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CHANGES IN LOWER LIMB COORDINATION ACROSS RUNNING AT DIFFERENT SPEEDS AND INCLINATIONS: CONTINUOUS RELATIVE PHASE ANALYSIS

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CHANGES IN LOWER LIMB COORDINATION ACROSS RUNNING AT DIFFERENT SPEEDS AND INCLINATIONS: CONTINUOUS RELATIVE PHASE ANALYSIS

ABSTRACT. The aim of this study was to evaluate the changes in segmental coordination when running at different inclinations and speeds. 18 recreational runners performed running trials at three inclinations (0°, 3° and 6°) and three speeds (preferred speed, fast and slow) were measured with Vicon motion capturing system. The phase angle, continuous relative phase (CRP) and variability of CRP (VCRP) were calculated. Statistical models were performed to compare means for each running condition at each gait point: one-way ANOVA with Bonferroni post-hoc analysis for those data points with homogeneity of variances and Welch ANOVA with Games-Howell post-hoc analysis for those with heterogeneity of variance. Effect size (ω^2) was computed to indicate whether the significant effects were trivial. Our results demonstrated that compared with the running speeds, participants who ran on different inclined surfaces showed higher Ankle-Knee CRP but lower Knee-Hip CRP and its variability, which is susceptible to running related injuries. These data suggest that runners should have a higher concern on joint loading and sports recovery when running at inclined surfaces.

KEY WORDS: treadmill running, continuous relative phase, coordination pattern, running with inclinations, running injuries

MODIFICĂRI ALE COORDONĂRII MEMBRELOR INFERIOARE LA ALERGARE CU VITEZE ȘI ÎNCLINAȚII DIFERITE: ANALIZA FAZEI RELATIVE CONTINUE

REZUMAT. Scopul acestui studiu a fost de a evalua schimbările în coordonarea segmentară la alergare cu diferite înclinații și viteze. 18 alergători de agrement au efectuat probe de alergare la trei înclinații (0°, 3° și 6°) și s-au măsurat trei viteze (viteza preferată, rapidă și lentă) cu sistemul de captare a mișcării Vicon. S-au calculat unghiul de fază, faza relativă continuă (CRP) și variabilitatea CRP (VCRP). S-au efectuat modele statistice pentru a compara mediile pentru fiecare condiție de alergare la fiecare punct de mers: ANOVA unidirecțională cu analiză post-hoc Bonferroni pentru acele puncte de date cu varianță omogenă și ANOVA Welch cu analiză post-hoc Games-Howell pentru punctele de date cu varianţă eterogenă. Mărimea efectului (ω^2) a fost calculată pentru a indica dacă efectele au fost semnificative. Rezultatele noastre au demonstrat că, în comparație cu vitezele de alergare, participanții care au alergat pe diferite suprafețe înclinate au prezentat CRP mai mare în zona gleznă-genunchi, dar mai scăzută în zona genunchi-șold și variabilitatea acesteia, care este susceptibilă la leziuni legate de alergare. Aceste date sugerează că alergătorii ar trebui să pună un accent mai mare asupra încărcării articulațiilor și recuperării atunci când aleargă pe suprafețe înclinate.

CUVINTE CHEIE: alergare pe bandă, fază relativă continuă, model de coordonare, alergare pe suprafețe înclinate, leziuni legate de alergare

MODIFICATIONS DE LA COORDINATION DES MEMBRES INFÉRIEURS LORS DE LA COURSE À DIFFÉRENTES VITESSES ET INCLINAISONS : ANALYSE DE PHASE RELATIVE CONTINUE

RÉSUMÉ. Le but de cette étude était d'évaluer les changements dans la coordination segmentaire lors de la course à différentes inclinaisons et vitesses. 18 coureurs récréatifs ont effectué des essais de course à trois inclinaisons (0°, 3° et 6°) et trois vitesses (vitesse préférée, rapide et lente) qui ont été mesurées à l'aide du système de capture de mouvement Vicon. L'angle de phase, la phase relative continue (CRP) et la variabilité de la CRP (VCRP) ont été calculés. Des modèles statistiques ont été réalisés pour comparer les moyennes de chaque condition de course à chaque point de marche : ANOVA unidirectionnelle avec analyse post-hoc de Bonferroni pour les points de données présentant une homogénéité de variances et ANOVA de Welch avec analyse post-hoc de Games-Howell pour ceux présentant une hétérogénéité de variance. La taille de l'effet (ω^2) a été calculée pour indiquer si les effets significatifs étaient insignifiants. Nos résultats ont démontré que par rapport aux vitesses de course, les participants qui ont couru sur différentes surfaces inclinées ont présenté une CRP cheville-genou plus élevée mais une CRP genou-hanche plus faible et sa variabilité, susceptible de provoquer des blessures liées à la course. Ces données suggèrent que les coureurs devraient se préoccuper davantage de la charge articulaire et de la récupération sportive lorsqu'ils courent sur des surfaces inclinées.

MOTS CLÉS : course sur tapis roulant, phase relative continue, modèle de coordination, courir sur des surfaces inclinées, blessures liées à la course

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INTRODUCTION

Treadmill running is a popular fitness activity for recreational runners because of the low cost, few restrictions on space, and improvement of cardiovascular capability. This running is also widely used as supplementary training in elite athletes [1]. However, the poor running technique may cause chronic injuries in the knee and lower leg. Data showed that 33% to 50% of runners received at least 1 injury annually [2]. Most running injuries occurred in the joints of the lower limbs (Over 80%), including the legs, hip and feet, but knee injuries were the most common [3]. In studies over the past few years, high-impact forces from running have been identified as a significant cause of running injuries. Knee flexion and rotation could be effective in reducing joint impingement [4]. In response to incline running, the coordination of the movements of the small and large leg in the sagittal plane and the phase relationship produced flexion and extension suitable for the knee joint. In the frontal plane, the leg and foot coordinate their movements to produce anterior and posterior rotations of the subtalar joint as a means of ensuring stability of movement [5]. It could be found through existing studies that coordination between joints is necessary to ensure running and joint changes due to impact forces may be a dangerous movement pattern that predisposes runners to injury [3].

Running is a complex motor skill that involves numerous interacting joint segments or degrees of freedom; but coordination determines how these degrees of freedom are organized in an appropriate way [3]. Coordination analysis can provide insight into the mechanisms of running conditioning and running injury. Since the high frequency of joint movements presented by running and the relative positional relationships it brings, which are difficult to find out the relative positional differences between joints by kinematic analysis of single joints alone. Therefore; using a model of coordination, it helped researchers to gain further insight into the positional characteristics between the joints of the lower limbs in the running condition and to better understand the motor performance of the lower limbs during running movements [6]. Funato *et al*. concluded from an analysis of joint coordination during running that as the stride frequency increases, close relationship among the joints, reducing the production of joint degrees of freedom and leading to joint variability that can cause reduced performance and even injury [7]. In addition, the value of motor coordination for insight into running has been analyzed in several investigations by calculating continuous relative phase (CRP) angles. For example, by analyzing the coordination of the shank-foot and thigh-shank couplings in sagittal plane, it was found that the magnitude of coordination variability was significantly greater in backward running than in forward running, indicating that more degrees of freedom were involved in backward running [8]. CRP angles and CRP variability were calculated for key lower extremity kinematic couplings. It was found that subjects with lower limb injury disorders (iliotibial band syndrome) had abnormal segmental coordination patterns in running, particularly coupling involving knee abduction and tibia internal/external rotation. It was also suggested that changes in CRP in injury-prone runners may be associated with abnormal segmental coordination patterns [9]. Therefore, prospective studies assessing motor coordination will contribute to our understanding of the interplay between coordination, pain and running injuries. Since current methods in coordination assessment required multiple biomechanical variables, building an approach which can be measured and calculated in an easy way became critical in human dynamic analysis.

Commonly, therapists chose motor control and development mechanism in assessing motion performances and those theories emphasized the regulation of central nervous system [10]; however, some researchers suggested that the dynamic systems theory (DST) is a better explanation of how motor learning was optimized [11]. DST deems that motion behavior and its coordination are the outcomes of complex interactions within multiple segments and joints and it can be quantified by continuous relative phase (CRP), which is calculated by phase angle (PA) of a distal segment subtracting a proximal one through the time series of coupling angular displacements and velocities [12]. Several studies also approved that CRP is a practical protocol to investigate coordination of two coupling joints that fit the DST theory of interactions [11, 13].

In recent years, the effect of running speeds and inclinations on the lower limb coordination have been reported. When comparing biomechanical changes in long distance-running at different speeds, Aljohani *et al*. found a decrease in coupling angle variability in the sagittal plane of the knee joint and an increase in the proportion of hip flexion/extension movement patterns when speed was increased by 30%. This study concluded that speed changes were significantly correlated with an increase in risk factors for running-related injuries [14]. Bailey believed that increased movement speed affected coordination patterns and coordination variability. It was found that CRPV in the thigh decreased significantly with increasing speed and that this change was associated with an increase in the knee coupling range [15]. As the incline increases, the body adjusts its center of mass by leaning forward on its own to ensure the stability of movement. The length of the limb shortens in the oscillator and this change depends mainly on the movement of the knee joint, therefore the increase in incline reduces the range of motion of the knee joint [16]. Telhan *et al*. assumed that running on level and moderately inclined inclinations appeared to be a safe component of training regimens and return-to-run protocols after injury [17]. However, how the factors of speed, inclination and interaction would affect movement coordination during treadmill running was still vague.

This study aimed to investigate the effect of incline and speed on lower limb coordination during treadmill running. According to the current knowledge, Lam *et al*. investigated the effects of inclined motion on lower limb kinetic and kinematic variables. With increasing incline, peak vertical impact and loading rates, stride length and ankle coronal range of motion decrease, with the lowest sagittal knee mobility at an incline of 3°. Thus, running with a high incline resulted in more altered biomechanical variables compared to running with a low incline [18, 19]. The increase in speed produced a moderate change in the frequency of movement patterns, mainly in the form of changes in pelvic-trunk coordination. In addition, changes in each coordination pattern were only observed with increased velocity, suggesting that the effect of velocity on coordination depends not only on the amount of change but also on the direction of change. Therefore, to analyze the effect of coordination patterns on joints, the relationship between speed and coordination needs to be further investigated [18]. Hence, we hypothesized that both two factors would change the lower-limbs coordination patterns while running. For instance, the inclination would limit that of Knee-Ankle coupling, while speed would raise the range of motion of Hip-Knee coupling. Both those changes would be identified through the coordination pattern.

EXPERIMENTAL

Methods

Participants

18 healthy recreational male runners took part in this study. Their average age was 20.9±1.9 years with average mass and height of 70.4±6.3 kg and 1.79±0.07 m, respectively. They had an average running experience of 6.0±2.4 yrs, with current running exposure of 15.0 ±7.8 km/wk. None of the participants suffered from any musculoskeletal injuries at least six months prior to their participation. All study procedures complied with the principles of the Declaration of Helsinki for ethical research in human participants. Written informed consent was obtained from each participant prior to data acquisition.

Data Collection

After the 15 min warm-up, reflective markers (diameter 14 mm) were placed over the following anatomical landmarks: left and right sides of anterior superior iliac spine (ASIS) and Posterior superior iliac spine (PSIS), hip joint center, medial and lateral epicondyles of femur, medial and lateral malleolus, three calcaneus markers (posterior upper, posterior lower and lateral aspect of calcaneus), two-foot tracking markers (medial side of the first metatarsal head, upper side of the second metatarsal head and lateral side of the fifth metatarsal head) and two 4-marker rigid clusters which were attached to the thigh and leg segments (Fig. 1). A motion capture system of 10 cameras (200 Hz, Vicon, Metrics Ltd, Oxford, UK) was used to capture lower limb kinematics data for entire experiment.

An instrumented treadmill (Bertec Corp., Columbus, Ohio) was provided. The participants were first instructed to run at three inclinations (0°, 3°, 6°) with their preferred speed. The preferred speed of individual participant was determined by asking participants to run on the treadmill whilst gradually increasing the treadmill speed without letting them know the exact speed. They were instructed to verbally identify a running speed, which were the most comfortable and matched their preferred speed for an endurance run [20]. In the process of exploring the influence of inclination on running coordination, the preferred speed was determined at 0°, the same preferred speed was used for both 3° and 6° condition. The average preferred speed was 2.54 ± 0.34 m/s. After the completion of three inclination conditions, another fast speed (preferred speed +10%) and slow speed (preferred speed -10%) were performed with the level inclination. At least 1.5 min recording for running data was required in each test and 5 min rest was available between two tests. The order of inclination and speed conditions were randomly presented across participants.

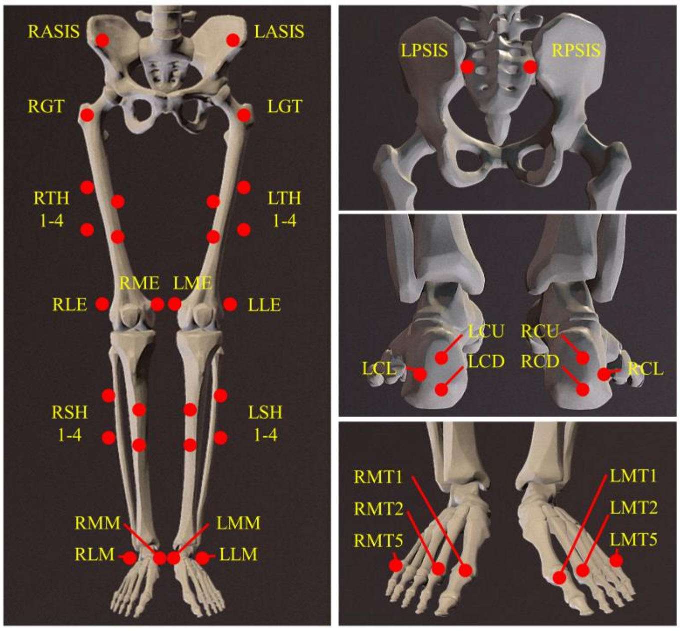

Figure 1. Demonstration of Markers' Installation

Data Processing

The biomechanical data were processed with Visual3D software (C-Motion Inc., Ontario, Canada) to define body segments and joint kinematic variables. A spline interpolation was performed to determine the minor missing data using three frames before and after the missing data. The contact phase was defined as the initial contact and toe-off by the force platform (Bertec Corp., Columbus, Ohio). A fourth-order Butterworth low-pass filter with cut-off frequencies of 10 Hz was used to filter the high-frequency noise. Each set of discrete joint angle data was normalized to 100 points using cubic spline interpolation which donated 100% of the gait cycle.

Continuous relative phase calculation procedure: Some researchers suggested that the dynamic systems theory (DST) is a better explanation of how motor learning was optimized [11]. DST deemed that motion behavior and its coordination are the outcomes of complex interactions, within multiple segments and joints, and it can be quantified by CRP which was calculated by the phase angle (PA) of a distal segment subtracting a proximal one through the time series of coupling angular displacements and velocities [12]. Several studies also approved that CRP is a practical protocol to investigate coordination of two coupling joints that fit the DST theory of interactions [11, 13].

We used Hilbert transform to calculate CRP by following four steps, which was introduced by Lamb [11].

(1) Shifting the center of phase portrait around zero

$$\theta_c(k) = \theta(k) - \min(\theta(k)) - \frac{\max(\theta(k)) - \min(\theta(k))}{2}, \ (k = 1, 2, 3 \ldots 100) \quad (1)$$

where $\theta(k) = \{\theta(1), \theta(2), \theta(3) \ldots \theta(100)\}$ denotes the interpolated 100 points Euler joint angle vector, and $\theta_c(k)$ refers to the Euler angle vector without zero-frequency component.

(2) Generating the analytic signal $\zeta(k)$ of $\theta_c(k)$ using Hilbert transform

$$\zeta(k) = \theta_c(k) + iH(k) \quad (2)$$

where $H(k)$ is the Hilbert transform of $\theta_c(k)$

(3) Computing the joint PA $\varphi(k)$ at each time k

$$\varphi(k) = \tan^{-1}\left(\frac{H(k)}{\theta_c(k)}\right) \quad (3)$$

(4) Calculating the continuous relative phase $CRP_{(1-2)}(k)$ between two joints

$$CRP_{(1-2)}(k) = \varphi_1(k) - \varphi_2(k) \quad (4)$$

where $\varphi_1(k)$ represents the PA of the proximal joint and $\varphi_2(k)$ represents the PA of the distal joint.

According to Equations (1) – (4), joint PA (hip, knee and ankle), Ankle-Knee CRP and Knee-Hip CRP of left and right lower limbs were calculated respectively. Ten successful trials were selected and averaged for each tested condition. An increasing CRP demonstrates that distal joint rotates faster than the proximal joint. Oppositely, a decreasing CRP represents that proximal joint rotates faster than the distal joint. This reversal tendency represents a change in relative rotation relationship between the proximal and distal joints. Furthermore, we computed standard deviation for each subject across 100 data points, among all participants as the variability of CRP (VCRP) [9], which represents a degree of variation in coordination between two joints [3].

Statistics Analysis

Since there were no significant differences between left and right leg data, the left and right leg data were merged for further statistical analysis. To investigate the impact of speed and inclination on lower limb coordination during running, analysis of variance (ANOVA) was used to explore if there was any difference between conditions. This method is a general method for evaluating differences in time series and has been applied by other scholars [21]. Due to the relatively small sample size (about 36 samples/group) and non-normal distribution of data at a small number of points, Brown-Forsythe's test was chosen to test the null hypothesis that the variances are equal across the three groups of data at three inclinations/speeds. For those points with homogeneity of variance, one-way ANOVA with Bonferroni multiple comparison test was performed to identify the significant difference. For those points for which the assumption of variance homogeneity was violated, Welch ANOVA was applied as it is proved to have a more robust performance than other non-parametric tests (Kruskal Wallis) [22] and post-hoc Games-Howell test was then applied for pairwise comparisons, which has greater power than traditional method. In addition, to estimate the degree of difference, effect size (ω^2) was computed at each point, which has less bias than (η^2) when heterogeneity of variance [23], interpreted as small ($\omega^2 < 0.06$), medium ($0.06 < \omega^2 < 0.14$), or large ($\omega^2 > 0.14$) [24].

For further investigation of the data, the running gait cycle was divided into four stages: (1) loading response (1%-20%), (2) mid-terminal stance (21%-60%), (3) initial swing (61%-80%), (4) mid-terminal swing (81%-100%) [25]. Furthermore, those points with significant differences ($p < 0.05$) were accumulated at each gait cycle stage separately between three conditions [26] and denoted by %P. Those points with large or medium effect ($\omega^2 > 0.14$ for large effect, $\omega^2 > 0.06$ for medium effect) were accumulated at each stage and denoted by %ES. All statistical analysis procedures were performed using MATLAB (R2020a, MathWorks, USA) with a significance level of 0.05 and a confidence interval of 95%.

RESULTS

Phase Angle (PA) Variables

As shown in Fig. 2, in terms of tendency, both speed and inclination affect the PA in knee rather than in ankle and hip, but slight off-set existed within loading response and early stance phase (around 0%-40% gait cycle) for ankle PA and whole stance and early swing (around 2%-80% gait cycle) for hip PA. With the running faster, knee PA increased; while slope became steep, knee PA decreased.

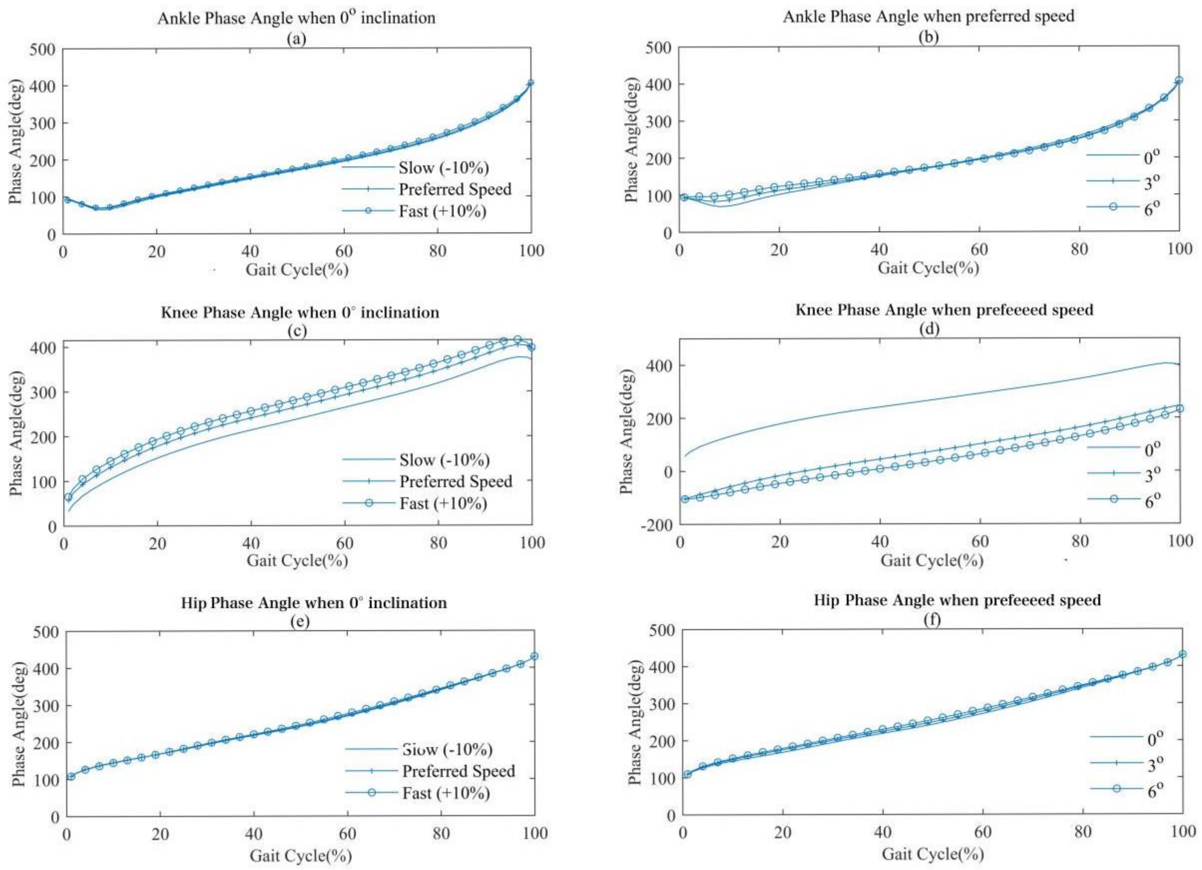

Figure 2. Curves of ankle (top), knee (middle) and hip (bottom) phase angle during running at different speeds (left panel) and inclinations (right panel)

Continuous Relative Phase (CRP) Variables

According to Table 1 and Fig. 3(a) and (b), in terms of speed, percentage of point (%P) and effect size (%ES) for both Knee-Hip and Ankle-Knee showed no significant differences or large effects among three speed conditions (fast, preferred and slow at level surface) across the entire gait cycle (Sig. %P = 0, %ES = 0 for both Ankle-Knee and Knee-Hip). But we found a statistically significant difference for those two couplings when inclination increased. In terms of CRP in Ankle-Knee, significant variations existed in 21-100% gait cycle (Sig. %P range 20-25, %ES around 20); however, CRP in Knee-Hip showed significance across the entire gait cycle (Sig. %P range 19-20, %ES range 7-20).

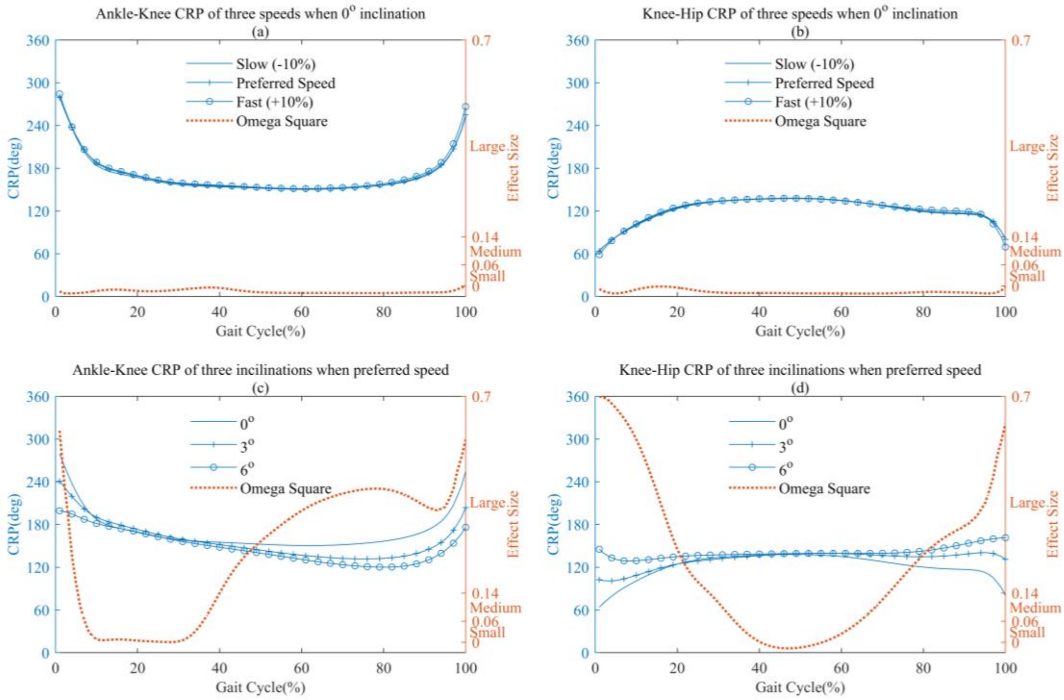

Figure 3. Curves of ankle-knee (left panel) and knee-hip (right panel) continuous relative phase (CRP) during running at different speeds (top) and inclinations (bottom)

Variability of Continuous Relative Phase (VCRP) Variables

In terms of VCRP in Ankle-Knee and Knee-Hip, as running faster, significant differences were only found in mid-terminal stance phase (%P = 11; %ES = 0 for Ankle-Knee; %P = 24; %ES = 0 for Knee-Hip; $p < 0.05$, $\omega^2 > 0.14$) and initial swing phase (%P = 3; %ES = 0 for Ankle-knee; %P = 2; %ES=0 for Knee-Hip; $p < 0.05$, $\omega^2 > 0.14$). When inclination angle increased, there were significant differences across the whole gait cycle (%P = 20, %ES = 15 for loading response; %P = 31, %ES = 12 for mid-terminal stance; %P = 20, %ES = 20 for initial swing; %P = 20, %ES = 20 for mid-terminal swing, for Ankle-Knee; %P = 15, %ES = 1 for loading response; %P = 19, %ES = 0 for mid-terminal stance; %P = 20, %ES = 19 for initial swing; %P = 20, %ES = 20 for a mid-terminal swing for Knee-Hip; $p < 0.05$, $\omega^2 > 0.14$) (Table 1 and Fig. 4).

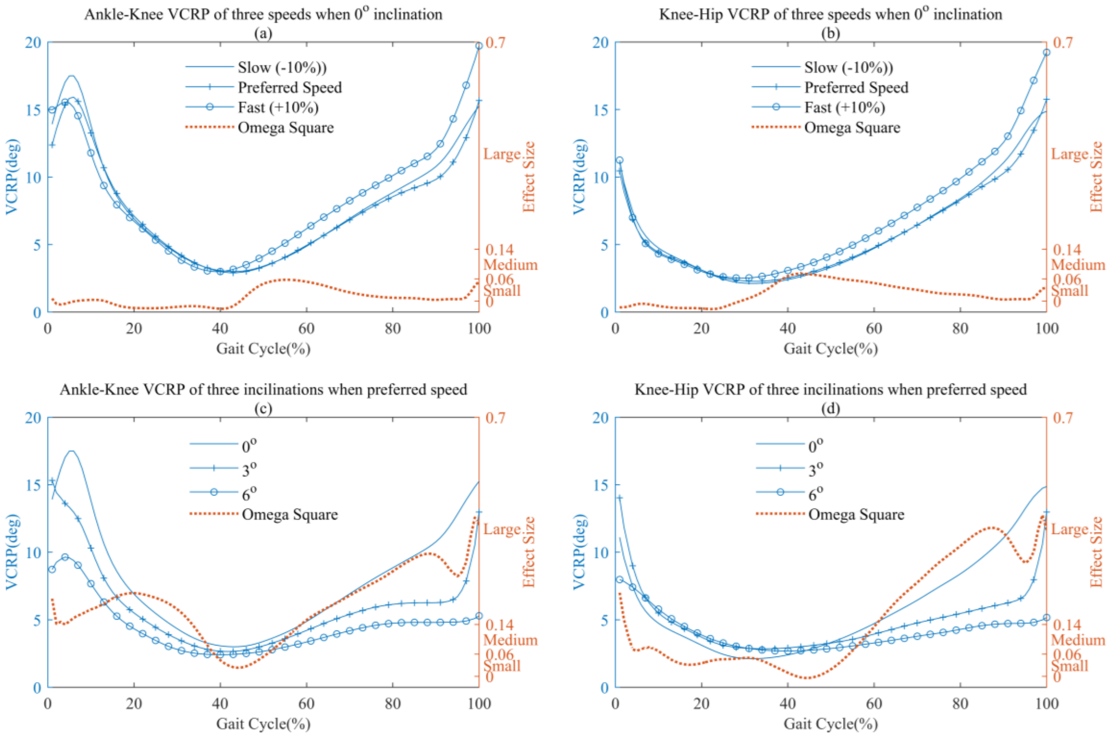

Figure 4. Curves of Ankle-Knee (left panel) and Knee-Hip (right panel) variability of continuous relative phase (VCRP) during running at different speeds (top) and inclinations (bottom)

Table 1: Statistical analysis results of CRP and VCRP

Item	Slope	Speed	Gait cycle												
			1%-20%			21%-60%			61%-80%			81%-100%			
			Mean (SD)	%P§	%ES* (%ES)**	Mean (SD)	%P§	%ES* (%ES)**	Mean (SD)	%P§	%ES* (%ES)**	Mean (SD)	%P§	%ES* (%ES)**	
CRP Ankle-Knee	0°	Slow	197.51(24.71)			154.9(8.91)			152.18(13.81)			180.31(25.10)			
	0°	Preferred	199.84(21.52)	0	0 (0)	155.87(8.50)	0	0 (0)	152.35(17.91)	0	0 (0)	181.44(32.85)	0	0 (0)	
	0°	Fast	200.90(20.78)			156.70(11.51)			153.66(11.51)			185.41(34.16)			
	0°	Preferred	199.84(21.52)			155.87(8.50)			152.35(17.91)			181.44(32.85)			
	3°	Preferred	195.77(19.43)	7	5 (7)	152.05(7.60)	25	21 (24)	133.01(11.31)	20	20 (20)	151.33(14.76)	20	20 (20)	
	6°	Preferred	182.68(18.90)			148.19(8.46)			123.89(10.70)			135.45(10.54)			
CRP Knee-Hip	0°	Slow	99.04(9.83)			134.56(8.11)			126.69(15.36)			111.44(23.94)			
	0°	Preferred	99.84(10.74)	0	0 (0)	135.17(7.83)	0	0 (0)	127.38(17.36)	0	0 (0)	112.54(30.32)	0	0 (0)	
	0°	Fast	100.12(10.57)			135.21(10.71)			127.83(10.71)			112.83(31.30)			
	0°	Preferred	99.84(10.74)			135.17(7.83)			127.38(17.36)			112.54(30.32)			
	3°	Preferred	110.53(9.41)	20	20 (20)	135.23(6.42)	19	7 (13)	136.62(9.87)	20	9 (16)	137.36(13.97)	20	20 (20)	
	6°	Preferred	132.42(13.45)			138.27(6.74)			140.18(9.24)			152.98(11.67)			
VCRP Ankle-Knee	0°	Slow	12.66			4.03			7.01			11.48			
	0°	Preferred	12.01	0	0 (0)	4.05	11	0 (0)	6.90	3	0 (0)	10.73	1	0 (0)	
	0°	Fast	11.45			4.29			8.31			13.38			
	0°	Preferred	12.01			4.05			6.90			10.73			
	3°	Preferred	10.00	20	15 (20)	3.45	31	12 (28)	5.39	20	20 (20)	7.01	20	20 (20)	
	6°	Preferred	7.29			2.86			4.18			4.86			
VCRP Knee-Hip	0°	Slow	5.35			2.89			6.59			11.56			
	0°	Preferred	5.04	0	0 (0)	3.01	24	0 (14)	6.56	2	0 (0)	11.04	1	0 (0)	
	0°	Fast	5.03			3.52			7.88			13.65			
	0°	Preferred	5.04			3.01			6.56			11.04			
	3°	Preferred	6.36	15	1 (10)	3.18	19	0 (6)	4.78	20	19 (20)	6.85	20	20 (20)	
	6°	Preferred	5.80			2.97			3.80			4.69			

DISCUSSION

This study explored the influences of speed and inclination on lower limb coordination while running on the treadmill. Generally, the present findings demonstrated that changing a small range of running speed (±10% of preferred speed) would not cause significant impact on CPR, but increased its variations as speed went up. However, lower limb coordination across different phases of gait cycle was significantly affected by the changes in inclination angle. For the choice of inclination angle: when running with an incline angle, we could observe the feature of change for lower limbs' coordination. So, our purpose was not to explore the influence of extreme incline angle on the running performance. Further, running with an incline larger than 10° would become dangerous for participants on the treadmill for several minutes, since their center of mass was significantly modified. In conclusion, analyzing these variations can gain insights into how the neuromuscular system and skeletal system work when coping with different speed and inclination conditions.

Our results suggested that speed had limited influence on the CRP in Ankle-Knee and Knee-Hip, but the VCRP increased as running speed was added. As indicated by Chiu and Lamoth [27, 28], the change of speed caused the adaptations and adjustments in steps, so as to maintain their running rhythm. Since, the lower speed (relative to preferred one) led to a shorter stride length, which then reduced range of motion of the knee joint, so smaller knee PA was observed [29]; vice versa for the higher speed. However, when running faster than preferred speed, VCRP in Ankle-Knee and Knee-Hip occurred during 21%-80% gait cycle; this phenomenon suggested that when running with higher speed, segmental kinematics in the lower limb required much higher variability to maintain the coordination pattern in an optimal state that works best for each participant [18]. Meanwhile, human body used inertia and gravity acceleration to optimize energy efficiency whilst running, which was by the principle of the lowest energy consumption [30]. Thereby, we assumed that preferred speed is more controllable and safer while running.

Changing the inclination angle demonstrated a larger impact on lower limb coordination. Our results showed that the effect of incline on the ankle-knee joint had a large significant difference from the middle to the end of the gait cycle (20%-100% GC), thus confirming our first hypothesis.

When walking uphill, the center of gravity of the human body moved forward to the front end of the sole. At the same speed, the higher incline had a faster step frequency, and the hip joint cannot reach the fully extended state like walking on flat ground. In order to keep the balance of body, the natural forward flexion of the hip and knee joint increased the flexion angle in the standing position, and reduced the range of motion of the knee joint. So, the PA decreased with the increase of the incline [31]. A similar finding was made by Baida *et al*. [32].

When systematically analyzing differences in exercise variability between healthy and sport-injured populations, it was found that 64% of the articles reported a greater VCRP in the injured population. CRP was more significantly influenced by incline compared to speed. The range of knee-ankle CRP was found to decrease during uphill exercise during the support phase (0-60% GC), indicating a limitation of relative knee-ankle movement [32]. Floria *et al*. found through their study that experienced runners exhibited a higher proportion of in-phase movements in pelvic-thigh and knee-ankle coupling and greater CRP in hip-knee coupling as the incline increased. This result was consistent with the results obtained in this paper [33]. As the inclination increased, the time required for the knee to complete a full range of motion was reduced. Particularly, at the initial foot strike (10%) and terminal swing stages (80%), the knee joint was in full extension, which increased both Ankle-Knee and Knee-Hip CRP. Hence, we postulated that, when coping with running inclinations, runners preferred to adjust knee rotation, rather than ankle and hip motion to keep running status. As coordination played an important role in the alteration of posture and movement patterns during running, the study of the effect of gradient on coordination was beneficial to our understanding of the changes in the neuromuscular and skeletal systems during exercise. This had implications for the rehabilitation of lower limb disorders and for improving running safety.

The VCRP provided further support for this assumption. Since the VCRP reflects the stability within joints, VCRP corresponded to the capacity of the neuromuscular skeletal system to generate a stable movement. The low (high) VCRP indicated a stable (unstable) pattern in movement coordination [8, 34]. Our results showed that significant changes in Ankle-Knee and Knee-Hip VCRP across all four stages when the inclination changed, which implied that the adjustment between lower limb segments occurred in the entire running cycle. This coordination pattern increased the flexibility of lower limbs whilst coping with the inclined ground surface [19]; however, the high flexibility in fast running could be a potential risk factor, since highly varied coordination between ankle, knee and hip would have caused larger joint loading and thereby injury risks [12].

However, our study still had some limitations. Firstly, we did not consider the influence of speed in a higher intensity, such as ±20% preferred speed, as reported in Mehdizadeh's study [8]. Secondly, we did not include the fast (+10%) and slow (-10%) speed conditions at the two inclined surfaces (3° and 6°). If we included all the tests, the runner should have run a much longer time and fatigues were easily observed. So, we did not choose the orthogonal design.

CONCLUSIONS

Overall, higher incline running leads to higher ankle-knee CRP, versus lower knee-hip CRP and VCRP, so we speculate that these changes are a contributing factor to running-related injuries. At the same time, these data suggest that runners should be mindful of joint loading and recovery when running on inclines. It is safe for runners to choose a speed that is 10% faster than the preferred speed when running.

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DEVELOPING INNOVATIVE BALLET POINTE SHOES: A LEAN STARTUP AND DESIGN THINKING APPROACH

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DEVELOPING INNOVATIVE BALLET POINTE SHOES: A LEAN STARTUP AND DESIGN THINKING APPROACH

ABSTRACT. This study aims to explore the development of innovative ballet pointe shoes through the implementation of Lean Startup and Design Thinking methodologies. The research employs a multi-phase approach, including problem identification, concept development, market testing, and model refinement. Through iterative improvements and user feedback, the study seeks to create a model of pointe shoes that offers enhanced comfort, adaptability, and durability for ballet dancers. The research emphasizes the use of polymers and 3D printing in the manufacturing process, presenting opportunities for advancements in pointe shoe design. By incorporating new technologies and materials, the study contributes to the field of classical dance footwear. The proposed innovative solution holds potential to elevate the dancer's experience and performance in pointe shoes.

KEY WORDS: pointe shoes, innovation, Lean Startup, Design Thinking, 3D printing

DEZVOLTAREA POANTELOR DE BALET INOVATOARE: O ABORDARE TIP LEAN STARTUP ȘI DESIGN THINKING

REZUMAT. Acest studiu își propune să exploreze dezvoltarea poantelor de balet inovatoare prin implementarea metodologiilor Lean Startup și Design Thinking. Cercetarea de față implică o abordare în mai multe faze, care includ identificarea problemelor, dezvoltarea conceptului, testarea pieței și rafinarea modelului. Prin îmbunătățiri iterative și feedback de la utilizatori, studiul încearcă să creeze un model de poante care oferă confort sporit, adaptabilitate și durabilitate pentru dansatorii de balet. Cercetarea pune accent pe utilizarea polimerilor și imprimarea 3D în procesul de fabricație, prezentând oportunități pentru progrese în designul poantelor de balet. Prin încorporarea de noi tehnologii și materiale, studiul contribuie la domeniul încălțămintei pentru dans clasic. Soluția inovatoare propusă are potențialul de a crește experiența și performanța dansatorului la purtarea poantelor de balet.

CUVINTE CHEIE: poante de balet, inovație, Lean Startup, Design Thinking, imprimare 3D

DÉVELOPPEMENT DE POINTES DE BALLET INNOVANTES : UNE APPROCHE LEAN STARTUP ET DESIGN THINKING

RÉSUMÉ. Cette étude vise à explorer le développement de pointes de ballet innovantes grâce à la mise en œuvre des méthodologies Lean Startup et Design Thinking. La recherche utilise une approche en plusieurs phases, comprenant l'identification des problèmes, le développement de concepts, les tests de marché et l'affinement du modèle. Grâce à des améliorations itératives et aux commentaires des utilisateurs, l'étude cherche à créer un modèle de pointes offrant un confort, une adaptabilité et une durabilité améliorés pour les danseurs de ballet. La recherche met l'accent sur l'utilisation de polymères et l'impression 3D dans le processus de fabrication, offrant ainsi des opportunités de progrès dans la conception des pointes. En intégrant de nouvelles technologies et de nouveaux matériaux, l'étude contribue au domaine des chaussures de danse classique. La solution innovante proposée a le potentiel d'améliorer l'expérience et les performances du danseur avec des pointes.

MOTS CLÉS : pointes, innovation, Lean Startup, Design Thinking, impression 3D

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INTRODUCTION

In the present study, an examination is conducted into the historical progression and transformation of pointe shoes. This involves an investigation into their origination, contemporary status, and the concerns dancers have in relation to this type of footwear. The objective is to gain insight into the potential for innovation and constraints that arise when suggesting novel approaches.

History of Pointe Shoes

Dance has a rich historical background, originating from the Italian Renaissance and flourishing in France during the reign of Henry II and Catherine de Medici. In 1581, under Catherine's patronage, the first ballet in history, The Queen's Comic Ballet, was created, marking a significant milestone in the development of dance [1]. The subsequent growth of ballet occurred during the reign of Louis XIV, leading to the establishment of the Royal Academy of Dance in 1661, which later became known as the Paris Opera in 1780 [2].

In the early stages of ballet, dancers relied on high heels for their performances. However, this changed in 1730 when Marie Camargo introduced flat shoes that enabled dancers to execute intricate jumps and movements that were not feasible with heels [3]. It wasn't until 1832 that Maria Taglione captivated audiences by performing on the tips of her toes, utilizing the first pointe shoes during her rendition of La Sylphide, a choreography devised by her father [4]. Since then, they became a fundamental part of the repertoire and training of classical ballet female dancers.

Anna Pavlova (1881-1927) is credited with refining the design of pointe shoes as we know them today. Pavlova incorporated hard leather soles for enhanced support and stiffened the toe area, enabling dancers to achieve greater stability. Despite her innovative modifications, Pavlova faced criticism from her contemporaries who regarded her techniques as cheating [5].

The renowned Capezio brand played a pivotal role in establishing pointe shoes on the international stage. In 1887, Salvatore Capezio initiated his shoemaking career by opening a repair shop in New York. He subsequently began crafting sturdier and more supportive pointe shoes for ballerinas. In 1892, Capezio became the official shoemaker of the Metropolitan Opera House, and his brand flourished with the patronage of prominent figures like Anna Pavlova. During her inaugural United States tour in 1910, Pavlova purchased Capezio pointe shoes for herself and her entire company, contributing to the brand's resounding success [6]. Later, other significant brands emerged, such as Freed of London in 1929 and the Australian brand Bloch in 1931.

Developments and Current Status of Pointe Shoes

Despite the passage of time, pointe shoes have undergone minimal evolution since their invention in the 19th century [7]. Various brands emerged over the years, but they all utilized similar materials for manufacturing, including satin, hessian, canvas, suede, leather, cardboard, and paper [8]. Consequently, the durability of pointe shoes remains relatively low due to the moisture generated by perspiration, which weakens the fabric and paper layers supporting the toes, ultimately affecting shoe stability. On average, ballet pointe shoes last approximately 12 hours of use [9].

In the 1990s, former American dancer Eliza Gaynor Minden introduced a groundbreaking design for pointe shoes made from thermoplastic materials. This innovative development revolutionized the dance industry, significantly enhancing the durability of the shoes compared to traditional counterparts [10, 11]. Since 1993, numerous attempts have been made to introduce new pointe shoe models incorporating 21st century materials and technologies. However, many of these endeavours proved commercially unsuccessful and were subsequently withdrawn from the market, such as the Capulet, the Flyte, and the Mayer. Others remained as conceptual or theoretical projects, including the Nike Arc Angles and the P-rouette 3D printing pointe shoes [12].

More recently, brands like So Dança and Merlet have introduced models with resemblances to the concept proposed in this research. Additionally, a new brand called Act-Able has emerged, presenting a model of pointe shoes fabricated through 3D printing [12].

Pointe Shoes: Biomechanics, Parts and Manufacturing

Pointe shoes are a crucial tool in classical ballet, primarily used by girls. The appropriate age to start wearing pointe shoes varies, but generally, it is not recommended before the age of 12, unless specific physical and technical conditions are met [13, 14].

The biomechanics of the foot play a crucial role in the execution of pointe work. In classical ballet, the lower extremities rely on external rotation as the fundamental position, primarily originating from the hip joint. This foundational posture is commonly referred to as "*en dehors*" [15]. From this starting point of *en dehors*, dancers must strive for complete plantar flexion of the feet and ankles in order to rise onto pointe [13]. This intricate movement entails elevating the body onto the toes while maintaining the external rotation, gradually passing through demi-pointe before ultimately achieving the full pointe position (Figure 1).

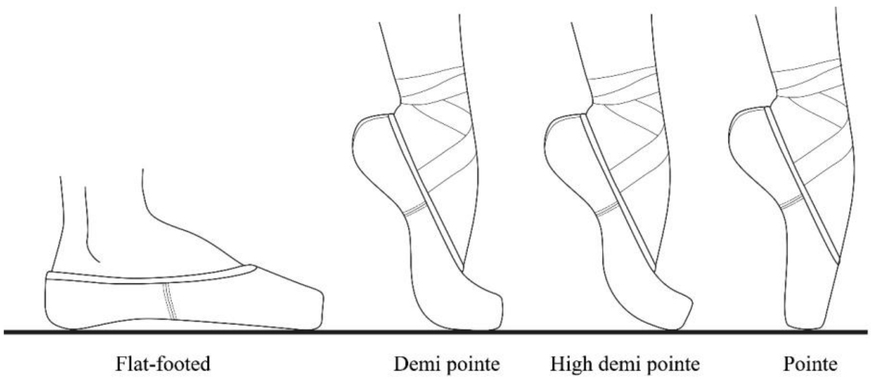

Figure 1. Biomechanics of getting over the pointe

A pointe shoe primarily consists of an internal structure composed of the box and shank, which provide support to bear the body's weight, and the textile component that covers the foot, known as the upper. Figure 2 illustrates the constituent parts of any pointe shoe.

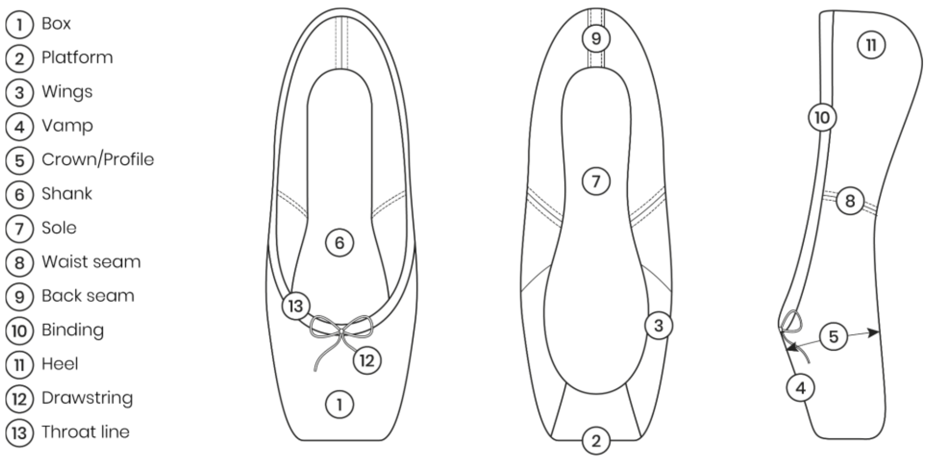

Figure 2. Parts of a pointe shoe

The upper is made of satin on the outside and a cotton lining on the inside [16]. The lining can be made from various moisture-absorbing or quick-drying materials to improve comfort.

The box (Figure 2), located at the front of the shoe, covers the dancer's toes, and provides support along with the shank. Traditionally, the box has been constructed using layers of paper or cardboard and burlap made from jute, glued together for rigidity. The box is the part of the shoe most affected by perspiration in terms of its durability. As reported by the Pittsburgh Ballet [17], an average professional ballerina exhausts approximately 100 to 120 pairs of pointe shoes per season. However, newer designs, like those pioneered by Gaynor Minden, fuse the box to the shank using elastomers, significantly increasing durability [18, 2].

The platform (Figure 2), the flat oval-shaped area on the bottom of the box, enables balance while on pointe. It is typically covered with satin, although some brands use suede. The platform's width has increased over time, potentially enhancing stability [18].

The side panels of a pointe shoe, known as wings (Figure 2), play a supportive role for the outer toes and sides of the feet when dancing on pointe [19].

Positioned on the lower front portion of the shoe, the vamp (Figure 2) covers the top of the toes. Its length is determined by factors such as the dancer's toe length, arch and ankle flexibility, and the type of instep they have.

The height of the crown (Figure 2) depends on the dancer's instep height and the compressibility of their foot [19].

Regarding the shank, located beneath the arch, it traditionally consisted of materials such as cardboard, leather, or a combination of both. However, modern pointe shoes utilize a variety of materials, including natural substances and synthetic components, to create shanks with different characteristics and properties [20, 12].

Pointe shoes are indispensable for ballet dancers, and their design incorporates biomechanical considerations and various components that provide support, durability, and comfort. A comprehensive understanding of these elements is crucial for both dancers and shoe manufacturers to optimize performance and minimize the risk of injuries.

EXPERIMENTAL

Methods

To undertake the development of innovative ballet pointe shoes, two methodologies will be combined.

The first of these is the Lean Startup methodology, developed by Eric Ries (2012), which focuses on creating and developing businesses in an agile and efficient manner [21]. Its aim is to minimise the risk in entrepreneurship by avoiding the development of products that customers do not desire or need. It is based on constructing a Minimum Viable Product (MVP) to obtain early feedback from customers and then iterate and pivot based on the results obtained [21, 22]. The idea is to quickly learn from the market and adapt to meet the real needs of users. Lean Startup also places emphasis on using metrics and data to make informed decisions rather than relying solely on intuitions and assumptions [23].

The second methodology is Design Thinking, which adopts a people-centred innovation approach [24]. It is based on deeply understanding users, empathising with them and their needs, and generating creative solutions through ideation and prototyping [24]. The methodology aims to address the real problems of customers and create meaningful and effective solutions that fulfil their needs and desires.

Both methodologies share a strong customer orientation and a mindset centred on experimentation and learning. Both approaches seek to deeply understand the needs, desires, and problems of users to develop relevant and effective solutions. Both Lean Startup and Design Thinking value iteration and rapid prototyping to obtain early feedback and validate ideas before investing significant resources [25]. Additionally, both promote an open and flexible mindset, allowing adaptation to changes and pivoting based on data and results obtained. Together, these similarities make the combination of both methodologies highly effective for generating new products and creating successful businesses.

According to Marion, Cannon, Reid, and McGowan (2021) [25], Design Thinking helps to better identify and understand customer problems and needs, providing a solid foundation for the development of the MVP in Lean Startup. By integrating both methodologies, a prototype can be quickly created based on the ideas generated from the Design Thinking process. Subsequently, this prototype is tested with customers, and Lean Startup comes into play to measure the response and learn from the results, which are analysed and used to make adjustments and improvements to the product. This create-measure-learn cycle is repeated until a product that satisfies the real needs of customers is achieved.

Phases of the Research

The research consists of 4 phases.

Phase 1: Identification of the Problems and Needs of the Users

This initial phase focuses on qualitative research, aligning with the principles of Design Thinking in its first stage, “empathize”. Firstly, qualitative interviews were conducted, recording audio with four professional dancers and thirteen classical dance students from different levels of a private academy in Valencia, regarding their training and use of pointe shoes. Secondly, two focus groups were conducted, recording audio with five 4^{th}-year and nine 5^{th}-year students from the Professional Degree of Conservatory of Dance in Riba-Roja de Túria. Finally, the latter group was asked to fill out a questionnaire after the focus group sessions, yielding 11 responses. This approach facilitates the identification of user needs and the evaluation of their relative importance. The results played a pivotal role in determining specific design requirements.

Phase 2. Definition of the Concept, Design and Testing of the MVP: Model 1

This phase focuses on the development of the Minimum Viable Product (MVP), aligning with the principles of the Lean Startup methodology. The first step involves defining the design concept, which addresses the problems identified in Phase 1. Subsequently, a concept test was conducted using a series of rapid prototypes to validate the concept with the participation of 24 dance students from the dance schools involved in Phase 1. Following the analysis of the test results, a usability test was conducted with several initial prototypes that were crafted by footwear industry professionals to be tested with 3 dance students and one professional dancer. Based on their feedback, relevant adjustments were made to proceed with the development of Model 1 as a validated MVP.

Phase 3. Market Testing of Model 1

As part of the Lean Startup methodology, this phase involved employing both qualitative and quantitative approaches for measurement and learning. Model 1, serving as an MVP, underwent thorough testing with 60 dancers of varying dance levels, who wore the shoes for a minimum period of one and a half months. An anonymous questionnaire was administered to gather valuable feedback, and conversations were held with certain dancers who reported specific issues, documenting them through videos and photos. The survey results were then analyzed to derive insights and make informed decisions for further iterations.

Phase 4. Redesign and Testing: Model 2 and 3

In this qualitative-focused phase, a redesign was undertaken to develop Model 2, which was subsequently tested at a summer dance campus involving 11 ballet students with varying skill levels. The students' usage of the model was meticulously observed, and they were queried about their experiences and sensations while dancing with the shoes. The results of this qualitative evaluation were then carefully analysed. These insights led to the conclusion that refinements and adjustments were needed to enhance the functionality of the product. Subsequently, to produce Model 3, several final design modifications were implemented based on the qualitative findings from the testing phase. The model 3 was then evaluated with 7 students from the Professional Degree of

Conservatory of Dance in Riba-Roja de Túria and two semi-professional dancers, who further contributed their feedback through specific questions about their experiences while dancing in the shoes. The combination of qualitative feedback from both phases served as a crucial guide to iteratively improve the pointe shoe design to better meet the users' needs and expectations.

RESULTS AND DISCUSSIONS

Phase 1: Identification of the Problems and Needs of the Users

The results of this phase were considered in two separate groups based on the user's profile, either a student or a professional dancer, as their knowledge, issues, and needs regarding pointe shoes differ.

Students

To analyse the outcomes of the interviews, focus groups, and questionnaires, two Design Thinking techniques were employed: the table for qualitative interview analysis (Table 1) and the empathy map (Figure 3).

These techniques considered the information gathered from the students who currently use or have used pointe shoes for a minimum of 3.5 hours per week during their training. This group comprised 21 students out of the total 27 participants. Six students from the private academy were excluded from this analysis as they use pointe shoes for less than 2 hours per week, indicating a beginner level.

The Table 1 allows to gather information from the interviews into a table, categorizing their needs, issues, and desires while assigning them a level of relevance.

Table 1: Qualitative interview analysis

	Needs	Problems	Desires	Observations
High relevance level	Prolonging the lifespan of pointe shoes when they are in the optimal state for dancing, as currently it's approximately one week.	Low durability in relation to their average price of €70: - 28.8% last between 2 and 4 weeks - 14.3% last between 1 and 2 months - 35.7% last between 2 and 3 months	Improved durability-to-price ratio. Incorporating reinforcement in the platform to enhance fabric longevity.	During performances, switching to new or old pointe shoes from those in good condition.
	Education to understand their foot characteristics and the necessary features for their pointe shoes. Pointe shoes that fit well, providing excellent support and mobility.	Lack of knowledge about the different parts of pointe shoes and their requirements.	Adjustable width to fit each foot. Pointe shoes to enhance the aesthetics of the foot.	Lack of awareness about the components of pointe shoes and the characteristics they should have based on their feet. Some students have 2 or more pairs available to alternate their use.
	Customization.	Differences in foot strength can result in one shoe softening or breaking before the other.	Having the option to select varying levels of hardness for each foot, as well as the color and finish of the pointe shoes.	Nine out of the eleven conservatory students who responded to the questionnaire affirm having one foot stronger than the other.
Moderate Level of Relevance	Adaptability.	Pain during use, especially when they are new or too soft.	Comfort.	Some teachers prohibit the use of toe caps. Students with bunions or the second longest toe experience more issues with pain and adaptability.
	The manufacturing process doesn't exert as much influence on the outcome.	The pointe shoes lack consistency and display variations with each purchase.	That the pointe shoes are consistently the same.	Traditional pointe shoes are crafted manually using materials susceptible to moisture. Consequently, the shoes may exhibit slight variations in shape and size with each manufacturing process.
	Thinner sole.	Lack of stability for flat feet.	Provide stability for flat feet.	This is particularly noticeable when performing a step called "*penché*".
	Providing effective guidance to reduce the likelihood of errors and expedite the process of finding their ideal pointe shoes.	Trial and error process to discover the suitable pointe shoes.	Finding their ideal pointe shoes on the first try.	Not all stores provide adequate guidance. None of the 21 participating students claim to have found their ideal pointe shoes.
	Minimize or eliminate the preparation time for the pointe shoes.	Time taken for sewing them.	Ribbons come sewn.	Out of the 11 surveyed students, 7 expressed a dislike for sewing them. In some instances, their mothers sew them instead.

	Needs	Problems	Desires	Observations
Low Level of Relevance	That the pointe shoes are prepared for immediate use.	Painful breaking-in process.	Painless breaking-in process.	Most of them soften them slightly with their hands or feet. However, only one student trims the shank and darns the base.
	Customization.	Difference in size between left and right foot.	Being able to purchase a pointe shoe of each size.	A student purchases two pairs simultaneously, each in a different size, intending to wear one on each foot. This practice is feasible due to the absence of left and right designations on pointe shoes. A majority of participants note that one shoe tends to feel tighter than the other, attributed to the inherent dissimilarity between our feet.
	Reduced noise generation.	Excessive noise from pointe shoes impacting the floor, especially noticeable during jumps.	Noiseless pointe shoes.	The noise level varies based on the brand. Professional dancers usually tap the shoes to soften them before wearing, reducing the sound.

The empathy map (Figure 3) enables the creation of a record that captures all the aforementioned information, along with the user's environment.

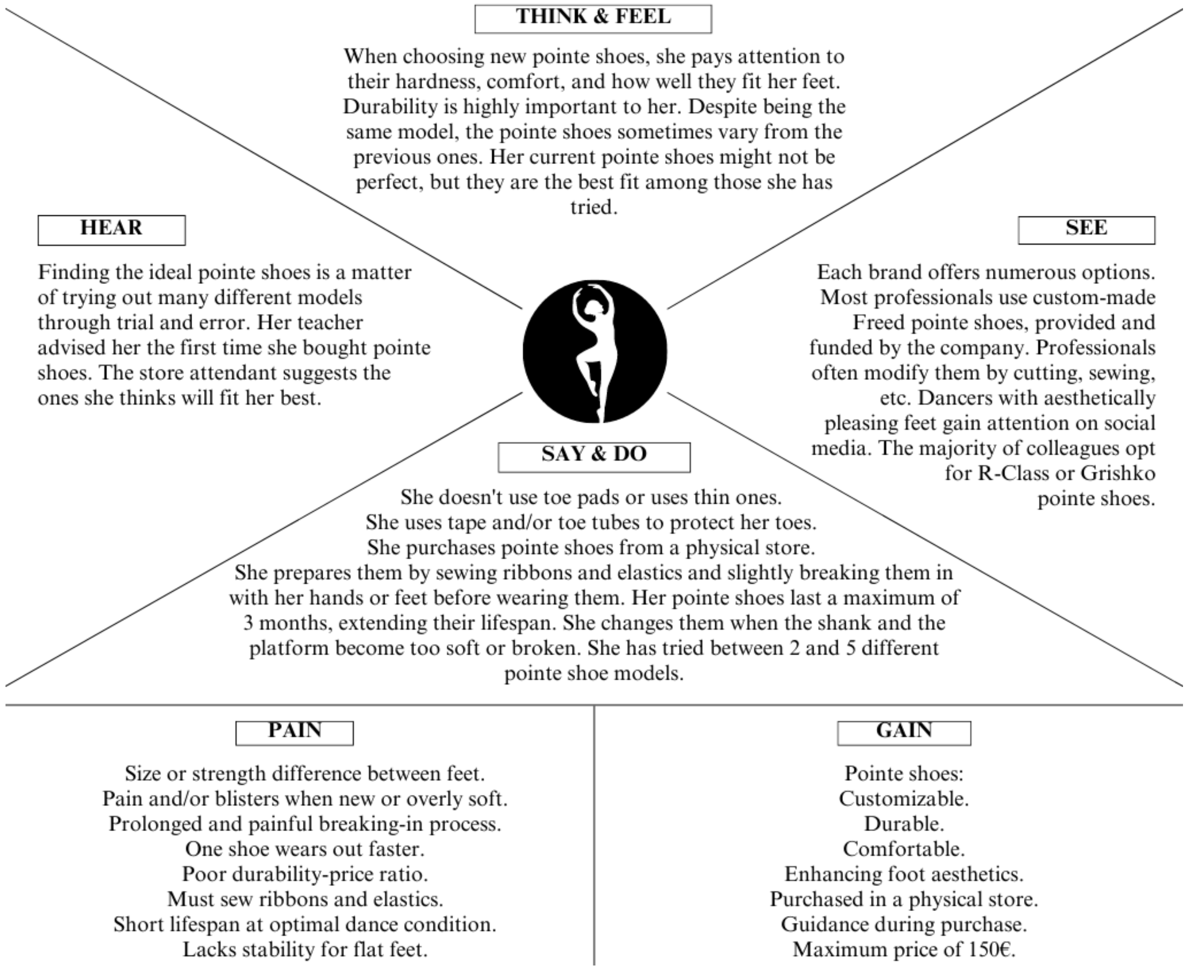

Figure 3. Empathy map

Professionals

The most common issues highlighted by the 4 professional dancers are flat-footed stability and lack of adaptability due to differences in foot strength. The most valued quality was determined using Equation 1.

$$P_T = \sum_{i=1}^{i=5} i \cdot \%_c \qquad (1)$$

where, P_T is the total score, i is the score from 1 to 5, $\%_c$ is the percentage of dancers who voted for each quality.

Comfort and aesthetics stood out as the most highly regarded attributes (Figure 4). While durability holds lesser significance due to the company covering shoe expenses, participants do acknowledge the limited longevity of pointe shoes in optimal dancing condition. Typically, a monthly allowance is allocated for pointe shoes, and in cases where this allowance is constrained, durability gains prominence. Colour holds no significant importance, since performers are mandated to apply makeup to diminish any shine.

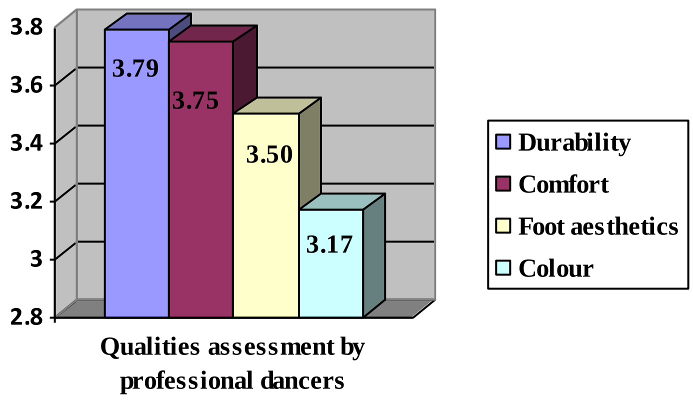

Figure 4. Score of the qualities valued in the choice of pointe shoes by professionals

List of Design Requirements

When defining the design requirements, students are considered as the target audience, as the market is much larger. There are more than 250,000 ballet students worldwide, as this number is examined each year by the Royal Academy of Dance (RAD), a British organization formed in 1920 that offers internationally recognized training certificates for different levels [26]. However, based on data obtained from the U.S. Bureau of Labor, Zippia, and the websites of the major companies in the US, Canada, Europe, and Russia, it is estimated that there are approximately 12,000 professional dancers worldwide [27, 28].

Therefore, based on the results obtained in the previous phase, a list of design requirements is proposed according to the target audience:

Table 2: List of design requirements

	Requirements
Durability	Pointe shoes should last a minimum of 3 months for dancers using them between 4 and 8 hours per week. Therefore, they must last a minimum of 72 hours
Comfort	Pointe shoes should be comfortable, so materials that enhance this characteristic should be considered in the design.
Adaptability	Pointe shoes should accommodate differences in foot strength; thus, they should be customizable in terms of hardness.
Foot aesthetics	They should enhance the aesthetics of each dancer's feet, so the goal will be to achieve customization of the shoe's point of curvature to adapt to the dancer's arch.
Colour	A traditional colour will be used as much as possible.
Price	It must be below €150.

Phase 2. Development MVP: Model 1

Concept Definition and Testing

Based on the user research findings, the following concept is proposed: pointe shoes with an internal polymeric structure and interchangeable shanks. This concept allows the dancer to use different levels of hardness or points of curvature for each foot and change them at will, according to the requirements of the moment or the choreography. In this way, the desired adaptability and increased durability are achieved.

Polymers are not affected by sweat; therefore, the durability will be significantly higher. To determine which polymer and manufacturing process are suitable for the internal structure, several tests were conducted, and quotations were requested. After evaluating the different options, 3D printed Polypropylene (Fused Deposition Modeling - FDM) was chosen for the box, due to its suitability in technical properties and cost. Additionally, laser cut and machined

Polyacetal was selected for the shanks, for the same reasons.

In order to validate the concept, several preliminary prototypes were created by separating the fabric from the internal structure.

Two focus groups were conducted at the dance schools that had participated in the previous phase. During these sessions, the prototypes were presented to the participants, and they were asked to simultaneously fill out an online survey (if possible) with general questions about pointe shoes and specific questions about the presented prototype. A total of 24 anonymous responses were collected to ensure the utmost sincerity from the participants.

The results of the survey show that durability is the most valued quality in pointe shoes, with a score of 3.79, followed by comfort with 3.75, foot aesthetics with 3.5 and colour with 3.16. The total score for each quality is calculated using Equation 1.

58.3% of the participants rated their interest in having different hardness in each foot with a score of 3 or more points (with 1 being the minimum and 5 being the maximum). However, only 16.7% scored their interest in using different sizes in each foot with 3 or more points.

Regarding the presented prototypes, 45.8% rated the usefulness of being able to change the shank with the maximum score (5), and another 50% rated it above 3.

An 87.7% expressed interest in purchasing the pointe shoes, of which 69.2% said they were willing to spend up to 150 € on pointe shoes that lasted longer, were more comfortable, and made their feet look beautiful. 72.2% considered a price range between 20 and 30 € for replacement shanks acceptable.

Out of the 24 participants, 70.8% were able to try the prototypes, of which 35.3% rated their comfort with a 5, and 52.9% with a 4.

Design and Testing of the MVP: Model 1

After the concept testing, Model 1 of the pointe shoes was designed. Two students and one professional dancer were selected to conduct the usability test using a functional prototype manufactured by footwear professionals. After a quick testing, it was determined that modifications should be implemented to improve the biomechanics of the pointe shoes: the thickness of the shanks was reduced to enhance flexibility in the metatarsal area, the sole rigidity was increased to prevent creasing in the arch area and the thickness of the lower wall of the box was reduced.

Finally, Model is represented and registered in the PCT/EP2021/052766 [29]. A detailed definition of each of its components is provided in Figure 5.

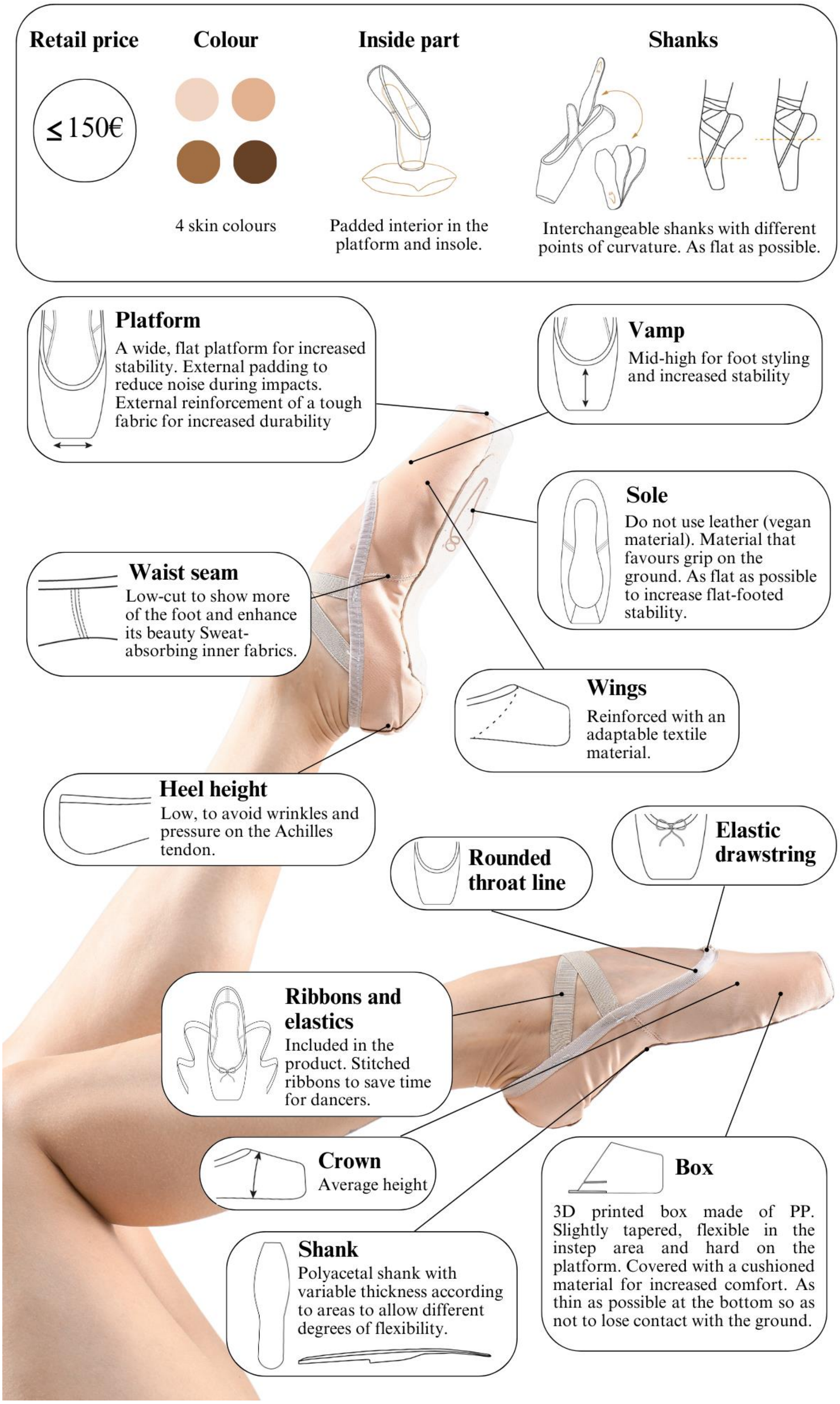

Figure 5. Description of MVP: model 1

Phase 3. Market Testing of Model 1

In the present study, a market test of the MVP was conducted with a group of 60 ballerinas who acquired and used pointe shoes for a minimum period of one and a half months. The purpose of this test was to evaluate the usability of the pointe shoes. To achieve this, a questionnaire was administered, guaranteeing anonymity in responses. Data from 33 ballerinas who completed the questionnaire were collected, while 5 left it incomplete, resulting in a total of 38 participants. Additionally, conversations were held with some of the respondents who directly reported their difficulties, documenting these issues through visual materials such as videos and photographs.

The results of the survey are presented below:

71.1% of the ballerinas expressed their intention to continue using these pointe shoes, while 5.3% showed lack of interest in continuing, and 10.5% were undecided. The remaining 13.2% chose not to respond to this question.

It was observed that 47% of the participants reported using pointe shoes for a weekly duration of 2 to 5 hours, while 41% indicated a usage period of only 2 hours. This distribution implies that a considerable portion of the participants might comprise beginner ballerinas or individuals engaging in ballet as an occasional recreational pursuit. Additionally, a minority of 12% reported using pointe shoes for over 5 hours on a weekly basis.

26% of the participants indicated that when stretching their feet, the pointe shoe did not adapt adequately, leading to undesirable aesthetic implications for ballet (see Figure 6).

Figure 6. Correct position on the left with a traditional pointe shoe and incorrect position on the right with pointe shoe model 1

44.7% of the ballerinas reported some kind of issue with the pointe shoes. The main problems were difficulty in correctly executing the rise onto pointe (34.2%) and the inability to roll down from pointe in a controlled manner (26.3%). Likewise, 15.8% of the respondents expressed difficulties in performing both movements.

Within the group of ballerinas who experienced problems when rising onto pointe, 61.5% were unable to perform the movement correctly (see Figure 1). On the other hand, the remaining 23.1% reported feeling a resistance that pushed them towards the ground, impeding the required biomechanical movement for the rise onto pointe.

10.5% of the respondents stated that the pointe shoes tended to stick to the floor during dance, while 18.4% indicated that this happened to a lesser extent but was tolerable. Given the relevance of this percentage, the possibility of modifying the material used in the base and sole was considered.

Another identified problem was the low heel height. 15.8% of the ballerinas experienced frequent slippage of the pointe shoes, 10.5% did so occasionally, and 26% had experienced this at some point.

The comfort of the pointe shoes was the aspect most highly valued by the ballerinas, with 47% rating their comfort with a score of 5 points (the highest) and 29% with 4 points.

Therefore, it was concluded that pointe shoe model 1 should undergo modifications to address the identified problems and improve certain functional aspects. However, the results were positive regarding the concept of pointe shoes, as a high percentage affirmed their desire to continue using them.

Phase 4. Development of the Model 2 and Model 3

Based on the market test results of the model 1, a series of changes were proposed to the internal structure of the pointe shoes with the aim of addressing the identified functional issues.

Design of Model 2

The box was modified by increasing the length of its cuts to enhance flexibility, and the base was slightly inclined to eliminate the need for the foot to reach a 90° angle to rise onto pointe (Figure 7).

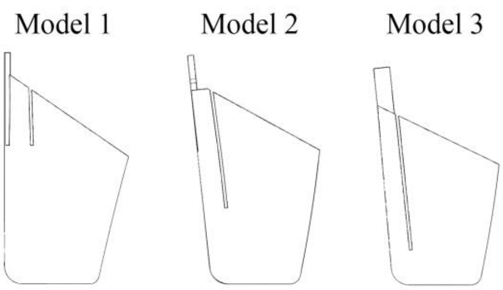

Figure 7. Box of the 3 models designed by the author

The last was redesigned to provide curvature to the sole of the pointe shoes, addressing the aesthetic issue of adaptability. To further improve this aspect, the wings were also shortened, as a trial conducted with two of the ballerinas who reported problems in the first phase revealed that the pointe shoes' aesthetics improved if they shortened the wings.

Regarding the platform reinforcement, another vegan fabric with better gliding properties was selected for testing.

With these changes, Model 2 was obtained.

Testing of Model 2

To conduct the testing of Model 2, the participation of 11 ballerinas was enlisted, who tested the ballet shoes during a two-week summer course. Among them, 5 dancers belonged to the beginner level (12-13 years), 3 to the intermediate level (14-15 years), and 3 to the advanced level (16-18 years).

Throughout this period, the performance of the ballerinas with the new pointe shoes was observed during their classes. At the end of the course, they were requested to complete a questionnaire detailing the positive and negative aspects of the shoes.

In the beginner level, 4 out of 5 students successfully adapted to the new pointe shoes, but some had difficulty fully supporting the platform while rising to pointe and controlling movements while rolling down. These shoes were perceived as somewhat soft.

In the intermediate level, none of the 3 students performed well with the new pointe shoes and only used them for one or two classes. They found the shoes too soft and inadequate for rising to pointe.

Among the advanced level, one dancer successfully mastered the new pointe shoes and continued using them. However, the other two dancers faced challenges due to the unflattering aesthetic and feeling insecure during movements from demi-pointe to pointe, finding the shoes too soft.

Figure 8. Beginner-level dancer, advanced-level dancers and intermediate-level dancer testing model 2

The test results conclude that while the pointe shoes fit better on the feet, achieving a fully elongated position has not yet been fully attained. It is suggested to reconsider the internal structure of shoe to improve the demi-pointe to pointe transition.

The platform material allowed sufficient gliding for turns but concerns regarding its durability were raised. Therefore, durability tests are proposed by combining the material with other fabrics to increase thickness and resistance. It was also identified as an appropriate moment to modify the shoe pattern, aiming to elevate the heel height to address issues raised during market testing, and lower the vamp height to reduce resistance during rising to pointe. Additionally, the proposal involves closing the throat line in the front, as it was observed during testing that it remained too open for most dancers.

Design of Model 3

For the development of Model 3, significant modifications were made to the internal structure of the pointe shoes.

The box was redesigned to enhance resistance during demi-pointe movements, making the transition to *en pointe* easier. The box's height was reduced, and the cuts were lengthened to improve flexibility in the toes (Figure 7). A rubber piece was added to the rounded edge that connects the sole to the platform, allowing slight deformation and providing support when the platform is not fully reached.

In regard to the shank, adjustments were introduced to augment its durability during demi-pointe motions. This component features diverse thickness levels, strategically chosen to attain the desired balance of flexibility and rigidity in various regions. To achieve this, the former practice of incorporating a metatarsal step to create thickness differentiation between the toe and arch sections (Figure 5) was replaced. Instead, a seamless curve was adopted, which not only bolsters resistance against flexion but also mitigates the buildup of tension. Consequently, this alteration diminishes the susceptibility to fractures within this specific area.

Regarding the upper, the patterns for the new last were designed, considering the conclusions obtained from the market testing.

With regard to the platform fabric, which is also used on the sole for aesthetic uniformity, various combinations were considered. The fabric tested in Model 2 was combined with other fabrics to provide increased resistance and thickness.

Testing of Model 3

Two testing modalities were conducted: one without direct observation and another with direct observation. In the first case, work was conducted with semi-professional dancers, managing remotely with feedback through photos, videos, and conversations. The second modality took place at the Riba-Roja de Túria Dance Conservatory, where students from different levels were selected: 2 students from 2nd-year, 3 from 4th-year, and 2 from 5th-year of Professional Grade. Their usage was observed, and communication was maintained for two weeks.

The semi-professional dancers performed well with the new pointe shoes, with one feeling better than her previous shoes and the other experiencing slight pressure on the foot pushing downwards. The

2nd-year conservatory students found the size and width of the shoes not ideal and chose not to continue using them after the observation period. However, the 4th-year conservatory students mastered the pointe shoes and decided to continue using them, praising their comfort and durability despite some difficulties in jumping. The 5th-year conservatory students had no issues with the shoes but preferred to stick with their current ones, with one student mentioning discomfort with the wide heel sole.

Figure 9. Semi-professional dancer, 2nd-year student, 4th-year student and 5th-year student testing model 3

In conclusion, based on the testing conducted, it can be affirmed that a design for pointe shoes suitable for 100% of the testers has been successfully developed. Among the 7 testers, 3 expressed a preference for the new shoes and intend to continue using them, whereas 2 testers opted to return to their previous models. Additionally, 2 testers found the new pointe shoes appealing, but they encountered sizing issues. Therefore, providing them with the correct size for evaluation will determine their continued usage.

Regarding the durability evaluation of different fabric combinations used in the platform, the continuous usage of the pointe shoes by the three 4th-year students during the testing and observation phase allowed to test these combinations. All combinations deteriorated in less than a month, with an average usage of 6 hours per week, except for one combination. The blend of microfiber fabric reinforced with polyester and cotton fabric demonstrated satisfactory durability. It was observed that the fabric undergoes gradual layer-by-layer breakage. The final layer experiences breakage after roughly 100 hours of use. Despite this, the breakage is minor, and the shoes continue to function adequately for an additional 45 hours. After surpassing the 145-hour mark, the breakage becomes substantial, necessitating a change of shoes.

Figure 10. Breakage after 61 hours, breakage after 100 hours and breakage after 145 hours

CONCLUSIONS

Ballet pointe shoes serve as essential tools for dancers, yet there have been limited advancements and innovations in the past century. This study addresses the creation of innovative pointe shoes through the implementation of Lean Startup and Design Thinking methodologies, whose combination has proven highly effective in developing new products within the field of classical dance. This research offers promising opportunities to enhance footwear and improve the dancer's experience. By adopting an experimental approach, the study successfully identified the needs and challenges of dancers concerning pointe shoes, leading to the generation of creative and viable solutions.

The research process was divided into four phases, each providing valuable information for iterative improvements in the shoe design. Through this iterative process, pointe shoes were developed, yielding positive results in tests with dancers, displaying a durability of 72 hours under ideal conditions (utilized on a linoleum surface), and featuring a manufacturing cost that allows for a retail price of €150.

These pointe shoes stand out for their comfortable design and adaptability to each dancer's requirements, facilitated by interchangeable shanks, without the need to go through the breaking-in process. This highlights their potential to enhance performance and the dancer's experience.

A significant finding was that the proposed model was not discarded due to internal structure failure, but rather due to the tearing of the fabric covering the platform. Remarkably, the shoe box remained intact even after more than 145 hours of use, demonstrating its resilience and durability. The shank's lifespan was estimated to endure at least 100 hours of intensive use.

Regarding materials and the manufacturing process, it was demonstrated that polymers are suitable for this type of footwear, offering increased durability and reduced impact noise. 3D printing emerged as the optimal manufacturing method for the shoe box, providing the advantage of variations and customization, while also being more accessible in terms of initial investment.

In summary, this study successfully produced pointe shoes that offer solutions to existing issues, leveraging new technologies and materials, thereby enhancing the dancer's experience. These innovations represent a significant advancement in pointe shoe design and pave the way for future enhancements and customizations in classical dance footwear.

It is crucial to emphasize that this study only marks the beginning of the journey towards innovation in pointe shoe design. Further research and additional testing are recommended to further refine the product and address any other issues or limitations that may arise.

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COMPETENCY OF *Acacia mearnsii* TANNIN EXTRACT FOR VEGETABLE TANNING USING ULTRASOUND TECHNIQUE

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COMPETENCY OF *Acacia mearnsii* TANNIN EXTRACT FOR VEGETABLE TANNING USING ULTRASOUND TECHNIQUE

ABSTRACT. This article describes the potential of *Acacia mearnsii* tannin extract for environmentally friendly vegetable tanning of leather using ultrasound. Vegetable tanning is a versatile but time-consuming process in the leather industry, particularly for heavy leather which needs more than one week for tanning using natural tanning materials. So, it is significant to develop new eco-friendly techniques employing ultrasound to speed up the vegetable tanning process without affecting the quality of the finished leather. In this study, the effect of ultrasound in vegetable tanning has been evaluated to enhance the tanning process. The effects of various parameters for example tannin dose, tanning time, temperature, and variable frequencies were studied. Tannin uptakes and other thermal properties were also investigated.

KEY WORDS: vegetable tanning, *Acacia mearnsii*, ultrasound, thermal stability, optimization

CAPACITATEA DE TĂBĂCIRE VEGETALĂ A EXTRACTULUI DE TANIN DIN *Acacia mearnsii* UTILIZÂND TEHNICA ULTRASUNETELOR

REZUMAT. Acest articol descrie potențialul utilizării extractului de tanin din *Acacia mearnsii* la tăbăcirea vegetală ecologică a pielii folosind ultrasunete. Tăbăcirea vegetală este un proces versatil, dar consumator de timp în industria pielăriei, în special pentru pielea grea, care are nevoie de mai mult de o săptămână pentru tăbăcire folosind materiale de tăbăcire naturale. Prin urmare, este importantă dezvoltarea unor noi tehnici ecologice care utilizează ultrasunete pentru a accelera procesul de tăbăcire vegetală fără a afecta calitatea pielii finite. În acest studiu, s-a evaluat efectul ultrasunetelor asupra procesului de tăbăcire vegetală pentru a îmbunătăți procesul de tăbăcire. S-au studiat efectele diferiților parametri, cum ar fi doza de tanin, timpul de tăbăcire, temperatura și frecvențele variabile. S-au investigat, de asemenea, absorbția de tanin și alte proprietăți termice.

CUVINTE CHEIE: tăbăcire vegetală, *Acacia mearnsii*, ultrasunete, stabilitate termică, optimizare

CAPACITÉ DE TANNAGE VÉGÉTAL DE L'EXTRAIT DE TANIN D'*Acacia mearnsii* PAR TECHNIQUE À ULTRASONS

RÉSUMÉ. Cet article décrit le potentiel de l'extrait de tanin d'*Acacia mearnsii* pour le tannage végétal du cuir par ultrasons respectueux de l'environnement. Le tannage végétal est un processus polyvalent mais long dans l'industrie du cuir, en particulier pour les cuirs épais qui nécessitent plus d'une semaine pour être tannés à l'aide de matériaux de tannage naturels. Il est donc important de développer de nouvelles techniques écologiques utilisant les ultrasons pour accélérer le processus de tannage végétal sans affecter la qualité du cuir fini. Dans cette étude, l'effet des ultrasons sur le tannage végétal a été évalué pour améliorer le processus de tannage. Les effets de divers paramètres, par exemple la dose de tanin, la durée de tannage, la température et les fréquences variables, ont été étudiés. L'absorption des tanins et d'autres propriétés thermiques ont également été étudiées.

MOTS CLÉS : tannage végétal, *Acacia mearnsii*, ultrasons, stabilité thermique, optimisation

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INTRODUCTION

Vegetable substances that can convert animal skin/hide into leather are called tanning agents or tannins. Vegetable tannins are astringent bitter plant polyphenolic compounds that are known to precipitate proteins, amino acids, and alkaloids [1]. The term tannin is used to mean any large polyphenolic compound containing enough hydroxyl groups and other suitable groups capable of forming complexes with several macromolecules [2]. There are mainly two classes of tannins: condensed tannins (catechols) and hydrolysable tannins (pyrogallols). Condensed tannins are oligomers and polymers of flavan-3-ol flavonoid monomers and hydrolysable tannins are esters of sugar, mostly glucose, and gallic acid or gallic acid derivatives [3].

Acacia mearnsii (Wattle) bark extract is well known vegetable tannin and used industrially to produce vegetable-tanned leather. The wattle bark proanthocyanidin oligomers contain 5-deoxy extender units that render the interflavanyl bonds resistant to acid catalyzed hydrolysis [4]. The bonding processes of vegetable tanning agents to collagen occurring during the interaction of tannins with collagen has drawn much attention for a long time. The bonding of tannins to collagen produces leather, which is more elastic than raw hide and shows more resistance to water, temperature, and microorganisms. Such bonds are formed only if the tannin molecules are large enough to join neighboring collagen chains and have enough phenols to form crosslinks in several places [5]. Using ultrasonic waves in vegetable tanning is as a potential viable option for solving this issue and speed up the vegetable tanning by binding collagen with natural tannin materials. Ultrasound is a sound wave with a frequency of 20 kHz-10 MHz that is generally used to enhance physical and chemical processes [6]. The tanning ability and quality of the aqueous solutions of tanning extracts, as a rule, increase after such treatment. This also happens during the treatment of tanning agents from a certain type of raw material, e.g., leaves or barks of *Acacia mearnsii*. This is apparently due to oxidative condensation of catechols [7]. It was found that the tannin molecule cannot penetrate in the tanning process or poorly penetrates the raw hide if it is too large. Therefore, it does not bind collagen or binds it very weakly [8, 9]. Tannins of molecular weight from 500 to 3000, especially 1000, are most responsible for tanning by phenolic compounds [10].

In vegetable tannage of light leather, the intention is to fill up the collagen structure and to confer weight and firmness. In heavy leather, the filling action and weight increase are important [11]. Hydrolysable tannins are used in combination tannages where specifically fewer toxic metals like titanium other than chrome are used to produce superior leathers that are eco-friendly [12]. This practice has been viewed as one of the best available techniques that will lead to increased production of leather products, environmental sustainability, and proper use of available natural resources [13]. This study aims at developing sustainable alternative technology for vegetable tanning process using ultrasound with natural materials.

MATERIAL AND METHODS

Materials

Raw materials used in vegetable tanning were divided into two categories: primary raw materials and auxiliary raw materials. The primary raw materials are cow pickled pelt and *Acacia mearnsii*. To operate the tanning process, different types of chemicals (laboratory reagent grade) were used besides the primary raw materials. The percentage of all chemicals mentioned here are on the basis of weight of pickled pelt.

Tanning Procedure of Pickled Pelt

Vegetable tanning was carried out in an ultrasonic bath with the help of a 600 mL glass beaker emerged in water. To investigate the vegetable tanning process with variable frequencies 10 kHz, 20 kHz, 30 kHz, and 40 kHz were used for a period of 5 hours.

Sample Preparation

The samples were cut into 2 inch × 2 inch taking from the equivalent lateral position of the pelt corresponding to the line of the backbone of the animal and weighed with an electronic balance (Shimadzu ATY224). The weight and area of the samples were almost (4.0 g) similar.

Vegetable Tanning

Vegetable tanning was performed using ultrasound and conventional techniques. All samples were divided into two parts for carrying out experiments with ultrasound and conventional methods. In the first group, the pickled pelt samples were taken in a beaker that was placed in a water bath to maintain the temperature exposed to ultrasound. Then, the pelts were vegetable tanned with 16%, 20%, and 24% of *Acacia mearnsii* for 5 hours. At the beginning of tanning half of the *Acacia mearnsii* was added to the pickling liquor (150%) and the other half was added after 30 min and was sonicated. Then sodium formate (1.5% of sample) was added as a masking agent. The tanning bath was then basified using sodium bicarbonate which was divided into three equal portions and was added within an hour. pH of the liquor was monitored (4.8 to 5.0) during adding sodium bicarbonate.

The second part of the sample was tanned by conventional method where a stationary glass vessel and rotary drum were used instead of ultrasound. A hotplate stirrer was used to control the temperature. In vegetable tanning an initial pH of 4.8 to 5.0 and the temperature of 80-98 °C was maintained.

Upon completion of tanning operation, the tanned leathers were covered by polythene and were piled up for several days to complete the fixation of tanning chemicals and dried in air. Tanned leathers obtained in both ultrasound and conventional methods were then used for analysis and characterization.

UV-Visible Spectrophotometry

The tanning content was determined by UV/visible spectrophotometry. The principle of this method is based on Lambert-Beer law, which shows that absorbance (A) is directly proportional to concentration for dilute solution. A SHIMADZU UV-1700 e spectrophotometer at 540 nm wavelength was used for the analysis. Once the characteristic peak was determined, the subsequent testing and calibration of this sample were conducted on this spectrophotometer. The data obtained from UV spectrophotometers was used to characterize the kinetics of tanning and to calculate the percentage of tannin uptake.

% tannin uptake at time 't' was calculated using the following equation:

$$\%Cr_{uptake} = \frac{Cr_i - Cr_f}{Cr_i} \times 100 \quad (1)$$

where Cr_i is the initial concentration of tannin liquor and Cr_f is the final concentration of tannin liquor.

RESULTS AND DISCUSSION

Vegetable Tanning of Leather

Vegetable tanning is a process that uses tannins derived from plant sources to convert raw animal hides into leather (Figure 1). *Acacia mearnsii*, also known as black wattle, is a tree species native to southeastern Australia. It is valued for its high tannin content in its bark. The use of ultrasound in vegetable tanning is an interesting aspect. Ultrasound can enhance the penetration of tannins into the hide, potentially improving the efficiency of the tanning process. The use of *Acacia mearnsii* tannin extracts and ultrasound in vegetable tanning suggests a specific research focus. This could include optimizing the tanning process for efficiency, exploring the quality of leather produced, or investigating the environmental impact of this method.

Figure 1. Vegetable tanned leather

Effect of Ultrasound on Tannin Uptake of Leather

Tannin uptake was studied during the tanning process for different tanning conditions. In this study, *Acacia mearnsii* tanning agent was used to perform the tanning operations with various frequencies for 5 hours. The tannin uptake of leather samples during vegetable tanning with ultrasound and conventional methods are shown in the Figure 2.

From the figure, it can be seen that the improvement of tannin uptake was more for the samples that had been tanned in presence of ultrasound than that of conventionally tanned samples. Ultrasound improved the penetration of tanning agents through the pores of collagen fibres and hence, enhanced the percentage of tannin uptake by the leather sample.

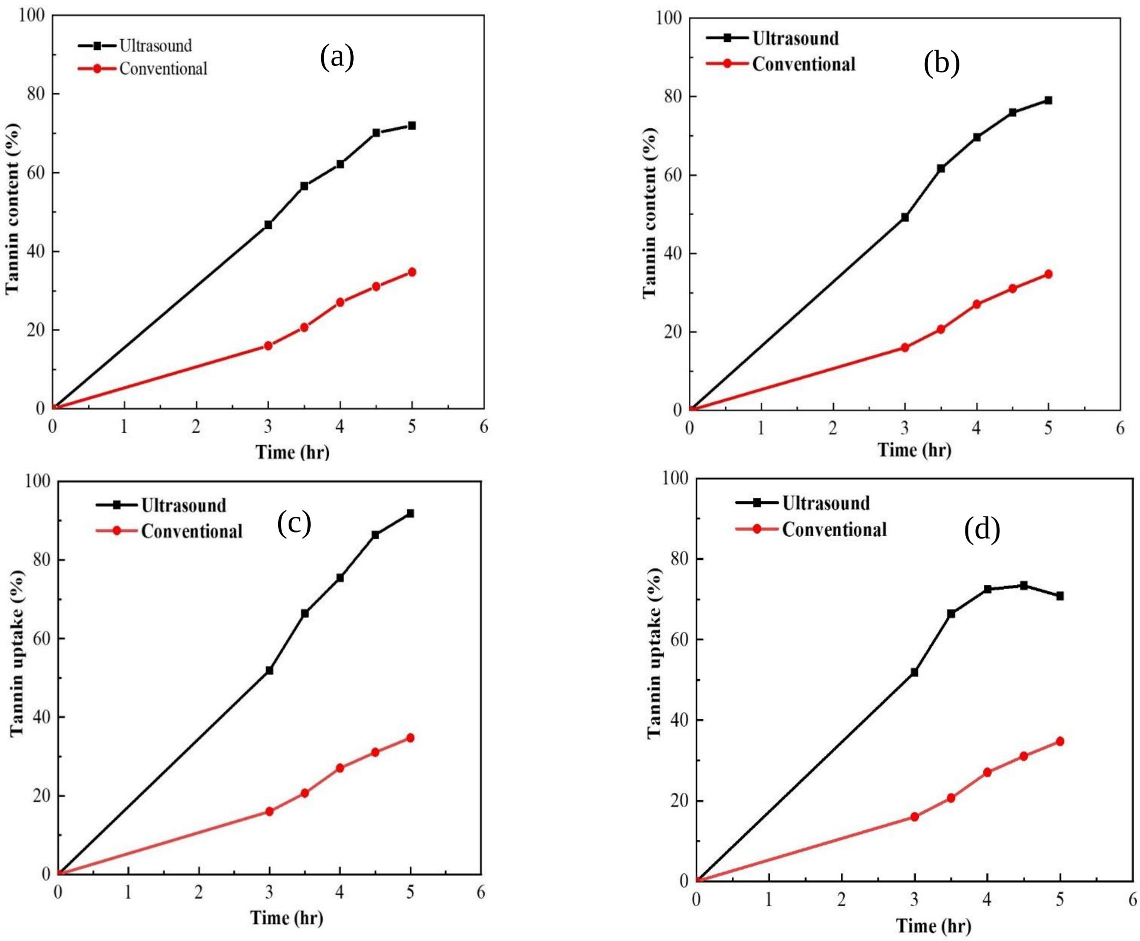

Figure 2. Tannin uptake of leather (%) as a function of time with ultrasound and conventional technique; ultrasound operated at frequency a) 10 kHz, b) 20 kHz, c) 30 kHz and d) 40 kHz

In this study, 71%, 79%, 91%, and 73% tannin uptakes were observed in case of tanning with ultrasound for tanning time of 5 hours using variable frequencies 10 kHz, 20 kHz, 30 kHz, and 40 kHz, respectively while only 34% tannin uptakes were observed in case of tanning with the conventional method for a tanning time of 5 hours. The results showed that the percentage of tannin uptake of the leather samples was increased up to 30 kHz operating frequency and then decreased. Because pickled pelts can absorb a certain maximum amount in a certain time and then it cannot absorb any tannin agent even the processing is carried out for longer time with higher frequency ultrasound. Thus, the use of 30 kHz US for 5 hours is the optimum condition for ultrasound-assisted vegetable tanning of leather.

Effect of Percentages of Tanning Agent on Tannin Uptake with Ultrasound

In the ultrasound-assisted vegetable tanning process, a comparative study was conducted using 16%, 20%, and 24% *Acacia mearnsii* as the main tanning agent. Figure 3 showed that using of 20% *Acacia mearnsii* was the optimum for the vegetable tanning process with ultrasonic waves. 16% *Acacia mearnsii* showed a lower penetration of tanning agents (< 15%) compared to using 20% Acacia. Again, 24% *Acacia mearnsii* gave a slightly higher penetration of tanning agents compared to using 20% of Acacia. Therefore, 20% of *Acacia mearnsii* was considered as the optimum composition of tanning agent in the vegetable tanning process.

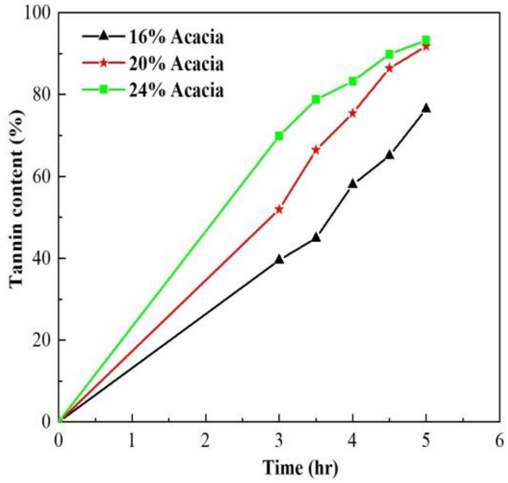

Figure 3. Effect of tannin uptake in various percentages of tanning agent within ultrasound

Thermogravimetric Analysis of Tanned Leather

The thermal degradation of leather tanned with and without ultrasound was compared to investigate the effect of ultrasound on leather tanning. The thermal degradation studies of the vegetable tanned leather samples were performed using thermogravimetric analyzer under N_2 atmosphere.

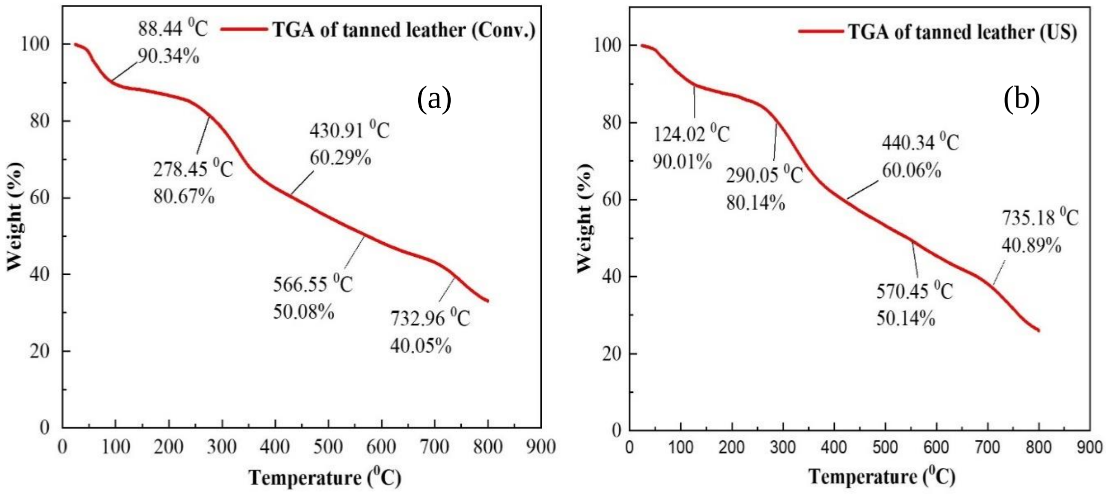

Figure 4. TGA of leather tanned with 10% tanning agent (*Acacia mearnsii*) for the total tanning time of 5 hours (a) with ultrasound, (b) conventional methods

Figures 4 (a) and (b) represent the thermograms of tanned leather with 10% tanning agent (*Acacia mearnsii*) for the total tanning time of 5 hours using ultrasound and conventional methods, respectively. It is seen from the Figures that temperature needed for 10%, 20%, 40%, 50%, and 60% loss of the weight of sample tanned with ultrasound were 124, 290, 440, 570, and 735 °C, respectively. On the other hand, 10%, 20%, 40%, 50%, and 60% loss of weight of the sample tanned with the conventional method under same tanning conditions were found at 88, 278, 430, 566, and 732 °C, respectively. These results reveal that thermal stability of the ultrasound-assisted vegetable tanned leather was greater than that of the conventionally tanned leather. It is assumed that the improvement of the thermal stability of ultrasound-assisted tanned leather occurs due to higher penetration of tanning agents through the pores and formation of tannin-collagen complexes which act as a barrier to the decomposition of leather samples.

DSC Analysis of Tanned Leather

The shrinkage temperature (Ts) of tanned leather is an effective indicator that can be used to evaluate the progress of tanning. Figure 5 showed that the shrinkage temperature of ultrasound-aided leather was higher than that of conventionally tanned leather. It is assumed that number of fixed tannin was increased due to ultrasound treatment. Thus the quality of fibre structure of tanned leather is not affected by the use of ultrasound.

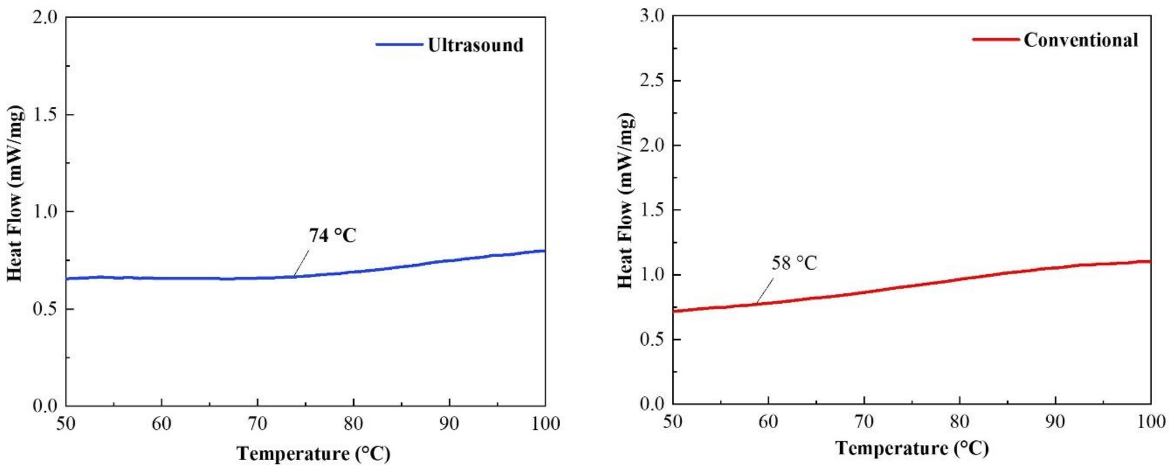

Figure 5. DSC thermograms of leather tanned with ultrasound and conventional methods

SEM Analysis of Tanned Leather

Fibre structure of the vegetable-tanned leather was observed by scanning electron microscope (SEM) and is shown in Figure 6. In micrographs, the darker the shade is, the higher the concentration of tannin agent. It can be seen that the tanned leather samples showed much uniform penetration of tannin agents in presence of ultrasound than that of tanned leather with the conventional method. In the process of ultrasound-assisted vegetable tanning the tanning agent completely penetrated into the full cross-section and grain surface of the leather.

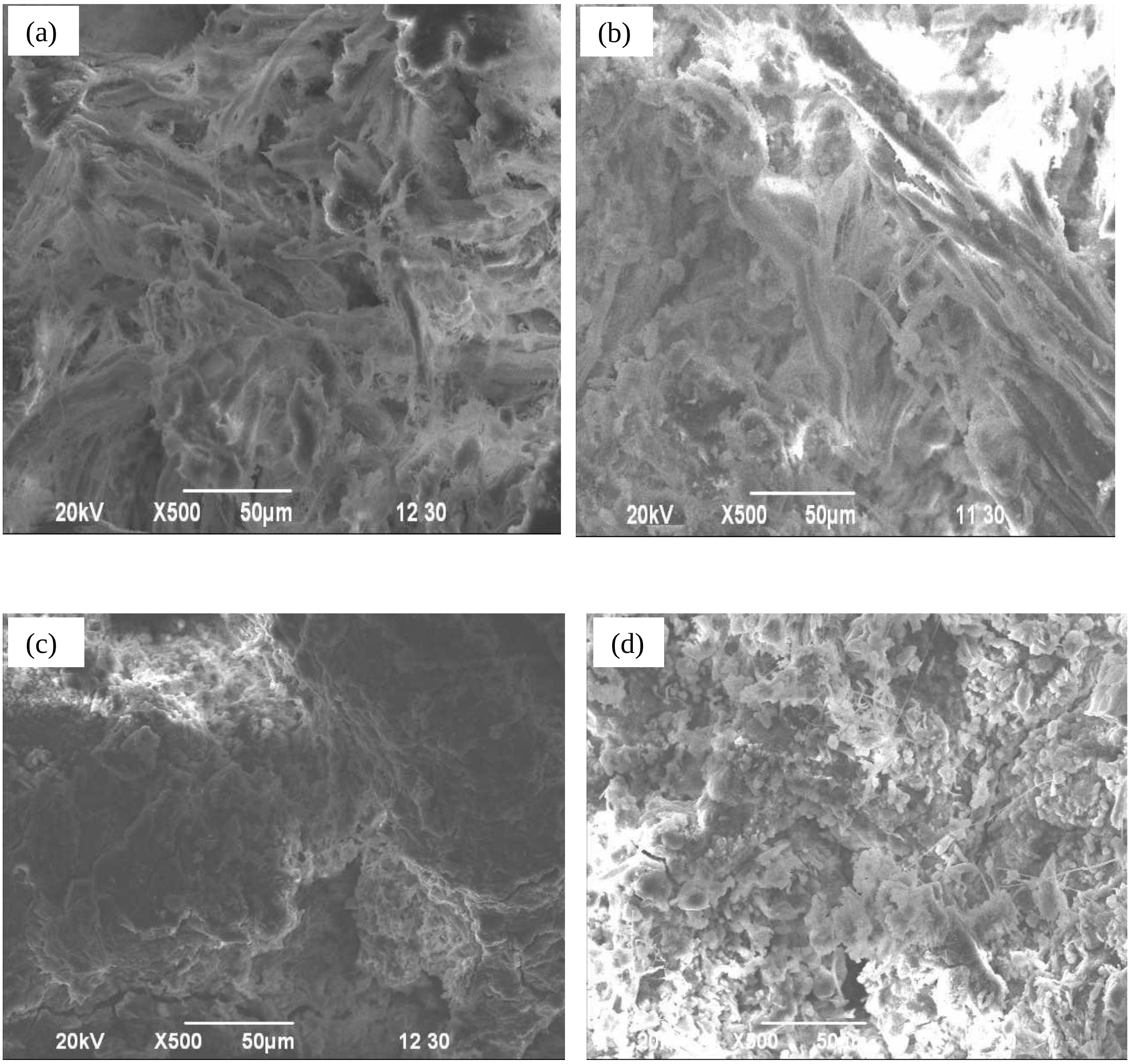

Figure 6. SEM images of cross-section of leather tanned with 10% tanning agent (a) with ultrasound, (b) without ultrasound; and surface view in presence of (c) ultrasound and (d) without ultrasound for 5 hours

The SEM images (Figure 6) also showed that the collagen fibrils are intact in the leather tanned with both ultrasound and conventional techniques. These results prove that the use of ultrasound in the tanning process did not damage the collagen fiber structures during the tanning period of 5 hours.

Diffusion of Tanning Agent

The images of the cross-sectional view of tanned leather obtained from the stereo microscope are shown in Figure 7. The depth of penetration of the tanning agent depends on the type of sample and the tanning agent used.

It is seen that in the case of ultrasound assisted vegetable tanning the degree of tanning agent penetration is higher compared to those samples tanned without ultrasound. It is due to the effect of acoustic cavitation which enhanced the diffusion rate of the tanning agent into collagen fibres. In addition, ultrasound aids in the uniform expansion of tannins by the inner part of the leather sample that is usually difficult in conventional method. Ultrasound helped to achieve a better penetration of tannin in the leather sample.

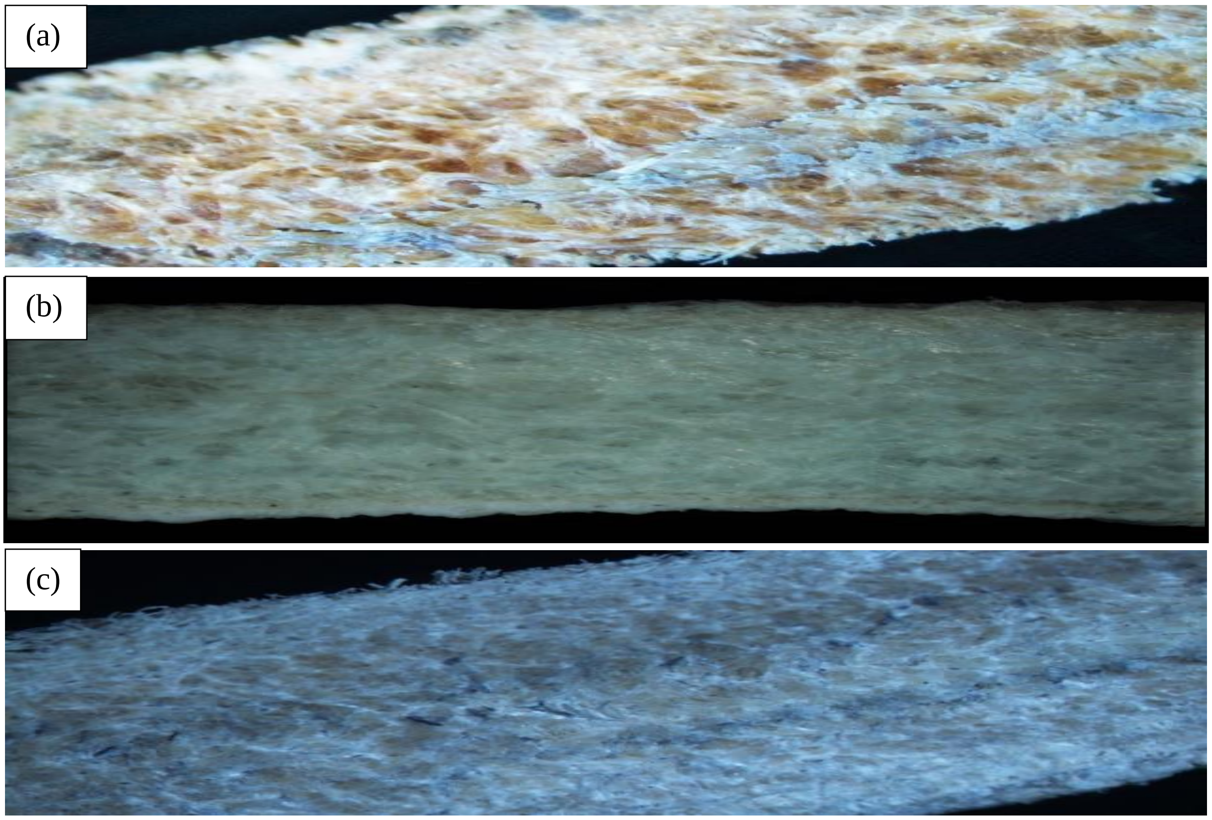

Figure 7. Photomicrograph (×25) of the cross-sectional view of (a) tanned leather in presence of ultrasound, (b) pickled pelt and (c) tanned leather with 10% tanning agent for total time of 5 hours in absence of ultrasound

Environmental Benefits

Ultrasound might be utilized as an efficient device for clean and green leather production. Ultrasonic waves can enhance tannin penetration through the raw hides even in static or ordinary room temperature using a high amount of tanning agent in vegetable tanning. The experiment was carried out with a variation of time under different operating conditions to observe the uptake of tanning agent in vegetable tanning. The results presented in the Table 1 revealed that ultrasound reduced the requirements of tanning agents' consumptions significantly. Therefore, vegetable tanning in presence of ultrasound with 30 kHz for 5 hours showed the optimum reduction (68%) of tanning agent.

Table 1: Amount of tannin in the spent tanned liquor

Tanning Time (hour)	Frequency (kHz)	Amount of tannin in the exhausted tanned liquor (ppm)		Reduction (%)
		Ultrasound	Conventional	
5	30	595	1865	68%
4	30	621	1589	61%
5	20	794	1913	58%
4	20	829	1731	52%

CONCLUSIONS

In the vegetable tanning application of ultrasound reduced the tanning time by 2 to 3 hours and increased the percentage of tannin uptake. Use of 30 kHz for 5 hours is the best condition for ultrasound-assisted vegetable tanning to afford the maximum percentage of tannin uptake. SEM and stereo microscopic images showed that the tanning agent penetrated more uniformly throughout the inner portion of the ultrasound-assisted tanned leather sample which was difficult in the conventional vegetable tanning. Again, thermal characterization of ultrasound-assisted vegetable tanned leather and conventionally vegetable tanned leather reveal that the thermal stability of ultrasound-assisted tanned leather is much better than those of conventionally tanned leather. The thermal stability of ultrasound assisted tanned leather was far better than that of conventionally tanned leather. It is also observed that vegetable tanning with the help of ultrasound of 30 kHz for 5 hours showed the reduction of tannin of 68%.

Authors' Contribution Statement

Professor Dr. Md. Zahangir Alam, Professor Dr. Md. Nurnabi and Dr. Md. Abu Sayid Mia planned and designed the research. Dr. Md. Abu Sayid Mia and Shamima Yeasmin conducted the experiments and wrote the manuscript. Professor Dr. Md. Zahangir Alam and Professor Dr. Md. Nurnabi supervised the whole research and revised the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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TESTING AND ASSESSING FUNCTIONALITY OF KERATIN HYDROLYSATE WITH AGRICULTURAL APPLICATION ON WHEAT SEEDS

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TESTING AND ASSESSING FUNCTIONALITY OF KERATIN HYDROLYSATE WITH AGRICULTURAL APPLICATION ON WHEAT SEEDS

ABSTRACT. This work aimed to obtain, characterize and evaluate keratin hydrolyzate with specific properties for applications in agriculture. The KerKAgr product, made by hydrolysing sheep wool with potassium hydroxide, was applied to wheat seeds. Physico-chemical analyses show that the keratin hydrolyzate obtained is rich in minerals, nitrogen and protein substances necessary in the plant growth process. Keratin hydrolyzate, KerKAgr, was used in treatments on Tamino and Mirastar wheat seeds, and the observations made showed an improvement in the germination rate and a stimulation of plant growth. KerKAgr 3% and 5% was used to treat wheat seeds and then germination and plant growth were monitored. The effect of keratin hydrolyzate was evaluated for 10 days on the two types of wheat (Tamino and Mirastar) treated with keratin hydrolyzate. The results of the treatments indicated an increased stimulation of seed germination by 10-20% compared to the control and a growth of wheat plants by 7.1-21.7% compared to the control. The biostimulating effect of keratin hydrolyzate has been highlighted. The good results obtained in the applications of keratin hydrolyzate in agriculture show that keratin hydrolyzate can be the basis for obtaining new biomaterials with various applications.
KEY WORDS: keratin hydrolyzate, biostimulator, seed germination

TESTAREA ȘI EVALUAREA FUNCȚIONALITĂȚII HIDROLIZATULUI DE CHERATINĂ CU APLICAȚIE ÎN AGRICULTURĂ PE SEMINȚE DE GRÂU

REZUMAT. Această lucrare a avut ca scop obținerea, caracterizarea și evaluarea hidrolizatului de cheratină cu proprietăți specifice pentru aplicații în agricultură. Produsul KerKAgr, obținut din lână de oaie prin hidroliză cu hidroxid de potasiu, a fost aplicat pe semințe de grâu. Analizele fizico-chimice arată că hidrolizatul de cheratină obținut este bogat în minerale, azot și substanțe proteice necesare în procesul de creștere a plantelor. Hidrolizatul de cheratină, KerKAgr, a fost utilizat în tratamente pe semințe de grâu, tip Tamino și Mirastar, iar observațiile făcute au arătat o îmbunătățire a ratei de germinare și o stimulare a creșterii plantelor. KerKAgr 3% și 5% a fost folosit pentru tratarea semințelor de grâu și apoi s-au monitorizat germinarea și creșterea plantelor. Efectul hidrolizatului de cheratină asupra celor două tipuri de grâu tratate cu hidrolizat de cheratină (Tamino și Mirastar) a fost evaluat timp de 10 zile. Rezultatele tratamentelor au indicat o stimulare crescută a germinării semințelor cu 10-20% față de martor și o creștere a plantelor de grâu cu 7,1-21,7% față de martor. Efectul biostimulator al hidrolizatului de cheratină a fost evidențiat. Rezultatele bune obținute în aplicațiile hidrolizatului de cheratină în agricultură arată că hidrolizatul de cheratină poate sta la baza obținerii de noi biomateriale cu aplicații diverse.
CUVINTE CHEIE: hidrolizat de cheratină, biostimulator, germinarea semințelor

TEST ET ÉVALUATION DE LA FONCTIONNALITÉ DE L'HYDROLYSAT DE KÉRATINE AVEC APPLICATION AGRICOLE SUR LES GRAINES DE BLÉ

RÉSUMÉ. Ce travail visait à obtenir, caractériser et évaluer un hydrolysat de kératine aux propriétés spécifiques pour des applications en agriculture. Le produit KerKAgr, obtenu à partir de laine de mouton par hydrolyse avec de l'hydroxyde de potassium, a été appliqué sur des graines de blé. Les analyses physico-chimiques montrent que l'hydrolysat de kératine obtenu est riche en minéraux, substances azotées et protéiques nécessaires au processus de croissance des plantes. L'hydrolysat de kératine, KerKAgr, a été utilisé dans les traitements des graines de blé Tamino et Mirastar, et les observations réalisées ont montré une amélioration du taux de germination et une stimulation de la croissance des plantes. KerKAgr 3% et 5% ont été utilisés pour traiter les graines de blé puis la germination et la croissance des plantes ont été suivies. L'effet de l'hydrolysat de kératine sur les deux types de blé traités avec l'hydrolysat de kératine (Tamino et Mirastar) a été évalué pendant 10 jours. Les résultats des traitements ont indiqué une stimulation accrue de la germination des graines de 10 à 20 % par rapport au témoin et une augmentation des plants de blé de 7,1 à 21,7 % par rapport au témoin. L'effet biostimulant de l'hydrolysat de kératine a été mis en évidence. Les bons résultats obtenus dans les applications de l'hydrolysat de kératine en agriculture montrent que l'hydrolysat de kératine peut être la base pour l'obtention de nouveaux biomatériaux avec diverses applications.
MOTS CLÉS : hydrolysat de kératine, effet biostimulant, germination des graines

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INTRODUCTION

The increase in population and the decrease in the area of arable land represented a challenge for the development of agriculture [1-3]. Ensuring the supply of sufficient and quality food is an important project of all countries in the world. The need for fertilizer application has played a critical role in agricultural production. It is estimated that 2.50×106 tons of fertilizers are used in agriculture every year [1, 2]. Application of these fertilizers can increase crop yield by 56%-58% and grain yield by 31%-32% [1-3]. The excessive application of chemical fertilizers directly results in the pollution of the agricultural environment, through soil acidification, soil hardening, nutrient imbalance and surface water pollution, etc. [4]. Some fertilizers also contain heavy metals; such as Zn, Cu, Co and Cr. Long-term use will lead to soil environmental damage and metal pollution [5, 6]. In order to mitigate environmental pollution, increase nutrient use efficiency, and develop sustainable ecological agriculture, eco-fertilizers have been widely produced [5-7]. Renewable materials are brought to attention because they could provide sustainable solutions for the production of ecological fertilizers, such as cellulose [8], chitosan [9, 10], alginate [11], starch [12, 13], and even branch waste of mulberry [14] and flax thread waste [15]. Besides the renewable natural materials mentioned, keratin derived from industrial by-products has started to be studied for use in agriculture [5-7]. Keratin is a biomass resource [16], which contains functional groups, it is renewable, degradable, non-toxic and has a low price. The protein substances that make up keratin can be a precursor of substances that restore humus and organic carbon in the soil [17]. It can also stabilize organic nitrogen in the soil [18].

A large part of sheep wool waste is produced in the processing of skins [19]. Sheep wool waste is one of the main sources of keratin, which presents some properties such as availability, non-toxicity, bio-degradation and bio-compatibility, etc. Keratin extracted by chemical methods is easily degraded by microorganisms into amino acids, which can increase microbial activity, improve soil structure and physical and chemical properties, and improve plant growth [1, 2, 19]. The use of waste for the production of fertilizers promotes industrial sustainability and the transition to a green economy [1, 2]. This research aims to provide an innovative strategy for resource utilization of sheep wool waste through its recycling and sustainable agricultural development. This study reported an environmentally friendly multifunctional fertilizer based on keratin from sheep wool waste. Keratin as a natural polymeric material is composed of amino acids that can increase the activity of microorganisms and improve the soil environment [1, 2, 19]. Keratin has recently appeared in various applications based on natural biomaterials. In addition to the potential to assemble into organized structures, keratin also consists of bioactive elements suitable for initiating biocompatible interactions with various substrates [20]. Keratin-rich wastes pollute the environment and are released in increasing quantities as by-products of agro-industrial or leather tanning processes [21-23]. Keratin from renewable sources in the leather industry is abundant, available and easy to harvest. Extracted keratin hydrolysates can be processed into different products using specific techniques established for a wide range of fields [24, 25]. Keratinous materials have a high protein content consisting of at least 17 amino acids that can be used in animal feed or agricultural fertilizers [19]. Degradation of keratin waste may therefore provide a cheap source of protein and amino acids [26]. The development of an ecological waste-based fertilizer is important in modern agriculture, due to the costly, incomplete degradation and supply restrictions of traditional fertilizers [4, 5, 7]. This could be an ecological multifunctional fertilizer rich in nutrients and with soil restoration action [4, 5, 7].

EXPERIMENTAL

Materials and Methods

In the experimental part, the obtaining, characterization and evaluation of keratin hydrolyzate with specific properties for applications in agriculture was pursued. Wool waste was purchased from sheep breeders in Constanța county, sodium carbonate and ammonia were supplied by SC Cristal RChim SRL, potassium hydroxide was supplied by Lachner. Keratin hydrolyzate was obtained from wool waste by alkaline hydrolysis with potassium hydroxide. All reagents used were for laboratory grade.

Obtaining Keratin Hydrolyzate

The wool recovered from the waste resulting from the processing of natural furs was degreased with 1% Na_2CO_2, 2% NH_3 (sol. 25%), 1% detergent, 1:10 water, 45°C, stirring, 3 hours, dried, shredded and hydrolyzed by the alkaline method, with 8% potassium hydroxide, at 97°C, stirring, 4 hours to obtain keratin hydrolyzate with protein macromolecular chains with a high degree of cleavage. The alkaline hydrolysis process consisted of the following stages: degreasing the raw wool, drying, shredding, alkaline hydrolysis, decantation, filtration and separation of the keratin hydrolyzate obtained. Keratin hydrolyzate, obtained by alkaline hydrolysis with potassium hydroxide, can be used in agriculture as a fertilizer to supply minerals and organic nitrogen in the development of plants grown on poor soils. The process of alkaline hydrolysis with potassium hydroxide by optimizing the technological parameters of temperature, reaction times, homogenization of the reaction mass and going through the sequence of work stages leads to obtaining keratin hydrolyzate rich in growth biostimulants and nutrients, important for ecological agriculture and as a rich source of organic nitrogen and mesonutrient sulfur for plants.

Characterization of Keratin Hydrolyzate

The keratin hydrolyzate obtained by alkaline hydrolysis was characterized by physico-chemical analyses regarding the content in: dry matter (SR EN ISO 4684:2006), ash (SR EN ISO 4047:2002), total nitrogen (SR ISO 5397:1996), protein substance (SR ISO 5397:1996), pH (STAS 8619/3:1990).

Physico-Chemical Analysis of Keratin Hydrolyzate for Applications in Agriculture

The physico-chemical characteristics highlight the functionality of the keratin hydrolyzate obtained with potassium hydroxide as follows: the content in ash (11.61%) shows that the keratin hydrolyzate is rich in mineral substances, total nitrogen (14.12%) and protein substance (85.49%) as an important source of organic nitrogen, the slow-release nutrient source for the development of plant crops (Table 1).

Table 1: Physico-chemical characteristics of the keratin hydrolyzate obtained by hydrolysis with potassium hydroxide for agriculture, KerKAgr

Characteristics	Dry substance, %	Ash, %	Total nitrogen, %	Protein substance, %	pH, pH units
No	1	2	3	4	5
KerKAgr	5.17	11.61	14.12	85.49	10.05

*The values for items 3 and 4 are related to the dry substance.

Analysis of Keratin Hydrolyzate by Electrophoresis

The keratin hydrolyzate obtained was characterized by determining the molecular weight distribution using SDS-PAGE electrophoresis. One of the most important factors in obtaining bioactive peptides with functional properties is their molecular weight. In the experimental study to determine the molecular masses of the proteins, the high polydispersity was taken into account, due to the presence of polypeptides, oligopeptides and free amino acids and generally having molecular masses between 3 and 198 KDa. KerKAgr was analyzed by acrylamide gel electrophoresis in the kuroGEL Verti 10x10 cm system, Vertical Dual-Gel Units, VWR Austria. Proteins were visualized by blue staining with Coomasie Blue Stain R250.

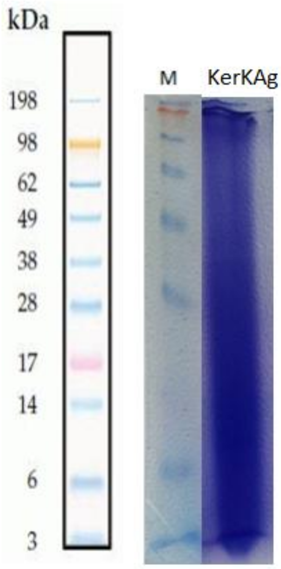

Figure 1. The range of molecular masses corresponding to the marker, M, and molecular mass distribution in keratin hydrolyzate, KerKAgr

The marker has a known molecular mass range of 3-198 KDa. Keratin hydrolyzate contains proteins with varying molecular masses, in the range of 3-198 KDa, throughout the marker domain. The electrophoretic pattern of wool keratin (Figure 1) shows the main two groups of proteins associated with keratin, intermediate filamentous proteins and matrix proteins. High molecular weight bands (45-60 kDa) attributed to filamentous proteins with a low sulfur content and low molecular weight bands attributed to proteins with a high sulfur content (20-10 kDa) and high glycine /tyrosine (6-9 kDa) content can be observed [27]. These considerations highlight the presence of proteins with a high sulfur content but also rich in glycine/tyrosine with low molecular masses in the keratin hydrolyzate extracted with potassium hydroxide, but also proteins with a low sulfur content and high molecular mass attributed to the proteins filamentous.

Determination of particle size by DLS

KerKAgr was analyzed with Zetasizer Nano ZS equipment, Malvern. Three measurements were made to determine the size of the particles and the Zeta potential. Two major populations were measured (Figure 2) at 164 nm and at 1106 nm, with an average of 527 nm and polydispersity of 0.739. These data confirm the analyzes obtained by the electrophoresis method of obtaining compounds with molecular masses lower than 20KDa, but also some compounds with high molecular masses.

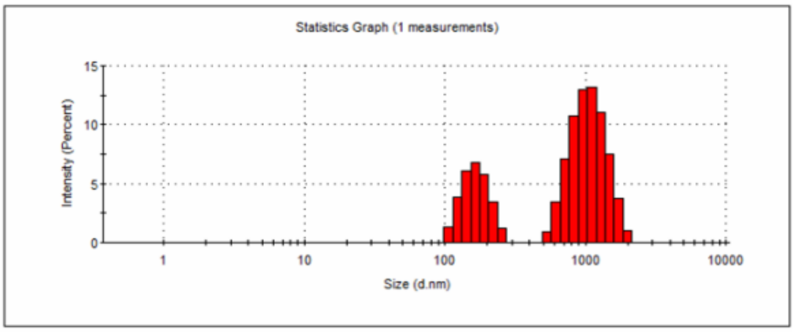

Figure 2. Histogram of particle size distribution in keratin hydrolyzate, KerKAgr

Zeta potential of -33 mV is an indicator of sample stability. A sample is considered stable if the potential value is outside the range (-30; +30 mV). The values included in this range suggest the tendency of agglomeration or deposition of particles. Also, the sign represents the type of charges on the surface of the particles, in the present case being negative charges (Figure 3).

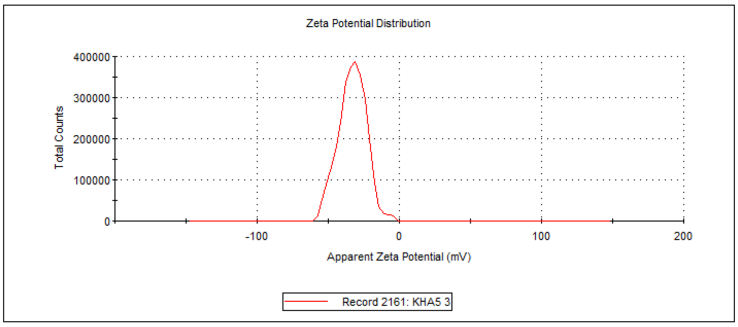

Figure 3. Zeta potential of keratin hydrolyzate obtained with potassium hydroxide, KerKAgr

RESULTS AND DISCUSSION

Testing and Evaluating the Functionality of Keratin Hydrolyzate on Wheat Seeds

The functionality of keratin hydrolysates has been tested and evaluated by using them in treatments applied to various types of wheat seeds. The keratin hydrolyzate obtained by alkaline hydrolysis in the presence of potassium hydroxide was used in different concentrations to treat the wheat seeds and then their growth was monitored.

Two types of wheat were treated with keratin hydrolyzate: Tamino and Mirastar. Wheat grains were treated with KerKAgr keratin hydrolyzate using the dilutions of 3% and 5% in water compared to the control sample germinated in water.

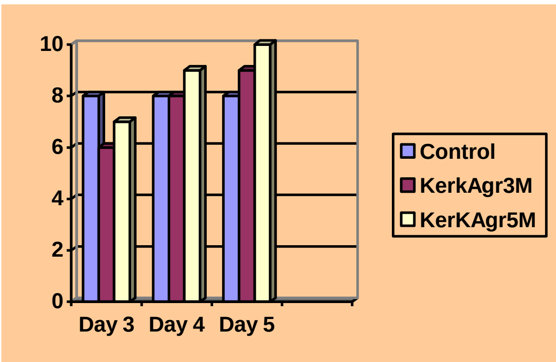

Figure 4. Germination rate for Mirastar wheat type

Mirastar and Tamino seeds treated with 3% and 5% KerKAgr had a higher germination rate on days 4 and 5 of the experiment compared to the control by up to 20% (Figures 4, 5). For the Tamino wheat type, treated with 5% KerkAgr, a higher germination rate is observed in all days of the experiment compared to the control (Figure 5).

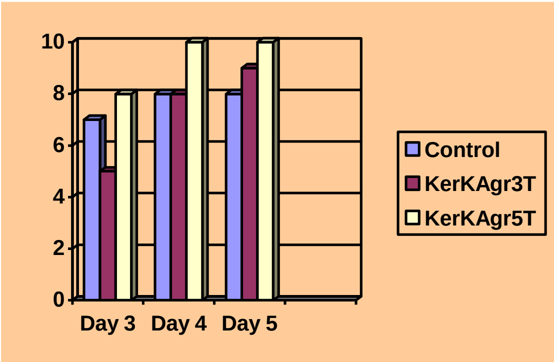

Figure 5. Germination rate for the Tamino wheat type

When measuring the length of the plants in the case of the Tamino type of wheat, an accelerated growth effect of the treatment with KerKAgr is seen compared to the control plants, in all days of the experiment, noticing a higher increase for seeds treated with 5% KerKAgr (Figure 6).

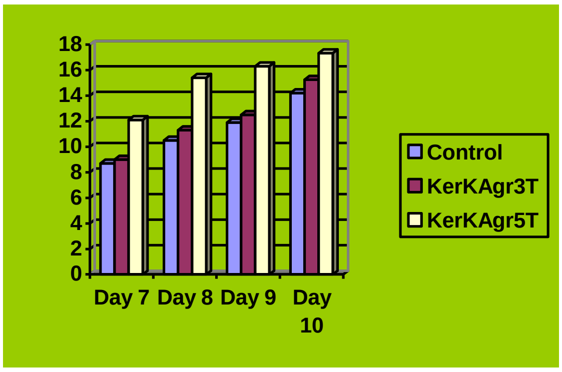

Figure 6. Average plant length (cm) for the Tamino wheat type

In the case of the growth of Mirastar wheat, an acceleration of the growth of plants treated with KerKAgr compared to the control is observed and plants continued to grow throughout the experiment (Figure 7).

The results of the treatments indicated a stimulation of the growth of wheat plants until 7.1% for Mirastar and 7.4% for Tamino wheat in the case of using the 3% dilution and 14.3% for Mirastar and 21.7% for Tamino wheat in the case of using the 5% dilution compared to the control (Figures 6, 7).

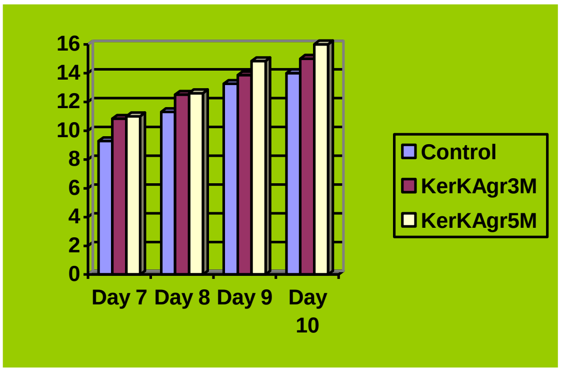

Figure 7. Average plant length (cm) for Mirastar wheat type

Keratin hydrolyzate has 10%-20% higher biostimulating effects for the germination of wheat seeds compared to the control sample and the growth of plant length was 7.1-21.7% higher than the control. The KerKAgr product made by hydrolysis with potassium hydroxide has specific properties for applications in agriculture. Physico-chemical analyses show that the hydrolyzate is rich in minerals, nitrogen and protein substances necessary in the plant growth process. KerKAgr keratin hydrolyzate was used in treatments on wheat seeds (Tamino and Mirastar) and the observations made showed an improvement in the germination rate and a stimulation of plant growth.

CONCLUSIONS

An eco-friendly multifunctional fertilizer based on keratin from sheep wool was prepared. Keratin hydrolyzate, KerKAgr, was obtained by alkaline hydrolysis with potassium hydroxide, and characterized physico-chemically. KerKAgr keratin hydrolyzate was tested and evaluated in treatments on wheat seeds and a 10-20% higher stimulation of the seed germination rate and a 7.1-21.7% higher plant length was observed compared to the control sample. The good results obtained in the applications of keratin hydrolyzate in agriculture show that keratin hydrolyzate can be the basis for obtaining new biomaterials with various applications. The utilization of wool by-products from the leather processing industry leads to a decrease in the amount of waste and the prevention of environmental pollution.

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RECENT DEVELOPMENTS IN ENVIRONMENT-FRIENDLY METHODS FOR VALUING LEATHER WASTE AS A MEANS OF PROMOTING THE CIRCULAR ECONOMY: A COMPREHENSIVE REVIEW

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RECENT DEVELOPMENTS IN ENVIRONMENT-FRIENDLY METHODS FOR VALUING LEATHER WASTE AS A MEANS OF PROMOTING THE CIRCULAR ECONOMY: A COMPREHENSIVE REVIEW

ABSTRACT. The leather processing industry produces a significant quantity of waste materials, which can be treated in a manner that is consistent with the concepts underlying the circular economy. This article provides an overview of ways to recycle substances or energy from tannery waste, such as thermal, biological, chemical and other procedures. These approaches have the potential to facilitate the recovery and recycling of a diverse range of recyclable chemical substances like chromium, fats, gelatin vitamins, hydrolysate and minerals, biomass, and microbial waste products for use in other manufacturing operations. All the methods related to leather waste valorization have been discussed in this study to illustrate the recent development in techniques and processes of leather waste. The incorporation of the concept of circular economy has also been depicted. The premise of the circular economy model is that any waste product from the leather industry may be recycled and utilized again in the leather-producing process or in other related sectors. This study demonstrates that the circular economy approach to leather production offers chances for collaboration and innovation across several industries. Collaboration among organizations may lead to the discovery of innovative methods to minimize waste, enhance productivity, and extract value from resources that would otherwise be disposed of. The overview also addresses the state of waste legislation today and how it affects the environment. Technologies for sustainable and intelligent valuation allow for high recycling levels without negatively impacting the natural environment.
KEY WORDS: tannery, waste, valorization, sustainability, chromium

PROGRESE RECENTE PRIVIND METODELE ECOLOGICE DE VALORIZARE A DEȘEURILOR DE PIELE CA MIJLOC DE PROMOVARE A ECONOMIEI CIRCULARE: O REVIZUIRE CUPRINZĂTOARE

REZUMAT. Industria de prelucrare a pielii produce o cantitate semnificativă de deșeuri, care pot fi tratate în concordanță cu conceptele care stau la baza economiei circulare. Acest articol oferă o privire de ansamblu asupra modalităților de reciclare a energiei sau a substanțelor din deșeurile de tăbăcărie, prin procese termice, biologice, chimice și alte procese. Aceste abordări au potențialul de a facilita recuperarea și reciclarea unei game diverse de substanțe chimice reciclabile, cum ar fi cromul, grăsimile, vitaminele din gelatină, hidrolizatul și mineralele, biomasa și deșeurile microbiene pentru utilizare în alte operațiuni de producție. În acest studiu s-au discutat toate metodele legate de valorificarea deșeurilor pentru a ilustra progresele recente privind tehnicile și procesele de gestionare a deșeurilor de piele. De asemenea, a fost descrisă încorporarea conceptului de economie circulară. Premisa modelului economiei circulare este că orice produs rezidual din industria pielăriei poate fi reciclat și utilizat din nou în procesul de producție a pielii sau în alte sectoare conexe. Acest studiu demonstrează că abordarea producției de piele în termeni de economie circulară oferă șanse de colaborare și inovare în mai multe industrii. Colaborarea între organizații poate duce la descoperirea unor metode inovatoare pentru a reduce la minimum risipa, a spori productivitatea și a extrage valoare din resursele care altfel ar fi eliminate. Prezentarea generală abordează, de asemenea, starea legislației actuale privind deșeurile și modul în care acestea afectează mediul. Tehnologiile pentru valorizarea durabilă și inteligentă a deșeurilor permit niveluri ridicate de reciclare fără a avea un impact negativ asupra mediului natural.
CUVINTE CHEIE: tăbăcărie, deșeuri, valorificare, durabilitate, crom

DÉVELOPPEMENTS RÉCENTS DANS LES MÉTHODES RESPECTUEUSES DE L'ENVIRONNEMENT POUR LA VALORISATION DES DÉCHETS DE CUIR COMME MOYEN DE PROMOUVOIR L'ÉCONOMIE CIRCULAIRE : UN BILAN COMPLET

RÉSUMÉ. L'industrie de transformation du cuir produit une quantité importante de déchets qui peuvent être traités d'une manière cohérente avec les concepts qui sous-tendent l'économie circulaire. Cet article donne un aperçu des moyens de recycler les substances ou l'énergie des déchets des tanneries, telles que les procédures thermiques, biologiques, chimiques et autres. Ces approches ont le potentiel de faciliter la récupération et le recyclage d'une gamme diversifiée de substances chimiques recyclables comme le chrome, les graisses, les vitamines de la gélatine, les hydrolysats et les minéraux, la biomasse et les déchets microbiens pour une utilisation dans d'autres opérations de fabrication. Toutes les méthodes liées à la valorisation des déchets de cuir ont été abordées dans cette étude pour illustrer l'évolution récente des techniques et procédés de gestion des déchets de cuir. On a décrit également l'intégration du concept d'économie circulaire. Le principe du modèle d'économie circulaire est que tout déchet de l'industrie du cuir peut être recyclé et réutilisé dans le processus de production du cuir ou dans d'autres secteurs connexes. Cette étude démontre que l'approche de l'économie circulaire dans la production du cuir offre des opportunités de collaboration et d'innovation entre plusieurs secteurs. La collaboration entre les organisations peut conduire à la découverte de méthodes innovantes pour minimiser les déchets, améliorer la productivité et extraire de la valeur de ressources qui autrement seraient éliminées. L'aperçu aborde également l'état actuel de la législation relative aux déchets et la manière dont elle affecte l'environnement. Les technologies de valorisation durable et intelligente permettent des niveaux de recyclage élevés sans impact négatif sur l'environnement naturel.
MOTS CLÉS : tannerie, déchets, valorisation, durabilité, chrome

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INTRODUCTION

Today's business model, which is founded on the idea of "take-make-waste," which is a continuous flow of energy and materials, leads to the fast utilization of natural resources and the creation of waste, the improper management of which damages the ecosystem. Thus, the sector needs solutions that will allow it to lessen its adverse environmental effects while meeting customers' demands [1]. The circular economy (CE), often known as the notion of environmental sustainability, is characterized by a cyclic movement of energy and materials, with an emphasis on refurbishment, restoring, and improving parts [2]. Using sources of renewable energy and reusing waste as additional resources, in simple terms. The concept of circular economy demonstrates more cost-effectiveness compared to the standard financial model due to its reduced reliance on power consumption and resources that are not renewable and more environmentally friendly (reuse of waste materials, reduced pollutant emissions). Its application promotes the growth of businesses through deploying novel technologies and increasing their reputations [3]. The manufacturing of leather is widely recognized as a highly polluting and resource-intensive sector. Approximately 25% of leather is derived from 100% raw materials, necessitating a water consumption ranging from 15,000 m^3 to 120,000 m^3. Consequently, this process results in the production of wastewater weighing between 15 and 50 mg, as well as solid waste ranging from 400 to 700 kg [4]. In addition to the aforementioned factors, it is important to consider the presence of smells, greenhouse gases (namely carbon dioxide, hydrogen sulfide, and ammonia), as well as organic compounds with volatile properties like amines, alkaline compounds, and hydrocarbons. The quantity of chemicals released is contingent upon the treatment methodology and technological processes employed for leather processing within a tannery [5]. The magnitude of the issue is illustrated by the fact that annual worldwide output of leather is predicted to reach 15 MT [4].

Tannery management of waste has hitherto solely involved landfilling and incomplete disposal due to financial constraints. When properly recycled, tannery scraps may serve as a vital component in advancing the cause of sustainable development. Waste disposal and pollution control expenses may be cut with CE plan adoption and leather waste valorization. Protein, fat, and water are the primary constituents of raw leather and processed waste, including trimmings, fleshings, and scouring (with the substances' moisture content reaching around 85%). [6]. The proteinaceous waste product possesses the potential to undergo hydrolysis by acidic, enzymatic or alkaline means, resulting in the extraction of collagen or gelatin. This process offers a cost-effective approach to get these substances, which can serve as valuable raw materials within the medicine and cosmetics sectors [7]. The use of tannery leftovers encompasses their potential for extracting oils and fats and their applicability in the creation of biodiesel [8]. The existing body of published material provides insights into potential avenues for the enhancing the value of waste generated by the leather industry. Several potential applications of leather waste have been identified in academic research. The scope of these applications involves the retrieval of activated carbon from waste derived from bio-collagen leather, with the purpose of purifying biogas, the fabrication of bio polymers from bovine hides, the development of sound-absorbing materials using leather collagen hydrolysates, the synthesis of surfactants being present from the protein portion of tanning wastes, and the creation of organic nitrogen-phosphorus fertilizers from the leather and chicken bones [9-12]. Producing ecological re-tanning compounds is another potential use for waste products from the leather manufacturing sector [13]. The oxidation of chrome Cr^{3+} to Cr^{6+} during the leather tanning process is a major contributor to pollution, and poses a health hazard to humans because of its oncogenic and cancer-causing properties. Contamination of soil and ground water can result from leaking chrome-tanned solid waste or high chrome contents in effluent [14]. Organic chelates can be used for successfully treating solid chromium leather waste, resulting in a 96% recovery rate [15]. Chromium can also be recovered with the help of acidic minerals like H_2SO_4, HNO_3, HCl etc. [16]. Thermal treatment of waste from tanneries can be employed as a means of extracting chrome in the form of Cr_2O_3, which can then be utilized in steel manufacturing within the metallurgy sector [14]. Tasca *et al*. conducted a study that focused on the environmental concerns associated with the tanning industry. The researchers specifically examined different procedures involved in the treatment of hides [17].

In their publication, Hu and his team offered a scholarly piece on the environmental treatment of tannery waste within the circular economy model [4]. Those researchers provided a comprehensive analysis of tannery pollutants and various dumping strategies, encompassing the decrease of effluent, solid garbage, salts and chrome. Pringle *et al*. [18] documented the difficulties associated with the implementation of circular economy (CE) principles within the leather industry. Their study primarily concentrated on the life cycle assessment of leather and the consequential waste produced throughout its manufacturing process. Additionally, they explored various recycling methods, including chemical, biological, and mechanical approaches, while also addressing the corresponding obstacles such as technological limitations, the value of retrieved substances, the existence of an additional market, and the economic feasibility of these recycling practices. A second researcher has proposed a way that could assist leather manufacturers achieve sustainability through optimization and improvement [19]. Specifically, Moktadir *et al*. addressed the problem of consumer consciousness and support from the government as predictors of the deployment of sustainable methods in leather items manufacturing in Bangladesh [20].

The objective of this review is to provide an overview of the most recent sustainable technical advancements pertaining to the leather sector, which is known for its high resource consumption. Additionally, this research aimed to examine the improvement made in managing waste from tanneries through the utilization of novel methods of treatment such as chemical, biological thermal, immobilization techniques. Using these techniques, several leather waste types have been converted to useful products like chromium, fats, gelatin vitamins, hydrolysate and minerals, biomass, and microbial waste products to promote circular economy. No contemporary study has focused specifically on the recycling of leather scraps, as far as we can recognize. In keeping with the principles of the sustainable or circular economy, these byproducts can be recycled for use in the tanning business or employed as a source of secondary raw materials in other industries (such as nutrients, biofuels, building, power, and pharmaceuticals). Entrepreneurs must balance the requirements of customers with ethical waste disposal in the face of rising global concerns about waste manufacturing and the consumption of basic supplies, calling for more study into the best possible method of tannery waste management with the hopes of learning how to most efficiently bring reused materials to the marketplace. Leather waste hydrolysates have potential as a replacement natural fertilizer ingredient. We have also examined the laws that are now binding, since their presence is crucial to the successful execution of massive amounts of technologies that are consistent with the CE plan.

THE WASTE GENERATED BY THE TANNING OPERATIONS

Tanneries generate wastes with a wide range of physical and chemical properties, which increases the complexity of waste management and necessitates a variety of approaches to trash recycling. There are several categories for the solid waste generated from tanned and untanned skins and hides. The quantity of wastewater (a liquid waste) produced is significantly higher. Figure 1 depicts several tanning waste streams and some of the ways in which this trash can be reused or recycled. To reduce the danger posed by ions of heavy metals along with other anions, and tannery residues can be processed using alternative valorization procedures that result in the extraction of high-value substances and components through recycling of materials. The features of various wastes, including their potential benefits and dangers, are shown in Table 1. The global legal categorization of waste generated by the leather industry is contingent upon its composition, particularly the presence of toxic elements such as chromium-containing substances and formaldehyde, as well as its production volume. The relevant legislation seeks to safeguard the well-being and protection of individuals and the natural surroundings by implementing guidelines pertaining to the containment and treatment of waste, stipulating emissions standards, and establishing thresholds for hazardous chemicals [21].

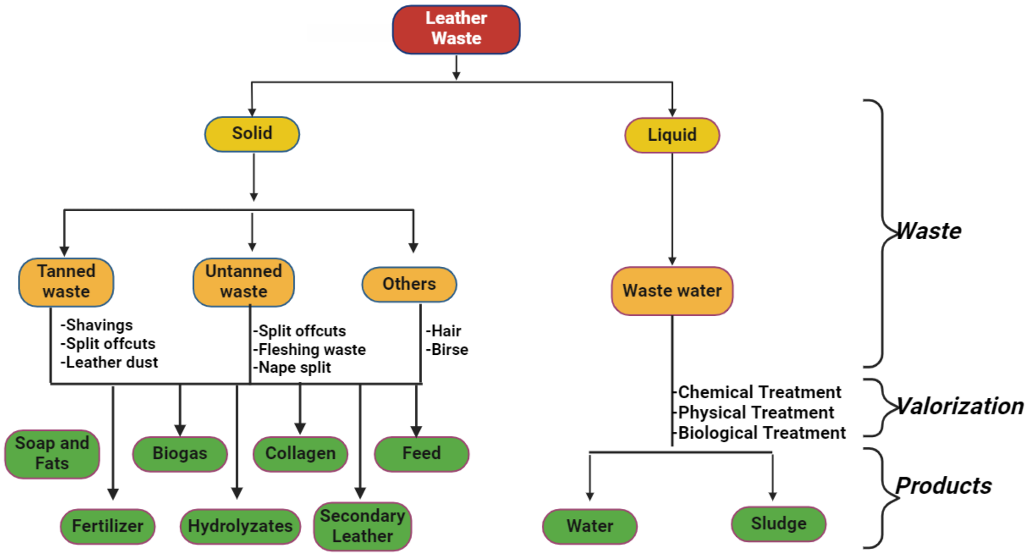

Figure 1. Tannery Byproducts and Potential Valorization Pathways (Source: *Authors compiled*)

Despite the absence of explicit rules pertaining to the tanning business within the European Union, this sector is subject to many requirements concerning the application of chemical compounds, animal by-products, specified dangerous compounds, as well as the promotion of those substances. The introduction of the Industrial Emissions Directive marked the implementation of a comprehensive strategy that emphasizes the integration and evaluation of the effects of commercial pollution and waste on the whole of the ecosystem [22]. Consequently, the defining of emission circumstances and levels in accordance with Best Available Techniques (BAT) has been reinforced. The pertinent papers include Regulation (EC) 1069/2009, the European Regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) and Commission Regulation (EU) 142/2011 [23, 24]. The European Trash Catalogue, which is outlined in the EU Commission Decision, serves as the primary reference for the generation of waste. According to the legislation, tannery related waste is categorized under label 04.01, which pertains to waste related to the tanning sector. The regulation of the European Union also provides explicit definitions for the maximum permissible levels of certain substances and components in leather goods. The inclusion of polychlorinated triphenyls (PCTs), arsenic, organotin chemicals as well as polychlorinated biphenyls (PCBs), and is strictly forbidden in tanning industry [21]. The highest recorded levels of heavy metals, namely Cd, Cr^{+6}, and Pb, are 100, 3, and 90 mg/kg, correspondingly. Particular attention is given to minimizing the usage of organic chemicals, namely pentachlorophenol, formaldehyde and azo dyes, due to their inherent hazards, especially to human health [17].

Table 1: Characterization of tannery waste

SL.	Waste/Residue	Explanation	Precious Component	Corresponding Risk	Methods of valorization	Prospective products after valorization	Reference
01	Effluents and wastewater	Liquid residue of leather treatment and pretreatment	Water	Chemicals such as colorful substances, sodium chloride, sulphate, inorganic and organic chemicals, and hazardous metallic substances, particularly Chromium derivatives.	Processes like filtration, coagulation, and precipitation are used to treat wastewater.	Sludge and clean water	[25], [13], [26]
02	Sludge from Tannery	The management of solid trash arising from the treatment of effluent and wastewater.	Mg, Ca	organic substances, coloring agents, chromium, and microorganisms that are harmful	burning, hydrolysis, leaching, and putting trash in landfills	Cinders/ash	[16], [27], [28]
03	Cuttings and splits	substantial waste produced during the shaping and cutting of leather that cannot be reused	Fat and protein	Organic materials, including colors and tanning substances, are commonly associated with the element chromium	digestion, combustion, and hydrolysis	Active carbon, ash, and collagen hydrolysate	[29], [30], [31]
04	Shavings waste	waste products from cutting and shaping leather.	collagen	chromium, tanning agents, and dyes	Basic hydrolysis	Hydrolyzed protein from collagen with less Cr	[32], [33], [34]
05	Buffing dust	Hazardous solid waste, consisting of micro fine powder of collagenous fibrils, is produced during the leather buffing process.	collagen	Synthetic fat, color, tanning substances, and Chromium	digestion by anaerobic processes, hydrolysis, and burning	collagen hydrolysate and activated carbon	[35], [36], [37]
06	Waste of fleshing	waste from the tanning process of hides that is made from the skin remaining after the tissue attached to the hide of the animal is removed	Fat and protein	NaCl, tanning substance	burning, hydrolysis, and extraction of fat	Soap, biofuel, and hydrolysate of proteins	[38], [39], [40]
07	Hair	Hair pulping results in the generation of solid garbage.	keratin	Not found	Decomposition, combustion, and land filling	Activated carbon, ash, and keratin hydrolysate	[41], [42], [43]

The case study of the leather sector in Bangladesh was employed to illustrate the many obstacles that contribute to suboptimal outcomes in the adoption and implementation of environmentally friendly technology [44]. Notwithstanding the implementation of novel facilities for treating wastewater, the existence of dated equipment and the utilization of significant quantities of substances presented formidable challenges. The assistance for the adoption of sustainable supply-chain management techniques in poor nations is lacking in both scientific and financial aspects from the state [45]. Insufficiently trained personnel, lacking awareness of environmental hazards, are employed in the operation of ineffective facilities with excessive emissions that fail to fulfill regulatory standards [46]. It is noteworthy that the absence of pressure exerted by globally recognized organizations fails to promote the promotion of cleaner manufacturing and minimized waste within the tanning sector.

THE ENVIRONMENTAL EFFECTS OF THE TANNING ACTIVITY

Enhancing the environmental quality via the use of cleaner manufacturing practices has a positive impact on the overall well-being and health of human populations. The achievement of long-term sustainability in the tanning industry requires a comprehensive strategy that encompasses several dimensions, including technological, financial, environmental, institutional, social, and legal elements [47]. The tanning business is known for generating significant quantities of trash, which, while not consistently, is often categorized as harmful. The heavy metals, organotin chemicals, formalin, PCBs, Azo dyes, PCTs, and phthalates are often cited as notable examples. These compounds often result in impairment of the kidneys, lungs, urinary, liver, and genital systems, as well as causing conjunctivitis and skin irritation. Their concentrations in the plasma and bloodstream are measured to detect their high levels [48]. Chromium, namely in the form of Cr^{6+}, is present in significant quantities within the effluent generated by the leather sector. This particular form of chrome exhibits notable attributes such as elevated mobility, assimilability and bioavailability [49]. Upon introduction into water and soil, this substance readily integrates into the ecological food web, hence exerting a deleterious impact. It has the potential to impede or hinder plant development, while also instigating various ailments in humans as well as animals. At high doses, it may potentially induce fatality [50].

Table 2 presents the various techniques used for the removal of Cr^{6+} from effluent, along with their respective efficiencies. Table 2 illustrates a wide array of effective techniques for the removal of chromium from tannery effluent. The efficiency of the system exhibits a range of values, often falling within the interval of 90% to 100%. Every approach has advantages and disadvantages. The process of sorbing chromium onto activated carbon or attaching it to organic matter by the process of biosorption akin to biological accumulation in fungus culture, yields significant removal rates. However, this approach presents a challenge in terms of chrome retrieval from sorbents or effective management of the sorbent material.

Table 2: The removal of Cr^{6+} from wastewater generated during the tanning process

SL	Cr^{6+} concentration before treatment (mg/L)	Cr^{6+} concentration after treatment (mg/L)	Removal Percentage	Removing Technique	Reference
01	100	9.50	90.5%	Activated carbon assisted sorption	[51]
02	2700	0	100%	Electric coagulation	[52]
03	2	0	100%	Photo-electrocatalysis	[53]
04	2920	3.46	99.9%	Biosorption	[54]
05	12.26	0.10	99.9%	Fungus Consortium bioremediation	[55]
06	544	19.00	96.5%	Electroplating	[56]
07	5010	75	98.5%	Hydroxides precipitation	[57]

The aforementioned approaches are characterized by their extended duration, which therefore renders them economically inefficient. The use of precipitating techniques necessitates the introduction of hydroxides, which result in the extraction of chromium and subsequent enrichment of alkali metals in the effluent. The use of electricity in methods that facilitate the precipitation of chromium in either metallic or oxide state is deserving of significant notice. By using this method, the retrieval and reintroduction of chromium into the production cycle may be effectively achieved, aligning with the principles of cleaner manufacturing. However, because to the exorbitant cost of power, the procedure is not economically viable [58]. CH_2O, primarily employed in the resinous state for the purposes of tanning and the preservation of leather, has carcinogenic characteristics. Consequently, it is essential to diminish or remove its usage and substitute it with substances such as mimosa extract, gallic acid or vegetable polyphenols. The proper handling of discarded or surplus leather necessitates the appropriate handling of its colors, particularly those belonging to the Azo group. The use of tanning agents is regulated, and the imposed restrictions on their usage are somewhat stringent. Non-harmful vegetable dyes have the potential to serve as suitable substitutes. The pigments found in flowers, fruits, and vegetables, notably carotenes, have a significant capacity for coloration [59]. In the event where synthetic dyes are the only means of coloring leather, it becomes necessary to subject the leather to decolorization after its usage, which may be achieved by the enzyme-mediated activity of fungus [60].

Furthermore, conventional techniques may be used to extract colors from leather, followed by the treatment of the resulting wastewater by processes such as adsorption using active carbon substances, flocculation, coagulation, and ion exchange for example [61]. The available literature also provides evidence of several additional substances, when employed in the process of tanning, may elicit detrimental impacts on both human health and the environment. Phthalates function as plasticizers, hence preventing the occurrence of fractures in crucial regions of leather. These chemicals have been shown to induce reproductive complications in both males and females. During the concluding phase of manufacturing, tanneries use biocides as a means of inhibiting the proliferation of microflora. Allergy or irritation to the skin may be induced by these substances, while high dosages may result in symptoms such as migraine or vertigo [48]. At the moment, the generation of energy is a major producer of greenhouse gasses, whereas recycling of materials and energy occurs at relatively low levels. Wastewater treatment, namely waste management, ranks as the second most energy-intensive procedure [62]. Similar to waste treatment, the process of tanning leather is characterized by its significant energy use. The leather tanning phase, including several discrete procedures conducted at reduced temperatures, accounts for roughly 90 percent of the total energy use [19]. The existing research indicates that the predominant methods used for recovering energy from solid tannery waste are gasification, hydrothermal treatment carbonation, and anaerobic fermentation [63]. Special consideration should be given to the potential risks associated with hazardous compounds, such as chrome, colors, and formaldehyde, due to their adverse effects on waste processing and the use of resultant intermediate materials. However, it is important to note that the storage of these chemicals might potentially result in leakage, leading to significant environmental pollution and the potential integration of certain compounds into the food chain. Furthermore, the aforementioned compounds provide a potential hazard to those employed in tanneries, since they may result in the development of skin disorders and respiratory difficulties, despite the use of protective clothing and footwear [64].

TECHNIQUES FOR THE MANAGEMENT OF BY-PRODUCTS DERIVED FROM THE LEATHER SECTOR

Through Chemical Methods

The first tanning process results in the generation of substantial quantities of solid waste. This includes around 7-8% of raw, unprocessed scraps. Proteins make up the bulk of these elements. The conversion of this particular waste into useful goods may be achieved using either acidic [65] or alkaline hydrolysis [32]. Proteins hydrolysate is derived via the application of acetic acid, with an ultimate concentration of 1.5 M, to untanned raw trimmings. The optimal process efficiency, which reaches around 80-85%, is achieved at a temperature of 80°C [31]. In a study conducted by Khatoon *et al*. several techniques were examined and compared in order to isolate protein constituents from chromium leather garbage. Protein and amino acid extraction was performed using alkaline techniques including sodium hydroxide (NaOH), calcium oxide (CaO), and magnesium oxide (MgO), as well as an acidic process utilizing sulfuric acid (H_2SO_4). The extraction process is adversely impacted by both elevated quantities of extractants and increased process temperature, resulting in the decomposition of proteins [66]. Like other heavy metals, chromium undergoes precipitation as $Cr(OH)_3$ under alkaline circumstances. The precipitate is collected using filter paper, followed by the separation of insoluble proteins by a reduction in temperatures to 4 °C. Optimal outcomes are achieved by using H_2SO_4 at a temperature of 40 °C and NaOH at 50 °C temperature. The agriculture industry has already been identified as a primary beneficiary of this invention, which includes things like fish food, feed for chickens, and organic compost. Important consideration must also be given to the recovery of amino acids from hide treatment wastewater produced during the unhairing-liming, soaking and curing stages. The protein portion obtained from the effluent is precipitated by using acidic conditions, specifically 2M H_2SO_4. This precipitated fraction is then exposed to a degreasing process using CH_2Cl_2 for a duration of 5 hours. Following the degreasing step, the protein fraction is hydrolyzed in the existence of HCl for a period of 24 hours. This hydrolysis process serves to minimize tannery waste and produce agents that are ecologically benign. The acetylation of a mixture of amino acids is the process that results in the production of surfactants [10]. Polypeptides were also extracted from the leather dust created during the polishing process. In an autoclave, NH_4OH is used to hydrolyze the dehydrated wastes (C_2HCl_3). There was a 55% increase in protein production. The addition enhanced the material's primary physical qualities [67].

The utilization of leather waste from processing as an economical collagen source is noteworthy due to its numerous uses in the cosmetic and medical sectors, as well as its potential to increase the mechanical qualities of composites [7, 68]. The type I collagen is the prevailing constituent found in the dermal layer of all animal skins, serving as a fundamental component in the formation of bone, tendon, and many types of connective tissues [69]. The solubilization of the skin matrix component was conducted using acetic acid and propionic at a concentration of 0.5 M and a temperature of 4 °C. The effectiveness of collagen extraction was found to be 94% and 85% in the two respective experiments. The component separated by each acid belonged to type 1 and shared similar chemical and physical characteristics [7]. Collagen-based waste-derived hybrid composites have been shown to have excellent biocompatibility. Due to their characteristics, they may be useful in the field of biomedicine [70]. Tannery waste collagen is used in several publications. Collagen hydrolysis produces sound-absorbing nanofibers. First, alkaline, acidic, and enzymatic hydrolyses occur. The efficiency research showed that alkaline hydrolysis yielded the most (64%) whereas acid hydrolysis enzymes did not impact the process. After electrically spinning with polyvinyl alcohol, polyacrylonitrile fills the hydrolysate layers. Acoustic studies showed that the composite material absorbed 1000–2500 Hz sound [71]. An additional illustration entailed the utilization of extracted collagen to extend the duration of gypsum's solidification process. Hydrolysis of tannery waste occurred at 90 °C in sodium hydroxide solution. The method was 85% efficient. Flocculation and diatomaceous earth eliminated chromium. Additional component lengthened gypsum setting time but decreased strength [72]. The production of alumina composites involved the use of collagen that was extracted by the process of acetic acid hydrolysis. Initially, the process of removing chrome in leather wastes involves the utilization of strong sulfuric acid. The samples that have been stripped are submerged in a mixture of HCl, ethylenediaminetetraacetic acid (EDTA), and C_2H_5OH, with a pH level of 8 for a duration of 3 days. Subsequently, the samples undergo acid hydrolysis for a period of 24 hours. The collagen powder obtained had a chromium concentration of around 6%. The composite material was subjected to the hybrid casting process after being mixed with alumina. The composite material exhibited a notable enhancement in both tensile strength and its hardness, with increases of 40% and 55% correspondingly [73]. Limed fleshing leftovers, which encompass skin tissue and the muscles, are abundant in protein content and constitute approximately 60-70% of the waste generated by tanneries. Traditionally, these residues undergo thermal, chemical, and enzymatic treatments to produce feed additives, glue, or biogas [74, 75]. The work conducted by Ammasi *et al*. introduced a novel technique with the objective of utilizing treated with lime fleshing residues to provide a feasible source of polypeptides to improve the quality of leather surfaces. To do this, an alkaline protease isolated from *Bacillus* crolab5468 is used in an enzymatic hydrolysis reaction. The garbage that was formerly produced is subjected to hydrolysis for a duration of 60 minutes at a temperature of 35°C, while the enzymes present in the waste are rendered inactive at 90°C temperature. The acquired polypeptides were tested on the skin of goat to determine their effect. Comparative analysis revealed notable enhancements in both visual aesthetics and mechanical strength characteristics when comparing treated leather samples to their untreated counterparts [66]. Protease uses the nitrogen and carbon in fleshing waste to digest the hide and remove the fur [76]. Lipids from flushing leftovers can be utilized to make biofuels [77]. The possibility of using tannery waste in the manufacture of biodiesel was also highlighted by Yuliana *et al*. [78]. Supercritical ethanol is used for lipid extraction. A remarkable output of 98 percent was accomplished.

Several research studies have identified novel avenues for the use of leather waste treatment. In their study, Yoseph *et al*. [79] demonstrated a methodology for the extraction of elastin, a crucial constituent of connection tissue that has substantial importance in the formulation of lotions, ointments, and anti-aging goods. They focused on isolating elastin from unprocessed cuttings. The mechanism involved in the extraction of this particular constituent from tannery effluents is inadequately comprehended. The waste materials are immersed in a mixture containing NaOH (5%), CaO (10%) and NaCl (5%) for a duration of 8 hours. The liquid portion is isolated, subjected to purification techniques, and subsequently subjected to evaporation. Insoluble elastin is acquired by the process of autoclaving, which is conducted under certain conditions consisting of a temperature of 120 °C, a pressure of 15 psi, and a duration of 20 hours. Since elastin has a specific amino acid composition, the characterization technique verified the accurate separation of proteins. The utilization of waste as a potential resource for re-tanning purposes is a viable application. The composition of these compounds mostly relies on formaldehyde, with concentrations reaching up to 50 mg per kilogram in leather. The researchers suggested the employing of a substance derived from discarded waste from tanneries cuttings. The residue underwent pretreatment by immersion in a hydrogen peroxide alkaline solution consisting of 7.5% w/w NaOH and 10% w/w H_2O_2 for a duration of 6 hours. The material underwent thermal hydrolysis at a temperature of 100°C for a duration of 5 hours. The product underwent neutralization using an acid that is organic with a pH of 8.5, followed by the process of spray drying. A comparative re-tanning experiment was done using a phenol condensate-based product. The test results demonstrated enhanced leather color intensity and heightened resilience to fracturing [13]. In their study, Majee *et al*. [11] introduced a novel fertilizer formulation that incorporates tannery waste as a constituent. They provided a detailed account of the methodology involved in the production of a NPK-based fertilizer utilizing, chicken bones, blue leather, and hyacinth water. The utilization of tannery trash, which has undergone a two-step alkaline hydrolysis process to remove chromium, is employed as a nitrogenous resource. The material undergoes acid hydrolysis, resulting in the formation of solid collagen. This collagen is subsequently pulverized and mixed with the meal of bones and dehydrated plant biomass. The study saw a 45% increase in soil nitrogen content when compared to unfertilized soil, and a 19% increase compared to soil treated with industrial fertilizer.

Chemical processes, such as the extraction process, hydrolysis, and enzyme-mediated hydrolysis are primarily employed for the valorization of leather waste. The provided illustrations demonstrate the process of isolating proteins or lipids and highlight the potential applications of the obtained components. The presentation of the management of by-products, namely chromium sludge that poses environmental risks, is not consistently addressed in relation to the enhancing the value of chrome leather waste. An innovative strategy involves utilizing waste materials as a viable resource for the production of means utilized in leather treating, and a supply of ammonium in macro element fertilizers. That specific recycling methodology aligns with the underlying principles of an economy that is circular and environmentally-friendly innovations.

Through Biological Methods

Instead of sending waste that is organic to a landfill, it can be composted for biological degradation [80]. The implementation of aerobic stabilizing techniques on tannery sludge offers significant benefits in terms of waste mass reduction, emissions mitigation, and prevention of landfill leakage. This approach is crucial for achieving ecological disposal practices [81]. The utilization of compost derived from a combination of tannery sludge and agricultural waste, when employed as a fertilizer for the purpose of cultivating ornamental peppers, is being investigated. There was a substantial augmentation in the quantity of leaves, vegetables and fruits, and chlorophyll content inside the leaves [82]. Vermicomposting is a biological process that facilitates the degradation and stabilization of organic materials, resulting in the production of a fertilizer that is abundant in nutrients. The remediation of sludge from tanneries through the utilization of earthworms necessitates the incorporation of other substances, such as manure, in order to diminish the concentration of chromium ions present in the initial material. This step is crucial as chromium is known to be harmful to earthworms. Co-vermicomposting is a method of composting that involves the simultaneous use of earthworms and microorganisms to decompose [83]. The utilization of vermicompost derived from the fleshing of waste from tanneries resulted in a notable enhancement in crop productivity, exemplified by a growth increase of over 10% in tomato plants [84]. Plant growth was stimulated by vermicompost made from tannery garbage, but there was no discernible rise in chromium levels in lovely bell pepper plants [85]. Nevertheless, the extended utilization of compost presents a potential risk of chromium ion buildup inside the soil. The findings of a decade-long investigation on the utilization of compost tannery waste revealed alterations in soil characteristics. The increase in the amount of organic elements and macroelements has a favorable outcome. Simultaneously, there is an increase in the concentration of chrome in the ground and a corresponding rise in its pH, leading to alterations in the composition of soil microflora. The period of highest magnitude in the augmentation of chromium concentration within the soil occurred within the initial five-year timeframe of the experimental study [86].

The process of breaking down organic materials by anaerobic bacteria is known as anaerobic digestion. Biogas is generated as a carrier of energy, while the resulting sludge, characterized by its elevated nutritional contents, can be utilized as a fertilizer. Anaerobic digestion (AD) has demonstrated promising results in the efficient breakdown of waste products generated by tanneries. Research conducted under semi-pilot settings has demonstrated that the utilization of biogas derived from this particular method has the potential to decrease energy usage by around 7% [87]. It is recommended to include tannery residues into co-digestion with other residues, mostly due to their elevated nitrogen-rich air content and the imperative to maintain an appropriate carbon-to-nitrogen proportion of 25:1 [88]. The inclusion of supplementary digestive components results in a reduction in the concentration of unwanted contaminants, such as chromium. Research has demonstrated that the digestion together of scraps and sludge from tanneries exhibits a significant reduction in power usage, surpassing 75% [89]. The existence of sulfides in leather fleshing waste necessitates cleaning prior to liquid entry into digesters, since this might raise hydrogen sulfide content in the production of biogas [90]. Microbial biological degradation has been identified as a viable approach for the breakdown of specific waste materials generated by the leather industry. The research findings indicate that *Brevibacterium luteolum* MTCC 5982 is a microbe with the ability to breakdown keratin derived from goat hair in an efficient manner. The highest level of hydrolysis was attained at the end of a 72-hour period, demonstrating an efficiency rate of 80% [41]. The degradation of high in protein chromium shavings may be effectively accomplished by *Bacillus subtilis* P13, a strain known for its production of keratinolytic serine protease. This particular strain exhibits a substantial capacity for enzymatic production, wherein a significant portion of the resulting product may be effectively allocated for pre-tanning applications [91].

Elevated levels of chrome in garbage have the potential to impede microbial activities; nonetheless, it is worth noting that organisms possess the ability to acclimate to platforms that incorporate this particular metal [92].

Microbial populations exposed to elevated levels of chromium have been observed to develop adaptive mechanisms, including biosorption, which involves the attachment of metal ions to cell wall polymers, and bioaccumulation, a complex process by which cells actively accumulate ions within their intracellular environment. The microbial breakdown of fleshing by *Clostridium limosum* not only led to a reduction in the amount of contaminants present, but also resulted in the concomitant synthesis of an extrinsic acid metalloprotease [93]. In a similar vein, *Synergistes* sp. has the capability to synthesize aspartate proteases. Proteases, being enzymatic catalysts, provide extensive utility throughout many sectors of the industrial landscape. The production in this particular scenario serves as an additional benefit to waste treatment [94]. The process of bioleaching has demonstrated its efficacy in the removal of chrome ions from tanning sewage [95]. The solubilization of chromium ions is facilitated by acid-producing microbes, specifically *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* and the resulting sludge, once separated, can be utilized in agricultural applications. By carefully selecting appropriate bioleaching circumstances, it is possible to achieve a significant increase in the leachability of chrome from waste products. In fact, for tannery sludge, the leachability can reach levels as high as 98% [96].

Finally, it can be said that valorization of tannery waste via biological means can be an intriguing alternate to conventional approaches. These technologies are crucial to the leather industry's waste management strategy since they allow for the effective recycling of valuable substances (organic substances, chromium, and fertilizer ingredients) and energy (biogas), as well as the development of new goods (enzymes).

Through Immobilization Techniques

Composites may contain waste tannery materials [97]. Cracking in asphalt is reduced when scraps of chrome-tanned leather are embedded in the material [98]. In the context of reusing tannery waste, leather-fiber composites were created through the blending of leather waste with artificial and organic fibers. The resulting yarn exhibited a high level of density, rendering it well-suited for utilization in the garment sector [35]. Insulation and acoustic panels made from leather scraps or their isolated components are among the “green building materials” now in use. The dried form of chromium chips and buffing dust has a very low heat conductivity and does not compromise the strength of building materials [99]. The thermodynamic simulations conducted on a building that was insulated using panels composed of a blend of leather (consisting of cleaning dust and chromium parts) and carpenter's trash have substantiated its significant thermal shielding efficacy. The examination of relaxation levels and usage of energy provides evidence that these panels have the potential to compete commercially with other substances such as polystyrene. The implementation of more than 7 mm in thickness coating of buffing dust results in a reduction of over 50% in the yearly energy usage [100]. Tudose *et al*. [101] demonstrated that the utilization of leather waste can yield materials possessing favorable thermo-insulating characteristics. The researchers conducted an analysis on the diffusion of heat properties of seven materials derived from tannery and woolen waste in their study. The untreated wool materials demonstrated the lowest values (6.0×10^{-8} m^2/s), followed by powder leather waste (8.5×10^{-8} m^2/s).

The performed feasibility research and environmental impact analysis have affirmed the suitability and satisfactory insulation qualities of the insulation material derived from mixed leather scraps, as well as the readily accessible insulation board composed of polyurethane. However, the determination of which technology possesses a more substantial environmental impact has not been reached. Simultaneously, the substantial upside potential of waste from tanneries was effectively showcased, underscoring the imperative for conducting comprehensive economic evaluations [102].

The examples shown demonstrate how, even in the absence of further processing, tannery waste treatment can add value to novel composite materials. The literature review reveals a lack of comprehensive understanding on the ecological and economic dimensions associated with the production of this particular material.

Through Thermal Methods

The utilization of solid leather waste as a potential feedstock for the production of energy is supported by its notable high higher heating value (HHV) of around 16 MJ/kg. Burning and pyrolysis are widely recognized as significant thermal methods of treatment for these wastes. The process of burning leather trash, characterized by its elevated nitrogen composition, results in the release of substantial quantities of nitrogen oxides (NOX). The co-incineration of plant materials, such as wood pellets, results in reduced emissions mostly due to their significantly lower nitrogen concentration. This reduction in nitrogen content ensures that the emissions of nitrogen oxides (NOX) meet the required emission criteria. It is necessary to conduct monitoring of the concentration of deleterious organic chemicals present in gases from the combustion process [103]. Energy and chrome substances can be recovered using pyrolysis heat treatment, which is believed to boost tannery savings (by a number of millions of dollars annually) [104]. When comparing combustion to pyrolysis, it is evident that the latter is highly influenced by many parameters such as temperature and heating rate. As a result, pyrolysis generates gas and liquid byproducts with significant energy content, making them suitable for use as fuel [28]. Gaseous, liquid, and solid end product mass ratios are greatly impacted by the ultimate pyrolysis temperature. At temperatures under 450 °C, the solid phase dominates, indicating inadequate breakdown of organic material. Additionally, a high gas phase with significant CO_2 concentration is detected. Raising the temperature around 500 °C increases the liquid phase share. While gas production declines with heat, calorific value of this increases because of greater hydrogen and methane concentration, achieving about 9.50 MJ/Nm^3 at a temperature of 500 °C [105].

Waste materials can also be gasified to produce energy. Syngas, the resultant higher-energy byproduct of this procedure, may be burned and used as a fuel replacement in tanneries [106]. During heat operations, the process of immobilizing Cr occurs in a solid state, hence facilitating its safe disposal. At elevated temperatures during combustion, there exists a potential hazard of transforming Cr^{3+} into the toxic Cr^{6+}. It is noteworthy that chromium undergoes a shift in its state of oxidation to Cr(VI) when exposed to high temperatures and oxidizing chemicals. To prevent this transition, it is advisable to do pyrolysis at temperatures below 600 °C [107]. The waste generated during chrome tanning of leather mostly comprises protein collagen and chromium. After subjecting the trash to pyrolysis at temperatures of 700 and 800 °C, chromium (Cr) was found to be abundant in the carbonate compound as Cr^{3+} [108]. The carbon matrix is strongly connected to trivalent chromium compounds. The results of leaching tests demonstrated that the trash was stable and did not leak into the surroundings [109]. The amounts of carbon and chrome found in tannery waste's carbonized pyrolysis products make them a suitable replacement for fossil coal in steelmaking. Carbonized leather scraps were used in place of coal in the production of iron ore pellets. By including leather scraps into the mix, we were able to boost the pellets' compressive property and Cr^{3+} content, resulting in a 50% recuperation of metal rate [110].

Activated carbons derived from leather garbage possess a notable capacity for adsorption due to their substantial porosity, rendering them suitable for a diverse range of usages. One of the most common environmental uses is for filtering out hazardous chemical compounds and dyes from water and air [111]. In addition to their application as adsorbent for aquatic contaminants, activated carbons enriched with gaseous nitrogen can function as electrode materials thanks to their high and consistent charging and discharging capability [112-114]. Other intriguing materials for energy storage systems, especially electrode materials, are multilayer porous graphitic carbon substances produced from leather waste [115]. Tannery garbage might be utilized to create heteroatom enriched aerogels made of carbon by activated burning, which could then be employed in electrode production [116]. Instead of using hazardous carbon black, rubber compound fillers may be made from carbons that are activated formed on CaO via limed fleshing pyrolysis [117]. Filler substances for lighter blocks of cement can be made from carbonated buffing powder from the leather industry. The addition of iron nanoparticles prevented Cr^{3+} from being converted to Cr^{6+}, hence enhancing the product's mechanical characteristics even more [118].

Their wide range of uses demonstrates the great potential of activated carbons, which are produced by pyrolyzing tannery waste. The potential applications are enhanced as waste usage becomes more efficient, aligning with the principles of a closed-loop economy and significantly contributing to the reduction of pollution in the environment.

Other Methods (Miscellaneous)

The utilization of tannery waste that contains chromium has the potential to be transformed into ceramic pigment. In order to get the desired outcome, waste material is subjected to a process of washing before to being subjected to temperatures exceeding 1000 °C. This process aims to produce a permanent greenish chromium pigment suitable for use in ceramics products [119]. The addition of minerals during vitrifying plasma results in a glass-like substance with minimal component leachability. The trash can be stacked away or even utilized as filler in building projects [120]. Reinforced biological composites made from leather scraps and cement have useful mechanical qualities and can be used in the building industry [121]. Bricks and other ceramics can be made from a mixture of tannery sewage and clay. Immobilized in a rigid matrix, chrome is harmless to ecosystems [122]. The utilization of leather waste generated by the tanning industry has the potential to enhance the efficacy of composite material manufacturing processes. The collagen structure that makes up leather has a multitude of polar groups that facilitate the formation of bonds with thermoplastic polymers. The incorporation of leather waste, namely fragments ranging from 10 to 500 µm, at a concentration of 7 to 23%, into thermoplastic starch leads to enhanced mechanical properties and increased longevity of the resulting composites [123]. The utilization of composites comprising polycaprolactone and residual leather particles exhibiting excellent characteristics holds potential for application within the footwear or leather products industry. The utilization of waste leather in the reinforcement of the matrix material offers a fully compostable solution that eliminates the need for high processing temperatures. This is particularly advantageous as it avoids the conversion of chromium in its trivalent state Cr^{3+} to its hexavalent state Cr^{6+} [124]. The effective dispersion of waste fibers inside the matrix is facilitated by their separation into individual fibers. This can be accomplished by the utilization of Solid-State Shear Milling (S3M) technology. As a direct consequence, the material exhibits enhanced its mechanical qualities [125]. Fabricating composites with aqueous polyurethanes resulted in an increase in mechanical characteristics. Hydrogen bonding within the matrix and the garbage cause these characteristics [72]. Polymers like polypropylene can be combined with chromium flakes to create acoustically absorbent composites. Over 90% sound attenuation was shown by Hemalatha *et al*. in the mid-frequency band [126].

The high chromium content of tanning effluent makes it a major environmental hazard. Ultrafiltration (which removes colloids and suspended particles), nano-filtration, and reverse osmosis (which removes ions containing chromium) are all membrane technologies that can be used to treat such streams effectively. High efficiency chromium recovery from effluent streams is guaranteed by carefully selecting separating parameters (pressure, the velocity of flow, and acidity) [127]. In order to retrieve chrome with a high selection effectiveness (above

90%), the membranes used for microfiltration might have their surfaces modified with substances like chitosan [128]. In addition to reducing COD and nitrogen-based pollutants, electrical membrane methods are also successful in recovering chromium. The retention rate of COD is between 87-92% and is affected by the kind of electrode employed in the electrocoagulation/ electrodialysis process, whereas NH3-N and chromium are removed with a 100% efficiency. The end result had the same levels of contamination as regular drinking water [129]. The utilization of a dual approach using microfiltration and a combination of reverse osmosis techniques to handle the treatment of wastewater from tanneries has been seen to yield a wastewater that has been treated that exhibits favorable suitability for application in aquaculture. This assertion is supported by scientific investigations conducted on the snail species *Pila globosa*, which serves as a reliable biomarker for assessing oxidative stress levels [130].

TANNING SECTOR AND THE CIRCULAR ECONOMY

The process of leather production results in significant quantities of waste, which might potentially serve as valuable resources for many sectors (see Figure 2). The available literature demonstrates that tanning residues undergo processing in order to generate re-tanning ingredients [13]. The aforementioned waste materials serve as a reservoir of chromium, which may be effectively repurposed in the manufacturing of leather following suitable treatment methods. The creation of fertilizer from tannery byproducts is an emerging method of waste-free manufacturing. In order to create a nitrogen-rich byproduct that may be used as an ingredient of NPK fertilizers, leather scraps are hydrolyzed in acidic or alkaline solutions [11]. The procedure allows for the elimination of chrome, the amount of which is restricted by law from fertilizer formulas [131]. Hydrolysis allows for the generation of a fertilizer byproduct and a chrome content, both of which have value and fit into the "circular economy" framework. The use of chemical fertilizers can be reduced or eliminated if this trash is recycled. This strategy is an eco-friendlier option. There are several upsides to implementing the strategies of environmentally friendly manufacturing and the circular economy. However, financial evaluation and technological feasibility assessment are just two of the many processes needed to put these approaches into action.

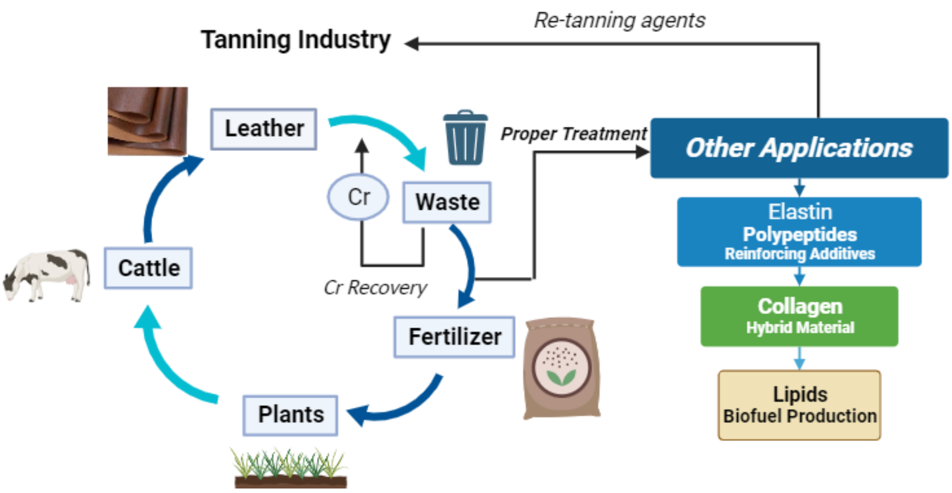

Figure 2. Concept of circular economy in leather sector (*Source: Authors compiled*)

CONCLUSION AND INSIGHTS

Waste from the leather tanning process presents a difficult management challenge due to its varied qualities. When it comes to the environment, nothing beats dumping trash in a landfill. By-products from the tanning industry can be dried, burned, pyrolyzed, and gasified; they can also be treated thermally or mechanically, as in briquetting; they may be utilized as a basis for methane fermentation. Novel biological processes include those that generate digestate, biogas, gelatin hydrolysate, fat, or fertilizers. Anaerobic digestion digestate can be employed for plant nutrition, and fermentation of methane allows for recovery of energy. The presence of chromium presents a significant challenge. Thankfully, there exist many techniques for the treatment of waste from tanning factories that contains the aforementioned ingredient. The preservation and cremation of tannery residues do not effectively mitigate the potential for secondary environmental contamination caused by chromium compounds. In order to mitigate this issue, several hydrolytic procedures such as alkaline, acidic, enzymatic, or mixed approaches are employed. One limitation of this approach is to the degradation of the collagen structure with subsequent depletion seen in the hydrolysate. Organic acid salts have the potential to serve as a viable option for the retrieval of chrome substances, hence facilitating the conservation of the collagen matrices. This preservation process is particularly valuable in the context of producing collagen hydrolysates.

The process of collagen extraction holds significant importance within the chemical, food, and pharmaceutical sectors. There is a need to improve the effectiveness of collagen regeneration. From a quantitative point of view, the primary concern within the leather business revolves around the presence of unprocessed leather and gelatin byproducts. The efficacy of these goods exhibits variability and is contingent upon the technical process and its respective phases. The practical application of by-products derived from wet tanning operations is limited. There is a need to develop a system for controlling chromium particles and chromium splits, which are substances generated during the latter phases of leather manufacturing. The valorization of trimmings of polished leather necessitates the implementation of appropriate design procedures.

Only by shifting away from a linear economy and toward an enclosed-loop economy, which ensures sustainable and less pollution, will the tanning industry be able to lessen its destructive influence on the environment and its high rate of energy consumption. It is extremely important for the leather business to have effective waste management since valuable components may be salvaged and recycled either within the same industry (chrome) or in other areas of the manufacturing sector (such as collagen, nutrients, energy carriers). The implementation of waste-free technology, in which every waste flow may be reused, is the largest obstacle. All material streams should be valorized, and new sustainable technologies should be compatible with the structure of waste management. Wastes bearing harmful chemicals such coloring agents, chromium, formaldehyde and phthalates must be changed immediately. It is scientifically demonstrated that this has a negative effect on the ecosystem as a whole. Natural dyes are one example of a biodegradable and safer option that should be explored. As a result, tannery staff and leather consumers will be safer and less pollutants will be released into the atmosphere. This review study is anticipated to provide guidance for future researchers who are fascinated in conducting studies during this interesting realm of wealth generation from leather waste.

Authors' Contributions

Md. Abdus Shabur: Conceptualization, Methodology, Writing – Original draft preparation. Md. Amjad Hossain: Reviewing, Editing and supervision.

Ethical Statement

Authors confirmed that no human or animal was harmed during collecting data. And this research work has not been published elsewhere and that it has not been submitted simultaneously for publication elsewhere.

Availability of Data and Materials

All data have been collected from Google Scholar and Scopus. Moreover, there is no individual person’s data in any form (including individual details, images or videos) in this study.

Competing Interests

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CHARACTERIZATION OF ENZYME-TREATED ECO-FRIENDLY IRON TANNED LEATHER

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CHARACTERIZATION OF ENZYME-TREATED ECO-FRIENDLY IRON TANNED LEATHER

ABSTRACT. Tanning is the process of converting putrescible raw hides and skins into non-putrescible leather. The most common chrome tanning process is not eco-friendly at all. But the increasing demand for leather leads us to find an eco-friendly tanning process. Therefore, the elimination of pollution due to the use of chrome and dyeing material is a matter of concern here. The primary objectives of this study are the reduction of pollution from using chrome and dyeing materials in the tanning process and their impacts on human life as well as the environment. In this study, different types of iron salts, combinations of different iron salts, and iron with chromium salts are used for tanning and no dyeing material is used to give color to the leather. On the other hand, various types of enzymes were applied for the completion of the beamhouse operation. Finally, the physical and thermal properties of various tanned leather were summarized to propagate an eco-friendly new tanning method.

KEY WORDS: enzyme, iron tanning, chrome tanning, physical properties, eco-friendly

CARACTERIZAREA PIEILOR TABĂCITE CU SĂRURI DE FIER ȘI TRATATE CU ENZIME

REZUMAT. Tăbăcirea este procesul de transformare a pieilor brute putrescibile în piele care nu putrezește. Cel mai utilizat proces de tăbăcire, cel cu săruri de crom, nu este deloc ecologic. Însă cererea tot mai mare de piele ne determină să dezvoltăm un proces de tăbăcire ecologic. Prin urmare, eliminarea poluării din cauza utilizării cromului și a materialului de vopsire este o chestiune de interes. Obiectivele principale ale acestui studiu sunt reducerea poluării în urma utilizării cromului și a materialelor de vopsire în procesul de tăbăcire și a impactului acestora asupra vieții umane, precum și asupra mediului. În acest studiu s-au utilizat pentru tăbăcire diferite tipuri de săruri de fier, combinații de diferite săruri de fier, precum și săruri de fier și de crom și nu s-a folosit niciun material de vopsire pentru a da culoare pielii. Pe de altă parte, s-au aplicat diferite tipuri de enzime pentru finalizarea operațiunilor umede. În cele din urmă, s-a făcut un rezumat al proprietăților fizice și termice ale diferitelor piei tăbăcite în vederea dezvoltării unei noi metode de tăbăcire ecologică.

CUVINTE CHEIE: enzime, tăbăcire cu săruri de fier, tăbăcire cu săruri de crom, proprietăți fizice, ecologic

CARACTÉRISATION DES CUIRS TANNÉS AVEC DES SELS DE FER ET TRAITÉS AUX ENZYMES

RÉSUMÉ. Le tannage est le processus qui consiste à transformer les peaux brutes putrescibles en cuir non putrescible. Le procédé de tannage le plus utilisé, celui aux sels de chrome, n'est pas du tout respectueux de l'environnement. Mais la demande croissante de cuir nous amène à développer un procédé de tannage écologique. Il est donc d'un grand intérêt d'éliminer la pollution due à l'utilisation de chrome et de matériaux colorants. Les principaux objectifs de cette étude sont de réduire la pollution liée à l'utilisation de chrome et de colorants dans le processus de tannage et leur impact sur la vie humaine ainsi que sur l'environnement. Différents types de sels de fer, des combinaisons de différents sels de fer, ainsi que des sels de fer et de chrome ont été utilisés pour le tannage dans cette étude, et aucun matériau colorant n'a été utilisé pour colorer le cuir. D'autre part, différents types d'enzymes ont été appliqués pour réaliser la rivière. Enfin, une synthèse des propriétés physiques et thermiques des différents cuirs tannés a été réalisée en vue de développer une nouvelle méthode de tannage écologique.

MOTS CLÉS : enzymes, tannage au sel de fer, tannage au sel de chrome, propriétés physiques, écologique

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INTRODUCTION

The leather making industry is one of the primitive industries in Bangladesh and plays a vital role to develop the gross domestic product (GDP) of the country [1]. Bangladeshi leather has a reputation across the world for its fine grain pattern, uniform fibre structure, and smoothness [2]. Currently, most of the leathers are tanned by the conventional method using basic chromium (III) salts. It is one of the most polluting and time-consuming steps in leather making [3].

Vegetable tanning materials used by the tanners are obtained from various plants. The tannins which appear to be by-products of the plants are water-soluble complex organic compounds [4-10]. Aluminum salts, in a dilute solution, hydrolyze in water with the formation of a colloidal precipitate of basic aluminum salts. As an example, aluminum chloride or sulfate in the solution has an acid reaction due to hydrolysis [11]. Iron tanning is done with the help of different types of iron salts. The properties of the leather are almost the same as chrome tanning and the cost of producing not putrescible leather is also budget-friendly [12]. Oil tannage has been used for the production of a specific type of high-quality leather. Zirconium is a metal belonging to the same group of elements as silicon and titanium. It accords with chromium in that it is sulfate and basic sulfate combines readily with the pelt.

A mixed ligand complex of iron with oxalic acid was synthesized and used for tanning experiments [13]. To continue this practice iron tanning as an eco-friendly process may play an influential role. Its outstanding ability to cross-link collagen with positive effects on leather filling and softness was emphasized in recent work [14]. As it contains no chrome in the tanning process so the disposal of iron waste is easier than chrome waste. To the aim of reducing chrome in this research, one goatskin is tanned with chrome and iron salt and the result is compared with iron tanning [15, 16]. It is an eco-friendly way as there is no dyeing material used in this iron tanning process. Dyeing materials also have negative impacts on human health as well as the environment [17, 18].

On the other hand, enzymes are an alternative to the conventional chemical process. Alkaline proteases from bacteria are used in the beamhouse operation due to their specificity, pH activity, and thermal stability. Various types of enzymes like alkaline protease, lipase, and keratinase, etc. are used in the leather industry to improve the final quality of the leather [19]. Enzymatic soaking, unhairing, and bating using alkaline protease, lipase, keratinase, and related kinetics were also studied.

EXPERIMENTAL

Materials and Method

Total seven (07) goatskin were taken and tanned with various techniques to compare the quality of the final product. $FeSO_4$ and Fe_2O_3 salts of iron and chrome salt are needed for tanning. Besides these, some of the chemicals are used in the conventional chrome tanning method but there are no dyeing chemicals used in this process for color. All processes are the same as conventional tanning instead of using chrome and dyeing materials. Five goat skins are taken and tanned with iron and a combination of iron and chromium salt. And another goatskin (S6) is taken and tanned with chrome tanning with dyeing materials.

- Goatskin (S1): Tanned with $FeSO_4$
- Goatskin (S2): Tanned with Fe_2O_3
- Goatskin (S3): Tanned with $FeSO_4$ + Fe_2O_3
- Goatskin (S4): Tanned with $FeSO_4$ + $Cr(OH)SO_4$
- Goatskin (S5): Tanned with $Cr(OH)SO_4$
- Goatskin (S6): Tanned with $Cr(OH)SO_4$ + acid dye

On the other hand, one goatskin (S7) is taken and tanned with various types of commercial enzymes that are used in the beamhouse operation, viz. Pelvit SPH for soaking, Erahvit MB for dehairing, and Ebranil PFE for bating. Enzymes are the catalysts of biological processes.

RESULTS AND DISCUSSION

Tanning has been done by using iron salts and without dyeing material to reduce environmental pollution and introduce a new cleaner technology for tanneries. All results of finished leather have been produced to be quite normal. It concluded that the leather produced using iron salt and a combination of iron and chromium salt were quite successful. It possesses good physical and chemical properties, whereas, the natural color of the finished leather is quite black or dark ash. It can be used easily in shoe uppers of natural color. It is very adaptable and easily competes in the domestic and global markets. On the other hand, goat skins were tanned by enzymatic treatment process to develop an eco-friendly processing technique. This result revealed that the physical and thermal properties of enzymatic-treated leather are highly appreciable (Figure 1).

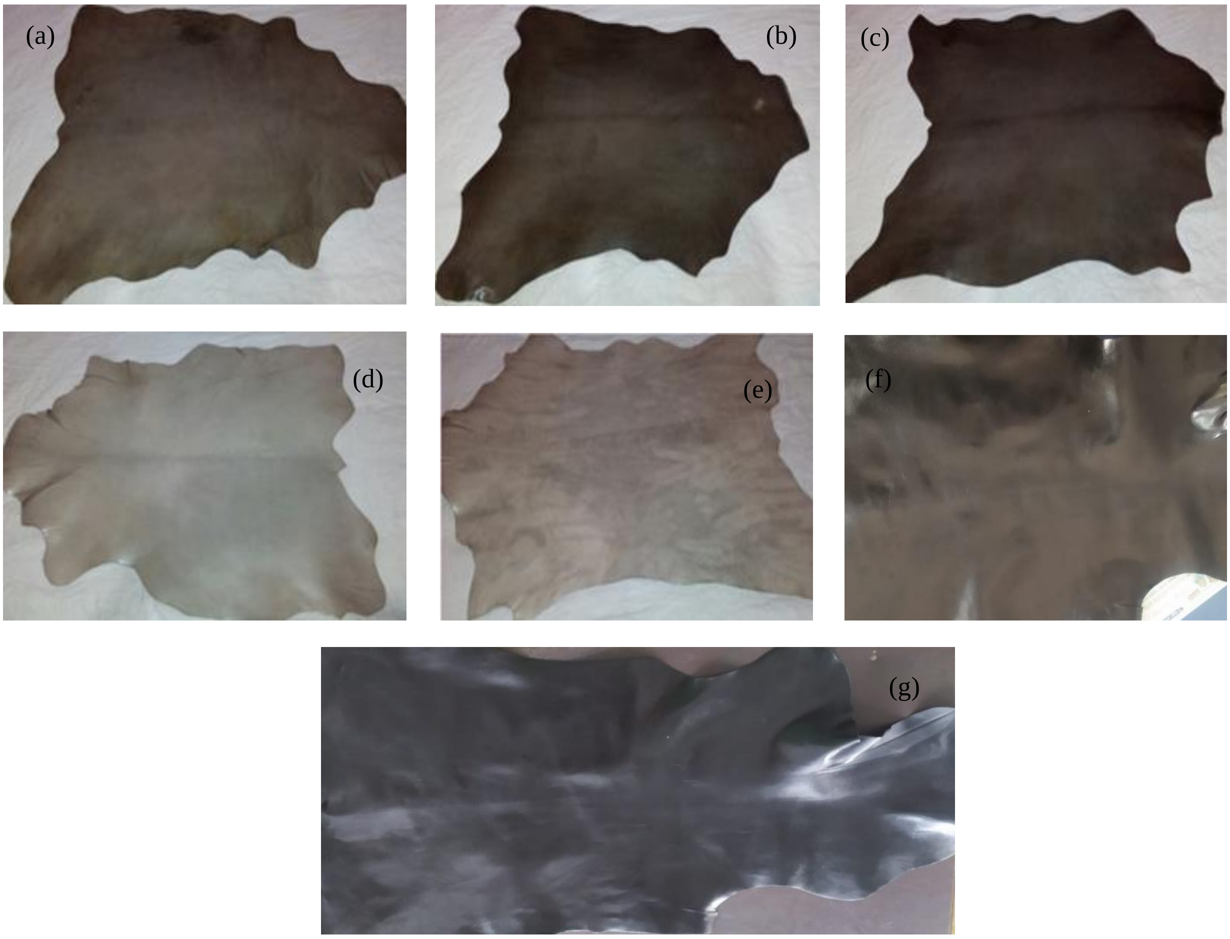


Figure 1. Final product images (a) tanned with basic chromium sulfate and ferrous sulfate, (b) tanned with Fe_2O_3, (c) tanned with $FeSO_4$ and Fe_2O_3, (d) tanned with $FeSO_4$, (e) tanned with basic chromium sulfate and with all this tanning this color is obtained without using any dyeing material, (f) tanned with $Cr(OH)SO_4$ + acid dye, (g) tanned with enzymes

Physical Properties

Physical tests of the iron-tanned, chrome-tanned, and enzymatic-treated leather namely tensile strength and percentage of elongation, stitch tearing strength, tongue tearing strength, split tearing strength, elastomer test, flexing endurance test, waterproofness test, bond strength test between leather and finish film, light fastness test, wet and dry rub fastness test, test for resistance to solvent of the finished film, moisture fastness test, water fastness test of finish film were determined according to ISO standard procedures and the results are summarized in Tables 1-11. It is observed that all physical properties of enzymatic-treated leather were found to be significantly higher than those of iron and chrome-tanned leather.

Tensile Strength

Tensile strength is the load required to break the unit cross-sectional area of the leather sample. 110 mm long and 25 mm wide specimens for testing each experiment were taken. The average thickness of the specimen was determined.

Table 1: Comparison of tensile strength

Tensile strength and % of elongation	S1	S2	S3	S4	S5	S6	S7
Result = Breaking load ÷ cross-sectional area (kg/cm^2)	250	164.8	168.5	265	240	200	280
% of elongation = (Final length-initial length)÷initial length×100%	120%	125%	125%	66%	54%	75%	52%

Stitch Tear Strength

Stitch tear strength is used for the determination of fiber strength. For this test, the load (kg) required to tear the sample of the leather between two holes of 2 mm diameter each and whose centers are 6 mm apart express its unit thickness (cm).

Table 2: Comparison of stitch tear strength

Stitch tear strength	S1	S2	S3	S4	S5	S6	S7
Result = load÷ thickness (kg/cm)	83.3	54.94	72.10	79.20	92	66.6	93

Tongue Tear Strength

Tongue tear strength is used to determine the fiber strength of leather. In this case, the load is required to tear a leather sample if the thickness is 1cm.

Table 3: Comparison of tongue tear strength

Tongue tear strength	S1	S2	S3	S4	S5	S6	S7
Result = load÷ thickness (kg/cm)	47.60	54.30	40.80	40.40	45.40	40.50	57.50

Bauman Tear Strength

To determine the fiber strength as in this test few fibers are ruptured at a time. In this case, the load in kg is required to continue the split in the leather specimen if the thickness of the leather is 1cm.

Table 4: Comparison of Bauman tear strength

Bauman tear strength	S1	S2	S3	S4	S5	S6	S7
Result = load ÷ thickness (kg/cm)	47.60	47.05	43.60	49.90	54.50	55.07	56.03

Lastometer Test

The bursting strength is an index of the overall strength of the finished leather. To know whether the leather will stand the load of lasting during shoe malling.

Table 5: comparison of lastometer test

Grain crack strength	S1	S2	S3	S4	S5	S6	S7
Result = load ÷ thickness (kg)	18	19	17.50	20	22	21	22.50

Waterproofness Test

A square test sample is bent into two V-shaped flanges that end in a trough. The trough is then immersed in water and the clamps oscillate at a steady rate so that the sample is bent repeatedly. The test is stopped when the water enters the test specimen.

Table 6: Comparison of waterproofness test

Waterproofness test	S1	S2	S3	S4	S5	S6	S7
Result after 15 minutes	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather	Water penetrates leather

Lightfastness Test

Half of the leather sample is covered with a starch-free cotton cloth. It is then kept in contact with sunlight or a Xenon lamp for 72 hours. Then a comparison is made by grayscale to the covered and uncovered portion.

Table 7: Comparison of lightfastness test

Lightfastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5	5	5	5	5	4

Color Rub Fastness Test

Starch-free cotton felt of dry-type felt rubbed with loaded into the leather. How much color is replaced in dry felt and wet felt is visually assessed.

Table 8: Comparison of color fastness test

Color rub fastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5	5	5	5	5	5

A Solvent of Finish Film Test

To carry out this test organic solvent such as Benzene, Ketone, Acetone, Alcohol, or chlorinated hydrocarbon is applied on the flesh side of the finished film of the leather. Then on the grain side, a dry rub fastness test is carried out and a comparison is made by grayscale to assess the color change. The color change rating should be 5-3. Excessive color change indicates a bad result.

Table 9: Comparison of a solvent of finish film test

Resistance to solvent of finish film	S1	S2	S3	S4	S5	S6
Grayscale	4	4	4	4	4	3-5

Moisture Fastness Test

Two samples are collected from the same leather. One is preserved in atmospheric conditions and the other is preserved in desiccators containing water at the bottom to ensure 100% relative humidity. Color rub fastness is carried out for both specimens or samples and the samples are compared with the help of grayscale.

Table 10: Comparison of moisture fastness test

Moisture fastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5	5	5	5	5	4-5

Perspiration Fastness Test

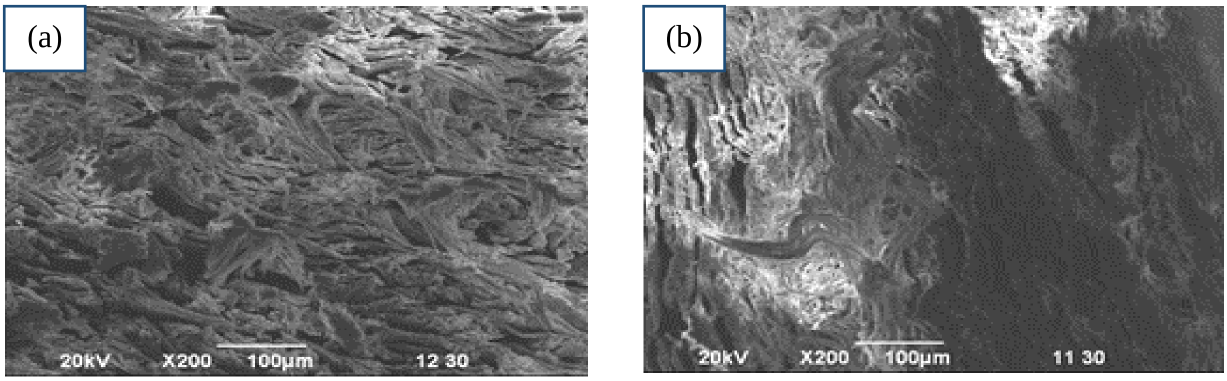
A piece of 100 ✕ 36 mm^2 specified undyed cloth is taken and wet with artificial perspiration. Then it is placed in the oven for three hours after drying the specimen and cloth assess the change with the grayscale.

Table 11: Comparison of perspiration fastness test

Perspiration fastness test	S1	S2	S3	S4	S5	S6
Grayscale rating	5-4	5-4	5-4	5-4	5-4	3-4

Scanning Electron Microscopic Analysis of Tanned Leather

Scanning electron microscopy test for tanned leather of $FeSO_4$ shows more uniform penetration of tanning material than Fe_2O_3. This test shows that chrome tanning penetration is good and fiber structures are more uniform than iron tanning (Fig. 2). On the other hand, Fig. 2g shows the cross-sectional view of the sample that has been treated with various enzymes in beamhouse operation. There was uniform penetration and the fibres structure was intact, and had a far better fiber orientation compared to iron and chromium-tanned leather. Hence, the enzymatic treatment leather shows better strength properties and greater surface area.



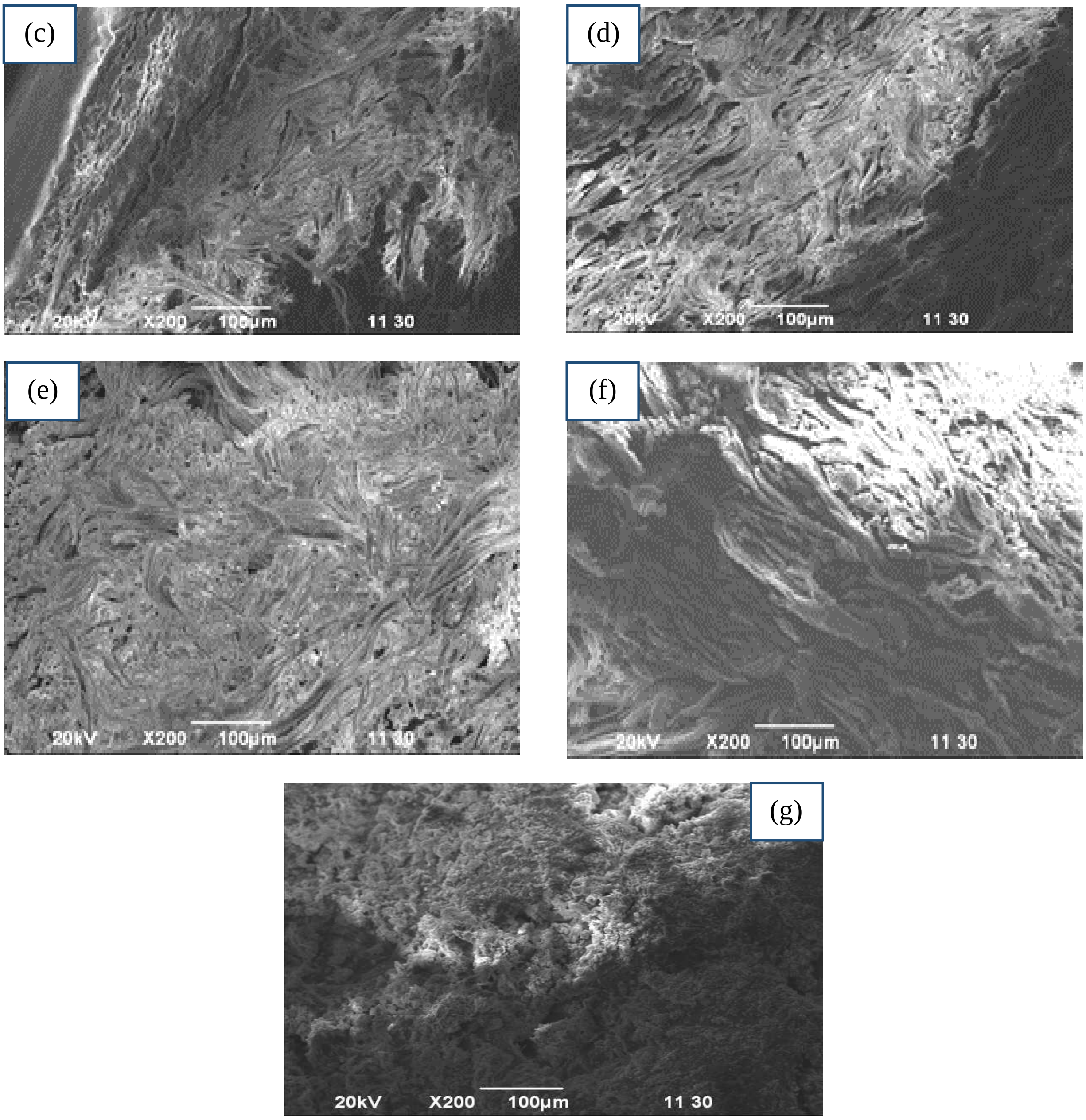
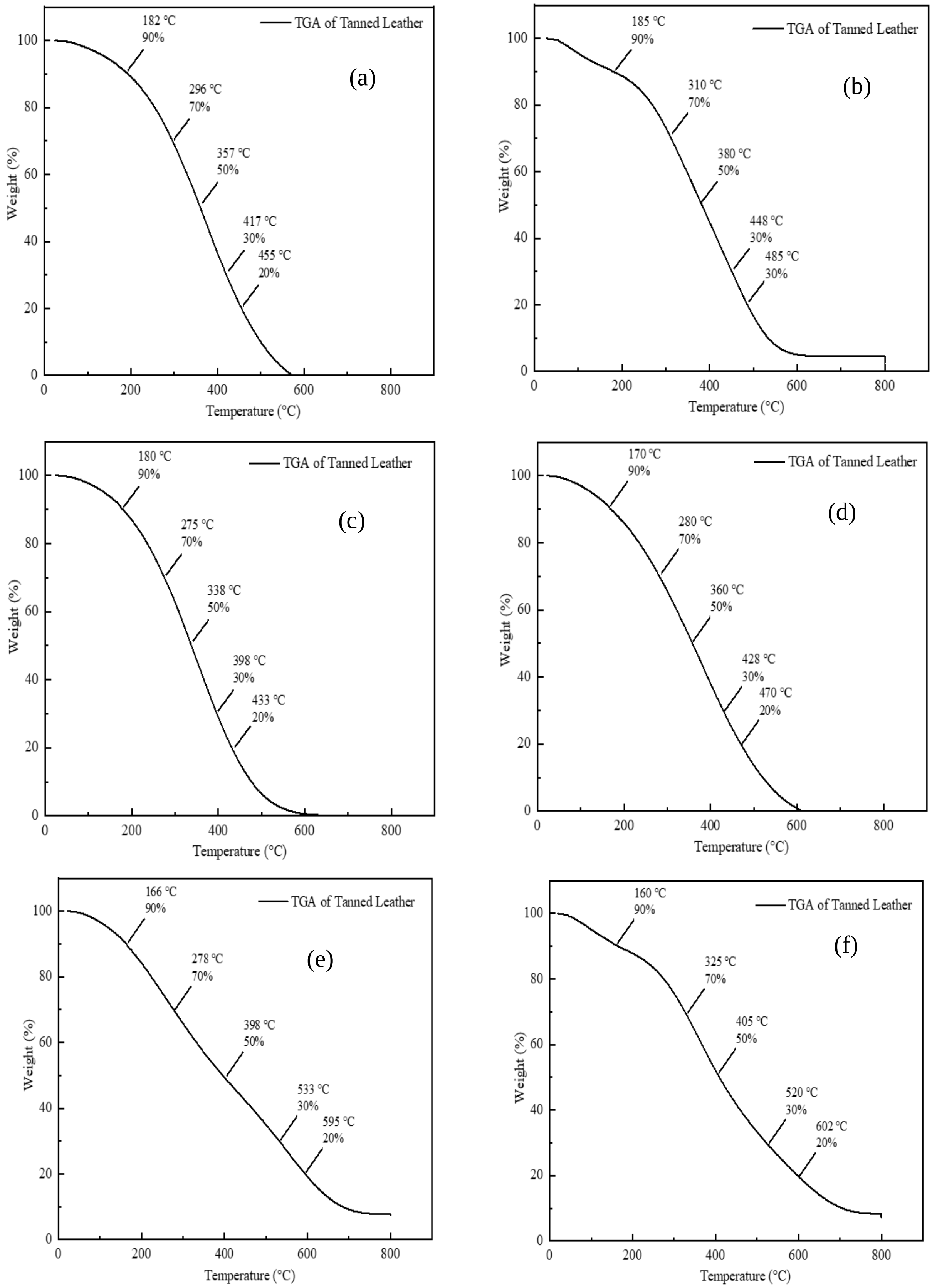


Figure 2. SEM images (magnification ×2000) of the cross-section of undyed leather tanned with (a) $FeSO_4$ (b) Fe_2O_3, (c) $FeSO_4$ and Fe_2O_3, (d) $FeSO_4$ and $Cr(OH)SO_4$, (e) $Cr(OH)SO_4$, (f) dyed with $Cr(OH)SO_4$, and (g) enzyme treated leather

Thermogravimetric Analysis for Tanned Leather

Thermogravimetric analysis is a thermal analysis technique in which changes in the chemical and physical characteristics of the samples provided are measured. Generally, a sample loses weight when heated as a result of decomposition, reduction or evaporation. The results of this work are highly promising indicating that iron salts and iron, chrome combination tanned leather using no dye also give good results (Fig. 3).

Fig. 3 (a) and (f) represent the thermograms of samples tanned with $FeSO_4$ and $Cr(OH)SO_4$ with acid dye, respectively. The temperatures needed for 10%, 30%, 50%, 70%, and 80% weight loss of sample tanned with $FeSO_4$ were 182, 296, 357, 417, and 455 °C, respectively while the same weight loss occurred at 160, 325, 405, 520, and 602 °C for the sample of $Cr(OH)SO_4$ tanned with acid dye. On the other hand, Fig. 3 (g) represents the thermograms of enzymatic-treated leather samples. The temperatures needed for 10%, 20%, and 30% weight loss of the sample were 268, 362, and 532 °C, respectively. Moreover, high temperatures are required for weight loss of enzymatic-treated leather samples due to the formation of strong tanning agent-collagen complexes.



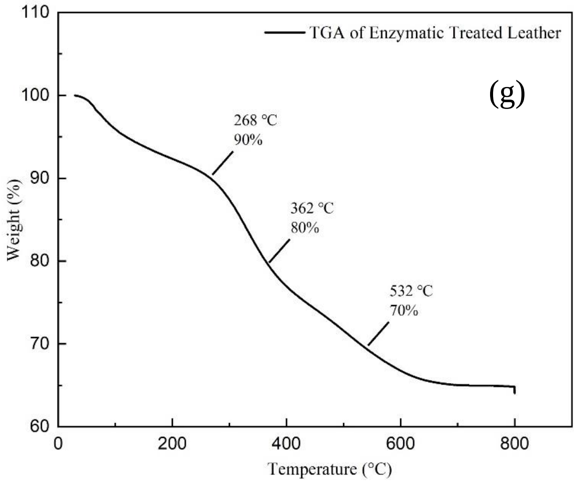


Figure 3. TGA of undyed leather tanned with (a) $FeSO_4$ (b) Fe_2O_3, (c) $FeSO_4$ and Fe_2O_3, (d) $FeSO_4$ and $Cr(OH)SO_4$, (e) $Cr(OH)SO_4$, (f) dyed with $Cr(OH)SO_4$, and (g) Enzyme treated leather

Differential Scanning Calorimetric Analysis for Tanned Leathers

A differential Scanning Calorimetry test here has been done to know about the shrinkage temperature of the tanned leathers. Fig. 4 revealed that the DSC thermograms of Iron, chromium, and enzymatic-treated tanned leather. The shrinkage temperature of enzymatically treated leather was far better than that of iron and chromium-tanned leather. Hence, enzymes act as catalysts to facilitate the chemical-free beamhouse operation without impairing the final quality of the leather. Therefore, the fixation of the tanning agents increased with the enzymatically treated pelt. All the leather passes the test result.

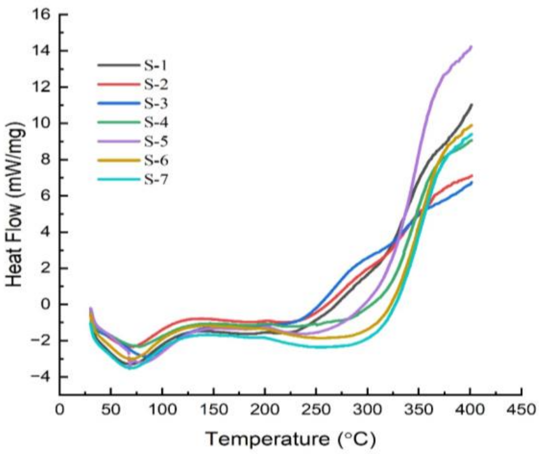


Figure 4. DSC thermograms of undyed leather tanned with (a) $FeSO_4$ (b) Fe_2O_3, (c) $FeSO_4$ and Fe_2O_3, (d) $FeSO_4$ and $Cr(OH)SO_4$, (e) $Cr(OH)SO_4$, (f) dyed with $Cr(OH)SO_4$, and (g) Enzyme treated leather

CONCLUSIONS

In this study, it is shown that different salts of iron and iron mixed with chrome-tanned leather give the best result, similar to conventional chrome-tanned leather, and here without using any dyeing material makes it more eco-friendly. Moreover, the enzymatic-treated leather showed the best result compared to other tanning methods. Various types of physical tests were carried out to compare the result of enzymatic-treated leather and other ones. Conventional methods for the tanning process discharge an enormous amount of pollutants due to the use of chemicals. Therefore, enzymatic treatment in beamhouse operation has been studied to facilitate the process without impairing the quality of finished products.

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Conflicts of Interest

The authors do not disclose any conflict of interest.

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EUROPEAN RESEARCH AREA

COTANCE NEWSLETTERS

Starting with January 2019, the COTANCE Council will issue a monthly ***COTANCE Newsletter*** with the purpose of **promoting an improved image of leather** to relevant decision makers and domestic stakeholders including Members of the European and National Parliament, Governmental authorities, Ministerial officers, Customers of the leather industry, Brands, Retail chains, Relevant NGOs, Designers, etc. The monthly newsletters present topics that tell the truth about a controversial aspect or a fact that is not well known by the general public to bring about a better understanding of leather and the European leather industry, as well as a positive predisposition to legislate in favor of the leather industry. The newsletters are available in seven languages at https://www.euroleather.com/index.php/newsletter, and were also published in the 2019-2023 issues of *Leather and Footwear Journal*. Newsletters 1-3 of 2024 are given below.

NEWS 1/2024

Leather in Fashion: An Obvious Choice for the New Generation of Designers

In the ever-changing world of contemporary fashion, leather has always been a key material. While trends rapidly shift, the value of leather remains unchanged. It is celebrated for its strength, luxury, and most importantly, its alignment with sustainable design and slow fashion principles. That is why it is no surprise that all over the world more and more young fashion designers chose to work with leather.

This is the case for **Ana Del Rio Mullarkey**, a young Spanish/British designer, who recently won the Real Leather. Stay Different. International Student Design Competition 2023 in Milano and now runs her own leather fashion brand "ANA DEL RIO" with the aim of leading "a Leather Revolution".

"Initially, I was attracted to leather due to its sustainability profile. As a designer trying to work with more natural materials, this durable and biodegradable solution which also adheres to

a circular economy model was perfect. Then, as soon as I started working with leather I felt an instant connection to this sumptuous material and decided to use it exclusively for all my designs", - says Ana.

Talking about her recent award-winning "El Domingo" collection, inspired by her Spanish heritage, Ana explains:

" "El Domingo" is inspired by the quintessential Spanish Sunday traditions such as visiting the Sunday antique market which I enjoyed when growing up in Madrid. The leathercraft techniques as well as the garments' silhouettes take references from traditional features such as the wall tiles inside classic Spanish bars or the elevated stonework surfaces on the facades of the historic buildings in my grandfather's town."


See more of Ana's work

Moving to Eastern Europe, we find Katarzyna Ostapowicz, a Polish footwear designer and manufacturer, who serves as an inspiring example of the value placed on leather in the footwear fashion industry. With a Master's Degree with honors in clothes, jewelry, and shoe design from the University of Fashion and Art in Lodz, Katarzyna has already earned widespread recognition as a shoe designer in Poland.

"As a designer, I am committed to ensuring that my products are of the highest quality and serve a good purpose. Natural leather possesses great advantages that meet my expectations. Footwear made from leather is comfortable, resistant to damage, and most importantly, safe for health. Natural leather is an exclusive, beautiful, and timeless material. Items made from it are always synonymous with luxury and elegance. Working with leather gives me the satisfaction and confidence of being able to offer a quality product", - says Katarzyna.

With her recent shoe collection crafted exclusively from leather, Katarzyna says: *"I partially customized it with my own prints using a UV technique. Once again, leather proved to be an unparalleled working companion, allowing me to merge my vision with this noble and irreplaceable material".*

Learn more about Kasia Ostapowicz's work

Leather's timeless nature is mirrored in humanity's own evolution and innovation. Even today, leather and its sustainable features keeps inspiring young designers worldwide who are not only striving to make a statement in the fashion world but are also committed to sustainable practices.

Their work with leather is a step towards a greener, carbon-neutral future, blending traditional craftsmanship with contemporary values. Thus, choosing to wear leather is not only historically justified, but also an environmentally responsible decision.

Ana: ***"My goal is to create contemporary, timeless leather garments and other pieces which defy fleeting trends and highlight leather's sustainable attributes. In this world of overproduction and mass consumption I would love people to join me on my Leather Revolution and to embrace unique leather garments which can be loved and which last for many lifetimes".***

Still unsure about choosing leather as part of your wardrobe? Discover 'Go for Slow Fashion - choose leather' and explore another story that will encourage you to embrace more leather into your life.

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Polish Chamber of Shoe and Leather Industry
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Polish Chamber of Shoe and Leather Industry (PIPS) | **Web**
Go for Slow Fashion - choose leather! | **COTANCE Newsletter 1/2022**

NEWS 2/2024

Leather - a Strategic Material in Military Clothing

On February 24, 2024, the World celebrated a very sorrowful anniversary - two years since the onset of the Russo-Ukrainian war. While you may have heard about the delivery of Taurus missiles, F16 jets, and Patriot systems to Ukraine, the significance of leather as a crucial material for the military sector is likely something you haven't heard much about.

First and foremost, leather is crucial in manufacturing military boots. Why? Because only leather ensures that soldiers don't have to worry about their feet getting cold in winter, sweating in summer, or becoming wet during heavy rains. These boots are almost entirely made from high-performance leather, usually heavy cattle hides, and their production follows demanding standards and meticulous quality controls to fulfill the stringent requirements set for military use. Only leather can make soldier’s boots breathable, durable, waterproof, ensuring the maximum wearing comfort day in day out.

Leather is also utilised for aviators' and military officers' jackets, handgun holsters, gloves, belts, and various military equipment components, as well as in prosthetics and other technical applications.

For this newsletter, we engaged in numerous conversations with Ukrainian leather industry operators, but for their safety, we won’t disclose their identities.

Director of the Ukrainian Industrial Company specialising in footwear for special and military purposes: “*I can’t say with certainty whether leather occupies a large share in military procurement, but there are definitively goods where you can’t do without it. For winter boots, leather is key, as it has better physical properties than any other material. Another example can be leather seats for land-based military and medical-related vehicles. Leather substitutes have proven ineffective* *in extreme conditions, such as explosions or shelling, where they become toxic and melt. Therefore, leather is irreplaceable on the battlefield*".

COTANCE had also the opportunity to interview a Sergeant Major, the chief of administration from the Khmelnytskyi district division, and a Senior Soldier of the King Danylo 24th separate mechanised brigade, 46th separate battalion fighting now in the Bakhmut direction.

When asked to identify military products made from leather, they all emphasized boots, whether winter or summer, which are exclusively made from leather, followed by handgun holsters. They both noted: *"Leather is simply practical, it doesn't need much care, it withstands extreme conditions, and is long-lasting". "In the 90s, as a soldier, I had more leather items, but a number of them have been replaced by other materials. Yet, when it comes to boots, nothing compares to leather"*, - **says Sergeant Major.**

According to **Ukrlegprom**:
By 2022, 339 enterprises and 30.5 thousand people (23% of the total number of people employed in the light industry TCLF) were employed in the production of leather and footwear in Ukraine.

Commenting on the current situation, the **Managing Director** of one of the largest tanneries in Ukraine says: *"There are not so many Ukrainian leather producers left, but there are over 1,000 workers in the sector making a significant contribution to Ukraine's effort to win in the war with Russia. We supply the leather for the production of military footwear, clothing and special products".*

Following the previous statements, the Managing Director adds: *"Yet, we have problems with the shortage of raw materials, chemicals and especially technologies for leather production. Difficulties with staff over the past 2 years are another challenge for leather production. Many people simply went abroad in 2022, and replacing them is a real problem, because training and preparing a specialist at any stage of leather production takes more than a month, or years, as in the case of production process technologists. But we continue to work despite this and contribute to our Victory".*

Our sources from the Ukrainian footwear sector regret that the blockade of the borders has a significant impact on logistics, which consequently impacts adversely on domestic production processes.

War is a tragedy. Yet, amidst all the suffering, leather emerges as a key material, ensuring protection and comfort to soldiers and serving as a reliable "comrade"; that does not fail at critical battlefield moments. Indeed, the current war makes us rediscover leather as a strategically important material for domestic defense capabilities.

This newsletter also serves to remind us of the significant support Ukraine continuously needs from all of us at all fronts, including in the area of leather availability.

At a time when Europe is reflecting on the crucial need for military sovereignty, it would not be out of place to give some thought to an EU-wide approach ensuring self-sufficiency in the supply of leather for Europe's armed forces.

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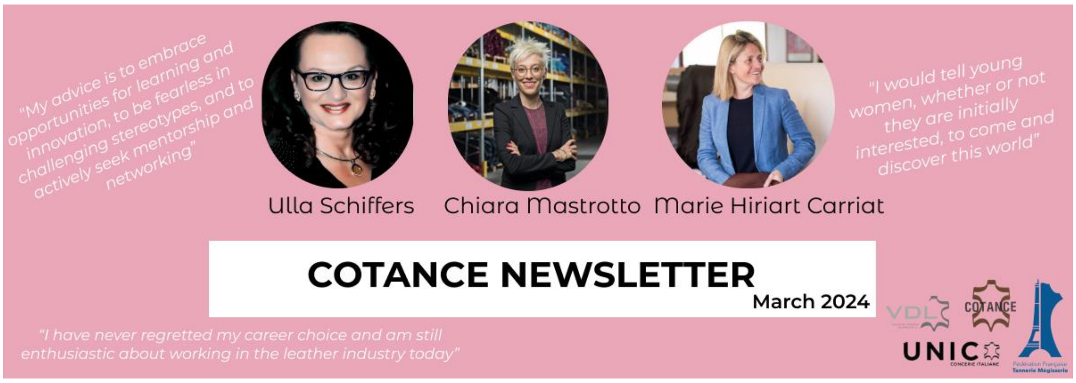

NEWS 3/2024

Women in European Tanneries: Transforming the Leather Industry Together

Conventional wisdom holds that leather production is a male-dominated industry. Indeed, the ratio of men to women in the sector supports this. But when COTANCE set out to explore the presence of women in the leather sector, we found that not only are women present, but that these women are more than exceptional.

In celebration of Women's Rights, which March is all about, and in partnership with our members VDL (Germany), UNIC (Italy), and FFTM (France), we dedicate our March Newsletter to the charismatic, bold, and exceptional women working in European tanneries. By sharing their personal stories, we want to encourage and inspire more women to join this vibrant industry, which still has so much to offer.

The tanning process (transforming skins and hides into leather) involves several labour-intensive steps, where men have traditionally outnumbered women. However, over the years, technological progress and process innovations have reduced the physicality of tasks and narrowed the gender gap, leading to more women working in tanneries.

Data, as highlighted in the 2020 Social & Environmental Report of the European Leather Industry, show that female personnel now constitute approximately 25% of the European workforce in tanneries. This figure can increase to 50% in certain companies where women are filling high-level management positions in marketing, communications and sustainability.

Moreover, women have a remarkable presence in European Leather Trade Associations, holding directorial roles in Italy (UNIC - Concerie Italiane), Spain (ACEXPIEL), France (FFTM), Hungary (AHLI), or Austria (FV TBSL). And in some cases, like France and Portugal, women are also chairing these organisations.

COTANCE had the opportunity to speak with some of these exceptional women in tanneries who are redefining the boundaries and expectations within this sector, and we are excited to share those conversations with you.

Women extending wet leathers on a drying device

As a fourth-generation descendant of tanners, **Ulla Schiffers** truly has leather in her blood. Having dedicated 42 years to the German leather industry, as a leather technician, her greatest ambition has always been *"to prove to male employees that women could bring the same competence and stamina to this challenging job"*.

Mrs Ulla Schiffers with her colleagues


Mrs Chiara Mastrotto

Leather also became a calling for **Chiara Mastrotto**, who, after pursuing a career in law, decided to leave it behind and join her family's business. Starting from "zero" and thanks to her collaborative leadership and can-do approach, she has advanced to become CEO and then the President of Gruppo Mastrotto. *"Each sector, including the leather industry, certainly has its specificities. However, I believe that in terms of opportunities, the most important aspect is to focus on merit. When merit is highlighted and becomes the driving factor behind hiring and promotions, the gender issue is also resolved"*, - says Chiara.

Marie Hiriart Carriat is the third generation of tanners from the Rémy Carriat tannery, located in Espelette, Pyrénées-Atlantiques, France. Founded in 1927, this independent, family-run business employs 70 people and specializes in the tradition of bull and buffalo leather crafting for the leather goods, footwear, and furniture industries. In June 2023, she was appointed President of the Fédération Française de la Tannerie Mégisserie (FFTM).


Mrs Marie Hiriart Carriat
photo by @TannerieRemyCarriat

"The REMY CARRIAT tannery has always been a place where women have played a pivotal role. My grandmother co-founded the tannery with my grandfather, Rémy Carriat. While he focused on production, she managed the administration. Subsequently, my mother worked alongside my father for many years, contributing significantly to the management and operation of the tannery. I began working with my father in 1992, initially as a sales assistant, before taking over as the head of the company in 1999", - says Marie.

Edited excerpts of the conversation with them follow.

- **How many women are employed in your company/tannery? If possible, could you compare the % of total female workers in the tannery to the % of women working at the management level?**

  Ulla: "I have been working in the chemical supply industry for many years, providing technical support for tanneries in Europe. There are hardly any other female leather technicians in these areas. The proportion of women in this job is perhaps a maximum of 5%. In our company, I am the only woman in technical support with several male colleagues."

  Chiara: "Currently, in Gruppo Mastrotto women constitute approximately 26% of factory workers and 51% of the office employees. In top positions, we reach over 57% of female executives, and among the board members we have perfect gender equality."

  Marie: "Today, at the Rémy Carriat tannery, there are 8 women working in production, 3 in quality control, and 5 in administration, totaling 16 out of the 75 employees in the company. This represents 21% of our workforce. Certain roles, such as those in our hand-patination studio and the quality department, are exclusively held by women."

Hand-patination at Tannerie Remy Carriat, France

- **The leather industry faces criticism for its environmental impact. How do you think the industry, and women in particular, can contribute to more sustainable practices?**

  Chiara: "Our industry has made significant strides in sustainability in the recent years, with companies like Gruppo Mastrotto leading by example through investment in water and chemical reduction, recycling initiatives, and renewable energy sourcing. By fostering innovation and adopting more sustainable tanning processes, we demonstrated our commitment to environmental responsibility. Women can play a pivotal role in driving this transformation, advocating for responsible production, and engaging with stakeholders to promote sustainability".

  Ulla: "Consumers need to be made aware that leather is an extremely durable product. So in terms of sustainability it contributes to "slow fashion". All of us who work in the leather industry, whether female or male, must do our best to better manage resources and avoid pollution".

  Marie: "The leather industry often faces criticism from individuals unfamiliar with our material or our processes. Addressing this misconception is crucial, regardless of one's gender. We are a sector that adheres strictly to REACH regulations, demonstrating our commitment to environmental and social responsibilities. Despite this, we face a significant image deficit and lack of support at the European level. In countries like France and Italy, decrees protect and uphold the 'Leather' designation, providing a level of defense for our products. However, this kind of regulatory support is absent at the European level, leaving a gap in our ability to safeguard our industry".

- **What characteristics or aspects of leather do you think should be promoted?**

  Ulla: "Leather is a fantastic natural product with outstanding properties - this uniqueness should be made clearer to the consumer".

  Marie: "Leather is a durable, natural, and ever-evolving material that accompanies us throughout our lives, being passed down from one generation to the next. It is an exceptionally pleasing material that engages all our senses".

Chiara: "Leather's sustainability, longevity, and its role within the circular economy should be emphasized, not just by tanneries but by fashion and design brands. As a by-product of the food and dairy industry, leather exemplifies sustainable practices through eco-friendly tanning and production methods, minimizing waste and environmental impact. Its durability and long-lasting nature, alongside efforts to correct misconceptions about alternatives, are key points that highlight leather's environmental credentials"

- **What advice would you give to young women interested in entering the leather industry?**

Chiara: "My advice is to embrace opportunities for learning and innovation, to be fearless in challenging stereotypes, and to actively seek mentorship and networking. Our industry offers a dynamic environment where sustainability, craftsmanship, and technology converge, providing a rich ground for professional growth and contribution. By advocating for inclusivity, sustainability, and innovation, women can play a transformative role in shaping the future of the leather industry.

Ulla: "I have never regretted my career choice and am still enthusiastic about working in the leather industry today. This industry impresses with its extremely informal character, its togetherness and the diverse career opportunities"

Marie: "I would tell young women, whether or not they are initially interested, to come and discover this world. Tanning is a profession that deserves exploration. Historically, it was primarily a male-dominated field, especially in bovine tanneries like ours, due to the physical demands of working with large, heavy leathers. However, the industry has undergone significant changes over the years, becoming much more welcoming to women, particularly due to the mechanization of some tasks. The tannery offers a wealth of career opportunities, whether in production, colour work, product design, research and development, quality control, customer service, environmental management, or corporate social responsibility... and the list goes on! There are so many ways in which you can apply your skills and introduce your feminine touch to the exciting world of tannin.

Traditionally perceived as male-dominated, the leather industry is experiencing a transformative shift with women increasingly occupying key roles in tanneries and directorial positions in trade associations.

Ulla Schiffers, Chiara Mastrotto and Marie Hiriart Carriat exemplify what women bring to the leather industry. Their stories of dedication, ambition, and success challenge stereotypes and highlight the importance of meritocracy, leadership, and sustainability.

The conclusion is clear: tanneries are not just places of opportunity for women; it is a sector where they are already making significant impacts and leading change. By highlighting their achievements maybe we inspire more women to join this exciting and evolving world of leather.

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