THE ANTIOXIDANT EFFECT OF COLLAGEN HYDROLYSATE ON IMPROVING LIGHTFASTNESS AND MECHANICAL PROPERTIES OF THE GRANOFIN EASY F90-MIMOSA-TANNED LEATHER

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ABSTRACT. The effect of antioxidants on the properties of Granofin easy-F90-mimosa-tanned leather is explored in the present paper. The fresh bovine hides were prepared through soaking, liming, de-liming, and bating processes before being tanned with Granofin Easy-F90 and mimosa. Granofin easy-F90 (G) and mimosa (M) were used as cross-linking agents and collagen hydrolysate (C) was used as an antioxidant. The molecular structure, lightfastness, mechanical properties, morphology, and shrinkage temperature (Ts) of leather were measured using Attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), Xenotest Alpha and Beta LM, tensile strength testing machine, Scanning Electron Microscope (SEM) and a leather shrinkage temperature tester, respectively. The results indicated that the lightfastness, shrinkage temperature, tear strength, tensile strength, and elongation at the break of the sample treated with collagen hydrolysate were improved. The Granofin easy-F90-mimosa-collagen hydrolysate (GMC) tanned leather sample offered a lightfastness, shrinkage temperature, tear strength, tensile strength, and elongation at break of 4, 95°C, 37.8N/mm, 25N/mm^2, 42%, and the Granofin easy-F90-mimosa-tanned leather sample gave 3-4, 91.5°C, 30.5 N/mm, 24.2 N/mm^2, 44.6%, respectively. Considering these results, it is proved that collagen hydrolysate had a positive impact on leather properties.

KEY WORDS: hydrolyzed collagen, F90, antioxidant, lightfastness

EFECTUL ANTIOXIDANT AL HIDROLIZATULUI DE COLAGEN ASUPRA ÎMBUNĂTĂȚIRII REZISTENȚEI LA LUMINĂ ȘI A PROPRIETĂȚILOR MECANICE ALE PIELII TĂBĂCITE CU GRANOFIN EASY F90 ȘI MIMOSA

REZUMAT. În lucrarea de față se explorează efectul antioxidanților asupra proprietăților pielii tăbăcite cu Granofin Easy F90 și mimosa. Pielea proaspătă de bovine a fost pregătită prin procese de înmuiere, alcalinizare, decalcifiere și sămăluire înainte de a fi tăbăcită cu Granofin Easy F90 și mimosa. Granofin Easy F90 (G) și mimosa (M) au fost folosite ca agenți de reticulare, iar hidrolizatul de colagen (C) a fost utilizat ca antioxidant. S-au măsurat structura moleculară, rezistența la lumină, proprietățile mecanice, morfologia și temperatura de contracție (Ts) ale pielii folosind Spectroscopia în infraroșu cu reflectanță totală atenuată (ATR-FTIR), Xenotest Alpha și Beta LM, un dispozitiv de testare a rezistenței la rupere, un microscop electronic de scanare (SEM) și un tester pentru temperatura de contracție a pielii. Rezultatele au indicat că rezistența la lumină, temperatura de contracție, rezistența la sfâșiere, rezistența la rupere și alungirea la rupere ale probei tratate cu hidrolizat de colagen au fost îmbunătățite. Pentru proba de piele tăbăcită cu Granofin Easy F90, mimosa și hidrolizat de colagen (GMC) s-au obținut valori de 4, 95°C, 37,8 N/mm, 25 N/mm^2, 42% pentru rezistența la lumină, temperatura de contracție, rezistența la sfâșiere, rezistența la rupere, respectiv alungirea la rupere, în timp ce proba de piele tăbăcită cu Granofin Easy F90 și mimosa a avut valori de 3-4, 91,5°C, 30,5 N/mm, 24,2 N/mm^2, respectiv 44,6%. Având în vedere aceste rezultate, s-a demonstrat că hidrolizatul de colagen a avut un impact pozitiv asupra proprietăților pielii.

CUVINTE-CHEIE: colagen hidrolizat, F90, antioxidant, rezistență la lumină

L'EFFET ANTIOXYDANT DE L'HYDROLYSAT DE COLLAGÈNE SUR L'AMÉLIORATION DE LA SOLIDITÉ À LA LUMIÈRE ET DES PROPRIÉTÉS MÉCANIQUES DU CUIR TANNÉ AU GRANOFIN EASY F90 ET MIMOSA

RÉSUMÉ. L'effet des antioxydants sur les propriétés du cuir tanné au Granofin Easy-F90 et mimosa est exploré dans cet article. Les peaux bovines fraîches ont été préparées par des procédés de trempage, de pelanage, de déchaulage et de confitage avant d'être tannées avec Granofin Easy-F90 et mimosa. Le Granofin Easy-F90 (G) et le mimosa (M) ont été utilisés comme agents réticulants et l'hydrolysat de collagène (C) a été utilisé comme antioxydant. La structure moléculaire, la solidité à la lumière, les propriétés mécaniques, la morphologie et la température de retrait (Ts) du cuir ont été mesurées à l'aide de la spectroscopie infrarouge à transformée de Fourier - réflectance totale atténuée (IRTF-ATR), du Xenotest Alpha et Beta LM, d'une machine d'essai de résistance à la traction, d'un microscope électronique à balayage (MEB) et respectivement d'un testeur de température de retrait du cuir. Les résultats ont montré que la solidité à la lumière, la température de retrait, la résistance à la déchirure, la résistance à la traction et l'allongement à la rupture de l'échantillon traité avec l'hydrolysat de collagène étaient améliorés. L'échantillon de cuir tanné au Granofin Easy-F90-mimosa-hydrolysat de collagène (GMC) a offert une solidité à la lumière, une température de retrait, une résistance à la déchirure, une résistance à la traction et un allongement à la rupture de 4, 95°C, 37.8N/mm, 25N/mm^2, 42%, tandis que l'échantillon de cuir tanné au Granofin Easy-F90-mimosa a donné respectivement 3-4, 91.5°C, 30.5N/mm, 24.2N/mm^2, 44.6%. Considérant ces résultats, il est prouvé que l'hydrolysat de collagène a eu un impact positif sur les propriétés du cuir.

MOTS-CLÉS : collagène hydrolysé, F90, antioxydant, solidité à la lumière

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INTRODUCTION

Since prehistoric times, leather has been a valuable material [1]. Leather is obtained from skin/hide through a series of processing stages such as soaking, unhairing, liming, de-liming, bating and, tanning. When exposed to the environment, including UV light, leather can undergo oxidation, resulting in the formation of free radicals that are reactive due to the presence of unpaired electrons [2, 3], leading to a reduction of the light fastness of leather and other physical-mechanical properties.

Vegetable-tanned leather is friendly to the environment; however, properties like shrinkage temperature (Ts), tear strength, tensile strength, and light fastness are reported to be poor [4]. When vegetable-tanned leather is combined with strong cross-linking agents, leather with enhanced properties is produced [5].

Granofin Easy F-90, an organically based tanning agent made of sodium p-((4,6-dichloro 1,3,5-triaz-2-yl) amino) benzene sulphonate, can be utilized as a cross-linking substance in leather processing [5]. The chemistry behind the reaction of F-90 with the collagen matrix is that the two chlorine atoms in F90 combine with the collagen matrix's attached amino groups to create covalent connecting bonds [6]. One of the chlorine atoms is hydrolyzed in water to form HCl, which drops the pH from 8 to 5 leading to the promotion of the sulfonate group's interaction with the collagen matrix's positively charged amine groups.

Additional crosslinkings are generated when F90 is re-tanned with mimosa, which induces an integrative tanning effect that causes a cross-linking bond formation between the amine of the collagen matrix, its carboxylic and hydroxyl groups. These cross-linking connections are formed across the collagen and the NH_2 group of the sulphonate benzene in the F90.

Despite the integrative cross-linking developed between F90 and mimosa, which leads to enhanced physical properties, the leather is still reported to have poor light fastness [7, 8]. With low light fastness, the resulting leather is prone to fading, leading to a reduction in the strength and lifetime of the leather [9]. Therefore, to lengthen the lifetime of the resulting leather, it is a recommended practice to use materials with antioxidant properties that can enhance the lightfastness and physical properties of leather.

Recently, various antioxidants have been reported to be active radical scavengers that provide a protective environment to products in textiles, leather, and other industries that are prone to the fading process [10]. It is accepted that collagen hydrolysate (C), a low molecular weight protein (1–30 kDa) with good biocompatibility and low antigenicity, can be used as an antioxidant [11, 12]. The availability of the aromatic amino acids and the histidine in the collagen hydrolysate which are hydrophobic amino acids gives the collagen hydrolysate properties of working as an antioxidant [12]. Various studies have worked on the antioxidant impact of collagen hydrolysate on human skin [5, 12, 13]. Nevertheless, there are no studies regarding the antioxidant effect on lightfastness and related leather properties through the application of collagen hydrolysate alone or in combination with other tanning agents on the F90-mimosa-tanned leather. Therefore, in this study, it is interesting to know whether the lightfastness could be improved by incorporating collagen hydrolysate in the F90-mimosa-tanned leather.

EXPERIMENTAL

Materials and Methods

Materials

Bovine hides were used in the tanning processes. Industrially produced, commercially available products were utilized as tanning agents in the present study. These include Borron A, Borron T, Preventol ZL, Oropon, and Erhavit MB from TFL, Lipoderm Licker A1, Decaltal ES FL, and Granofin Easy F-90 from Stahl, Burtral 30 WB from Buckman, Merpin 8020 from Carpetex, Mimosa tannin from Silvachimica S.r.l. Other chemicals and reagents used were provided by various suppliers and were of analytical standard.

Preparation of Materials and the Tanning Process

The raw fresh hide from bovine was processed following the stages indicated in Figure 1 before the tanning process. The chemicals used in this process were commercial grade, where F-90 was supplied by Stahl. The weight of the chemicals used in the main tanning was determined based on the weight of the limed pelt. Fresh hides were prepared and processed as per Yu *et al*. [14] with some modifications as presented in Tables 1 and 2.

Figure 1. Stages involved in processing the rawhide before the tanning process [14]

Analysis of GM and GMC Leather Samples' Physical and Mechanical Properties

The shrinkage temperature (Ts) was examined by a shrinkage tester (Heidolph MR 3001 K, SKU: RBN 22734) as per the official method (ASTM D6076-18 (2013)). From the leather sample, a thin strip measuring 50 by 10 mm was taken off and suspended in the water. The bath's temperature was raised by 2 degrees Celsius each minute, and the temperature of the first definite shrinkage was recorded. The tensile strength and elongation at break were performed using the tensile strength testing machine as per standard methods (DIN EN ISO 3376:2002(E) IULTCS/IUP6) using a LLOYD instrument (Erichsen Prüftechnik Wuppertal). Measurements of single-edge tear strength were determined as per DIN EN ISO 3377-1:2002 (E) IULTCS/IUP 40. Three trials were carried out per sample and the average value was calculated.

Fourier Transform InfraRed (FTIR) Analysis of GM and GMC Leather Samples

ATR-FTIR spectroscopy technique was applied to study the molecular changes of sample GM and GMC. The spectra were obtained at a wave number ranging from 400–4500 cm^{-1}, a resolution of 4 cm^{-1}, and 16 scans. To record spectra, a Nicolet iZ10, which is an extension of the Nicolet iN10 IR microscope, was used.

Scanning Electron Microscopy (SEM) Analysis of GM and GMC Leather Samples

Field Emission Scanning Electron Microscopy (FE-SEM Thermo Fisher FEI Quanta 250 FEG) was utilized to examine the leather samples' surface morphology. Samples from official sampling positions were used to create the experimental leather samples. Before being loaded into a sample holder, samples were immediately sliced into specimens of equal thickness and coated with gold. Using the SEM set at 100x magnification levels and an accelerating voltage of 10 kV, the micrographs for the cross-section were produced.

Colorfastness to Artificial Light by Xenon Arc Fading Lamp Test

The lightfastness measurements of the leather samples were tested for normal light and hot light as per the testing standard methods ISO 105-B02:2014 and DIN EN ISO 105-B06:2020 through subjecting at reflectance measurements using Xenotest Alpha and Beta LM, respectively. Together with a set of reference materials, a leather sample to be tested was subjected to artificial light from the Xenon arc fading lamp under controlled conditions. The test specimen's color change was compared to the reference materials to determine the color's fastness to light. The light fastness results were evaluated as per standard DIN EN 20105-A02. The ISO blue wool scale, which ranges from 1 to 8 along with an intermediate, served as the reference materials for ISO 105-B02 and its corresponding test procedures. Blue wool 1

indicates the lowest color fastness and 8 the highest. Nine levels, each occurring in two grey fields with their corresponding contrast, were chosen for the greyscale. As per DIN EN ISO 20105-A02: A grey scale for evaluating the color changes, nine possible values are considered including 5, 4-5, 4, 3-4, 3, 2-3, 2, 1-2, and 1. Grade 1 indicates a significant visual change (lowest rating) and Grade 5 indicates no visual color change (highest rating). The exposed portion of a sample was compared to an unexposed reference sample for the visual inspections.

Table 1: Soaking, liming, deliming, and bating

Process	%	Product	Temp	Runtime	pH	Comment
Dirt soak	150	Water, drain	25	20'		
	150	Water	25	20'		
	0.1	Borron A, drain				Wetting, dispersing & emulsifying agent
Main soak	400	Water				
	0.2	Sodium Dimethyl Dithiocarbamate (Preventol Z-L)	68			Bactericidal
	0.5	MgO (Merpin 8020 90)				Basifying agent
	0.2	Borron T			9.5	Degreasing agent
Liming	80	Water	20			
	1	Erhavit MB				sulphide-free liming agent
	0.1	$Ca(OH)_2$ (Lime)		20'	12	
	1	NaHS		30'		
	1	Na_2S		60'		2'/1'/run/stop
	1	Na_2S		60'		To complete hair removal
	0.5	Na_2S				
	1	$Ca(OH)_2$ (Lime)		45'		
	30	Water				
	1	$Ca(OH)_2$ (Lime)	20			
	0.1	Borron A		90'		
		Drain				
	150	Water, Flesh, split, weigh	25	15'		Wash 2 times
Delime	100	Water	25			
	2	Decaltal ES-N liquid (carboxylic acid esters)				
	0.05	Borron A				
	0.05	Borron T		60'	8	
Bating	0.6	Protease enzyme (Oropon ∞), wash		45'	8	

Color Index Measurements for Leathers Tanned with F90-Mimosa (GM) and F90-Mimosa-Collagen Hydrolysate (GMC)

Color measurements were performed using the Digi Eye color imaging system (Digi Eye, VeriVide Ltd, Great Britain), which consists of a digital camera and an illumination box with diffuse illuminant D65. The system was calibrated using digitizer calibration charts. Regarding the digital imaging techniques, the reference and tested leather sample's color difference was computed through the calculated CIELab values. The colorfastness grade was calculated according to the DIN EN ISO 105-A05 standard. In the CIE Lab color space coordinates, the color of the leather was represented by ΔL (Luminosity). This measures whether the sample is lighter (high L) or dark (low L). This shows no color information but only how light or dark the sample is. The coordinates (Δa and Δb), Δa represents redness or greenness, and Δb denotes yellowness or blueness. The color change or chromatic aberration (ΔE) between the light-subjected and un-subjected samples was used

to measure the specimen's luminosity. ΔE was calculated using Equation 1 [15].

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2} \quad (1)$$

L represents the difference between light and dark. a represents the difference between green (-a) and red (+a), and b represents the difference between yellow (+b) and blue (-b). A positive ΔL increment indicates that the color of the composite is lighter, while negative ΔL indicates that the color of the sample is dark after being exposed to light.

L, a, and b represent the difference between light and dark, -a (green) and red (+a), -b (blue) and +b (yellow), respectively. When ΔL is positive, the color of the material is lighter, while the negative value represents the darkness of the sample after exposure to light.

Table 2: Tanning, re-tanning, dyeing

Process	%	Dilution	Product	Temp	Time	pH	Comment
Tanning	80		Water				
	10		sodium p-((4,6-dichloro 1,3,5-triaz-2-yl) amino) benzene sulphonate (Granofin Easy F-90)	55	o. n	6	
	0.1	1:10	Burtol 30 WB				Fungicide, in hot water
	150		Water, drain, Samm, shave				Wash 2 times
Re-tanning	100		Water	40	40'		
	15		Mimosa			3.6-3.8	
	1		Tamol (naphthalene sulfonic acid)		60'		% based on mimosa weight
	50		Water		o. n	5.7	o.n. (overnight)
	5		Collagen hydrolysate		o. n	5.7	
Fatliquoring	4		Lipoderm liquor A1 (sulphited esters)		o. n	4.0-4.5	
	2		Ensul AM 90				
	100		Water, drain	25			Wash
Dying	100		Water	25			
	1		Dye (Avacor Brown MRZ)				Leave till penetration
Fixation	1.5	1:5	formic acid, drain		60'	3.5-3.6	3x @ 10+ 30
	200		Water		20'		
Top dying	1		Dye (Avacor Brown MRZ)				
Fixation	1.5	1:5	Formic acid, drain, wash, toggle		60'		3x @ 10+ 30

RESULTS AND DISCUSSIONS

Physical and Mechanical Properties for F90-Mimosa (GM) and F90-Mimosa-Collagen Hydrolysate (GMC) Tanned Leather

Figure 2 provides a schematic comparison between the physical properties of GM and GMC-tanned leather.

From the results, tear and tensile strength for the sample treated with collagen hydrolysate were higher than that without collagen hydrolysate. The increase was caused by stabilizing function through covalent intramolecular crosslinkers [16] of collagen hydrolysate functional groups, leather matrix, F-90, and mimosa. The results were in line with the physical requirements for shoe-upper leather [17].

The application of collagen hydrolysate reduces the elongation at break. However, the decrease was still above the physical standard requirements for shoe upper leather [16]. The applied collagen hydrolysate positively affected the fullness of leather and prevented over-elongation. These results show a similar trend to the study reported by Afşar *et al*. [18] regarding the impact of collagen hydrolysate on the physical properties of leather when it was used during the re-tanning process.

The shrinkage temperature for sample GMC was higher as compared to that of GM (Figure 2). The formation of the hydrogen bonding network and electrostatic interaction of collagen hydrolysate, leather matrix, and other tanning agents resulted in the higher shrinkage temperature [16]. The physical properties of the leather where the collagen hydrolysate was applied and its antioxidant capacity are reported to be related [16]. The antioxidant capacity of collagen hydrolysate is influenced by the available functional groups, such as hydrophobic amino acids in the peptide, which can stabilize free radicals through the donation of electrons or absorbing the free radicals electrons to reduce their reactivity [12]. The same functional groups play a role in improving other related leather properties [16]. Hence, collagen hydrolysate has a double impact as an antioxidant in improving light fastness and mechanical/physical properties of leather.

To assess the significance of variations, a Welch Two Sample t-test on two variables was used for the properties of GM and GMC-tanned leather. The dataset comprises four pairs of values for these properties. The results of the t-test demonstrate a p-value of 0.9207 and a t-value of -0.10379 with six degrees of freedom (df = 5.9986). The alternative hypothesis that the true difference in means is not equal to zero serves to conduct the test. The 95% confidence interval for the difference in means ranges from -55.29598 to 50.79598. Furthermore, the sample estimations indicate that GM's mean is 49.95 and GMC's is 47.70. Given the high p-value, there is no statistically significant difference between the means of GMC and GM.

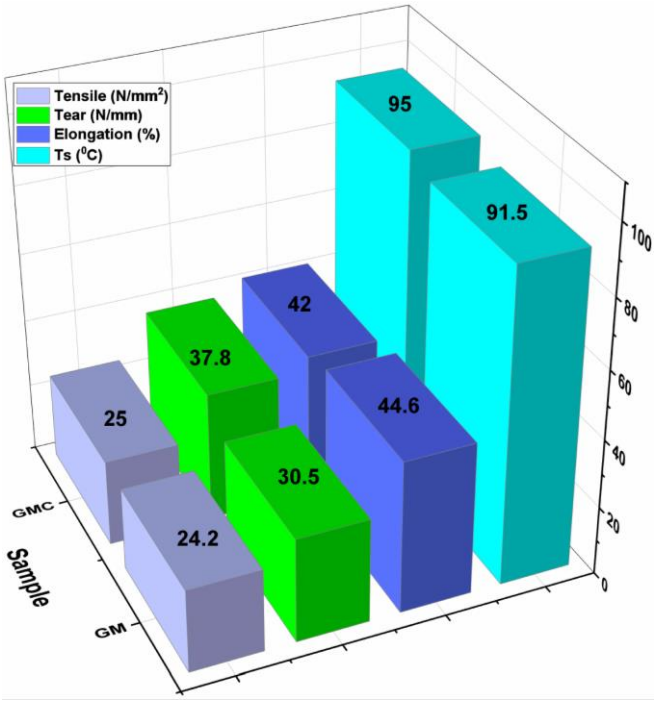

Figure 2. Properties of leather tanned with F90-mimosa (GM) and F90-mimosa-collagen hydrolysate (GMC)

Fourier Transform InfraRed (FTIR) of GM and GMC Leather Samples

The effective incorporation of collagen hydrolysate into the GM was verified by FTIR analysis, and the results are shown in Figure 3. The characteristic absorption bands at 3003, 2923, 1630, 1541, and 1234 cm^{-1} were observed in the FTIR spectra of GM and GMC. These were Amide A bands, observed at 3003 cm^{-1}, which represent the hydrogen bonding caused by N-H attached to a carbonyl group of the peptide chain[19]. The amide band B, due to CH_2 stretching, was observed at 2923 cm^{-1}. The amide band I, which represents the secondary structure of the protein, was seen at 1630 cm^{-1}. This is caused by hydrogen bonding due to the stretching of N-H and C=O. Amide II and III due to N-H bending vibration coupled with C-N and C-H stretching vibrations were found at 1541 and 1234 cm^{-1}, respectively. The absorption ratio between amide I and II, or 1451 $cm^{-1,}$ and amide III, which is equivalent to 1, confirms the existence of the triple helical structure of collagen [3]. The band observed at wavenumber 2853 cm^{-1} was influenced by the lipids from the fatliquors used during the tanning process.

A shift in the peak intensity of the absorbance was observed, and there was no shift in the wave number of the amide bands. The peak intensity for sample GMC increased as compared to GM. In FTIR, a higher peak intensity always indicates a higher concentration of the molecular bond's functional groups per unit volume [20]. The dispersion theory states that the square effective charge of the moving atom and the number of oscillators per unit volume are proportional to the absorption band's intensity [21]. The effective charge is influenced by structural changes and therefore, any changes in the peaks of the absorbance intensity indeed indicate structural changes.

FTIR of the tanned leather mostly displays the absorption band for collagen, therefore, a re-tanning of sample GM with collagen hydrolysate (which has the same composition as that of collagen) did not shift the band's wave number; rather, it only maximized the peak intensity of the spectra. The spectra exhibited features whose intensity changed after the addition of collagen hydrolysate, indicating a strong influence in defining the structure of the resulting leather.

The amide A's intensity change was associated with both intramolecular and intermolecular hydrogen bonds, indicating that a peptide's NH group should form the hydrogen bond [11]. The study's findings showed that the leather treated with collagen hydrolysate had a stronger hydrogen bond than the untreated leather. The outcomes demonstrated that following the addition of collagen hydrolysate, the leather's chemical characteristics were unaltered.

Concerning the influence of the functional groups on color fastness to light, collagen hydrolysate can penetrate inside the collagen fibers of leather due to its lower molecular weight [16]. Having the reactive amino, carboxyl, and hydroxyl groups (the functional groups), it can interact with leather collagen and other used tanning agents through hydrophobic, hydrogen, Van der Waals forces, and electrovalent bonds [22]. The peptides present in collagen hydrolysates function as electron donors to break down chain reactions in the leather matrix by reacting with free radicals to create more stable products [23]. The stable product, when exposed to light, will not be significantly affected by light, hence pronouncing the improved lightfastness.

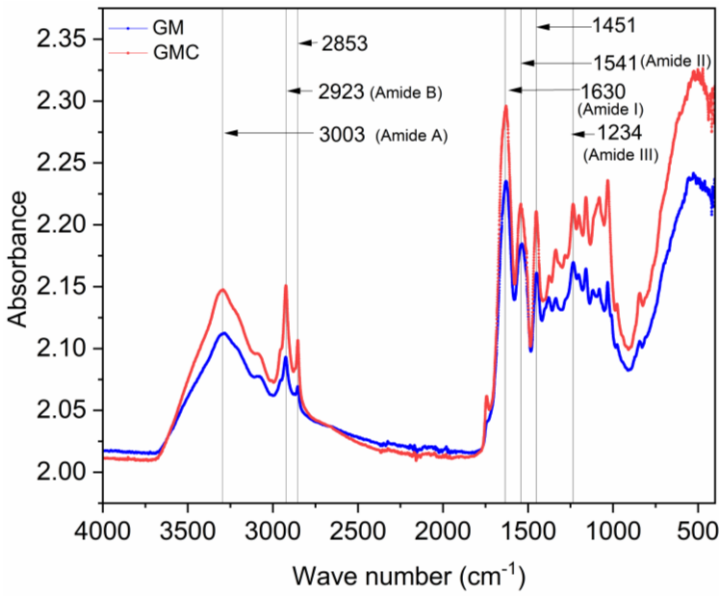

Figure 3. The FTIR spectra of GM and GMC

Scanning Electron Microscopy (SEM) for GM and GMC-tanned Leather Samples

The morphological structures of samples GM and GMC are shown in Figure 4. Scanning electron micrograph (SEM) analysis has been performed to investigate the fiber structure of the tanned leathers. Before the addition of collagen hydrolysate, the fiber bundles of F90-mimosa-tanned leather (GM) were tightly and closely packed (Figure 4a). After the addition of collagen hydrolysate, the fiber bundles of the tanned leather (GMC) were loosened, well separated, and opened (Figure 4b) due to the inside penetration of the collagen hydrolysate, which was also advantageous to the additional sites and the infiltration of dye. The opening of the fiber bundles was due to the interaction of collagen hydrolysate with F-90, mimosa, and leather collagen [22]. As an antioxidant, the opening of the fiber bundles improved the transfer of electrons to free radicals, leading to a stabilized structure of the leather matrix.

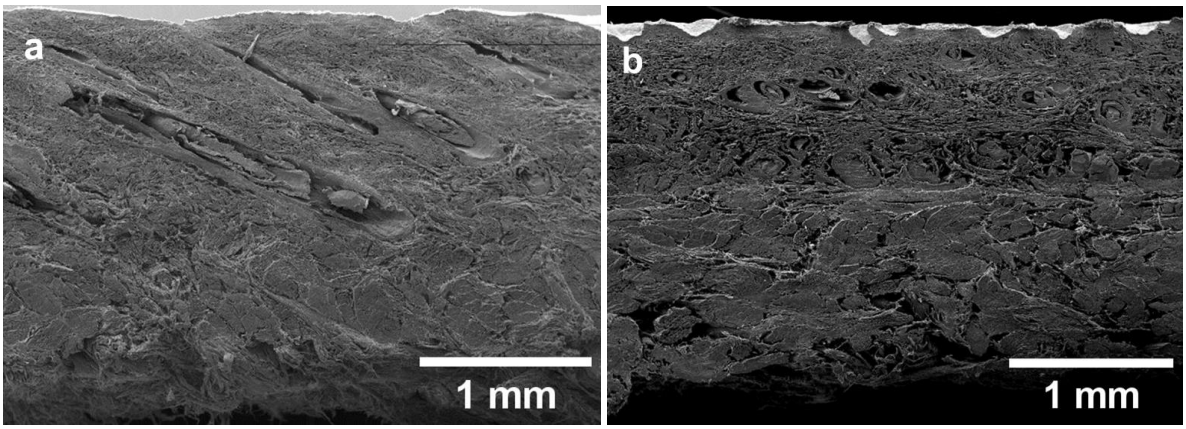

Figure 4. SEM images of (a) F90-mimosa and (b) F90-mimosa-collagen hydrolysate tanned leather

Colorfastness Test to Artificial Light by Xenon Arc Fading Lamp Test

The leathers tanned with GM and GMC show greater differences in their light fastness when exposed to UV light and hot light, as shown in Table 3. GMC had better lightfastness as compared to GM. This is due to the impact of collagen hydrolysate, which has an antioxidant effect on tanned leather.

Many studies indicate that most of the polymer's photodegradation routes are oxidative [3]. Auto-oxidation in leather is a process that is primarily triggered by UV radiations that are high in energy. Environmental pollutants or chemicals that function as radical initiators catalyze this process by splitting into free radicals when exposed to high-energy radiations. Since free radicals are so reactive, they react with oxygen present in the air to generate peroxide radicals. These peroxide radicals react with organic components of leather such as fat liquor, colorants, or dyes, tanning agents, and collagen leading to the deterioration/fading of the material [24].

Collagen hydrolysate neutralizes the propagation action leading to the prevention of the photodegradation process. The antioxidant mechanism of collagen hydrolysate can be attributed to its hydrophobic amino acids and aromatic side chains, which act as radical scavengers, neutralizing free radicals generated by UV exposure. This process likely stabilizes the leather matrix, reducing the degradation of colorants and structural proteins under UV light.

Table 3: Lightfastness for leathers tanned with F90-mimosa (GM) and F90-mimosa-collagen hydrolysate (GMC)

Sample	Blue scale	Greyscale
GM	3-4	1-2
GMC	4	3

Color Index Measurements for Leathers Tanned with F90-Mimosa (GM) and F90-Mimosa-Collagen Hydrolysate (GMC)

The images of the leathers processed with (GMC) and without collagen hydrolysate (GM) are presented in Figure 5 for visual assessment only and the dye used for both samples was Avacor Brown MRZ.

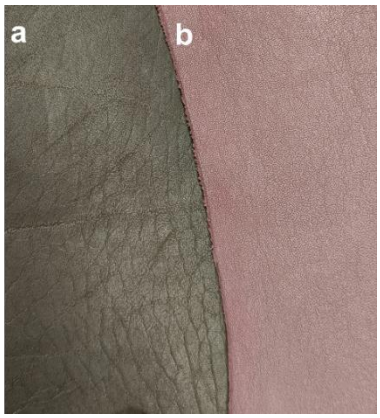

Figure 5. Image of leather tanned with (a) F90-mimosa-collagen hydrolysate and (b) F90-mimosa

For the color index measurement, the color changes or chromatic aberration (ΔE) of leather samples are shown in Figure 6. For all leather kinds, good color resistance to fading under hot or normal light is required [25]. The resistance to yellowing can be investigated by the change of chromatic aberration (ΔE) [28]. By comparing the ΔE values for GM which are 3.56 and 7.81 (normal and hot light exposure, respectively) and for GMC which are 1.55 and 3.38 (normal and hot light exposure, respectively), the values were a bit lower for the sample GMC, confirming that it is more resistant to yellowing than GM [7, 26]. This also implies that, when GM and GMC are exposed to light, GM will be affected (prone to yellowing) more than GMC. The greater resistance to the yellowing of the GMC sample was influenced by the incorporation of collagen hydrolysate (an antioxidant) and it confirms that GM and GMC exhibited differences in their light fastnesses. So here, we can pronounce that F90-mimosa-collagen hydrolysate (GMC) tanned leather has higher light fastness properties than F90-mimosa (GM).

Looking at the ΔL, Δa, and Δb values for samples GM and GMC, it is experimentally determined that the two samples do not match in color. Considering the ΔL, it is evident that sample GM is lighter than sample GMC, which was dark in color. The greater lightness of sample GM was influenced by serious photodegradation and photooxidation [27], leading to the disorientation of the structural network of the leather. Chroma values (Δa and Δb) in GM were higher than in GMC, suggesting that GM underwent a considerable yellowing upon exposure to light. The addition of collagen hydrolysate may have brought about these variations between GM and GMC. ΔE value is the total color difference that represents the distance of a line between the sample and the standard. Comparing the ΔE value, GM has a higher value than GMC, where the lower the value of ΔE of a sample implies the closer the sample is to the standard and the less the change in color after exposure to UV light [28].

To evaluate the significance of differences between the color index values (ΔL, Δa, Δb, ΔE) of GM and GMC tanned leather, the Welch Two Sample t-test on two variables was conducted. The dataset comprises four pairs of values for the samples. For normal light, the t-test results indicate a t-value of 0.57723 with 10.313 degrees of freedom, and the p-value was found to be 0.5762. The 95% confidence interval for the difference in means ranges from -6.094725 to 10.380440, and the mean of GM was found to be 5.101429, while the mean of GMC was 2.958571. The result indicates no significant difference between the two sample means, as the p-value exceeds the common significance threshold (0.05). For hot light, the test results show a t-value of 0.83435 with 10.343 degrees of freedom and a p-value of 0.4229. The 95% confidence interval for the difference in means ranges from -5.207864 to 11.487864. The mean of GM was found to be 6.375714, while the mean of GMC was 3.235714. Since the p-value is greater than the typical significance level of 0.05, the result suggests no statistically significant difference between the means of the two samples.

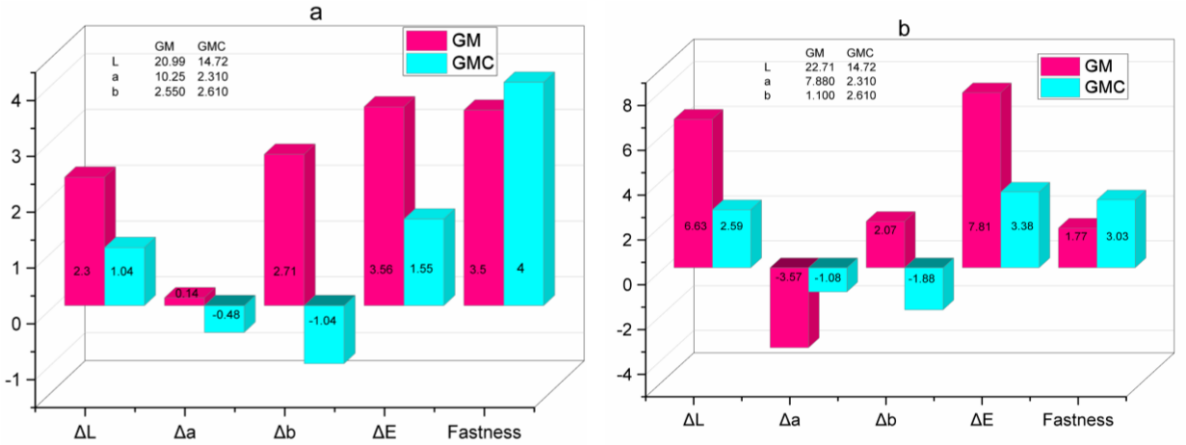

Figure 6. Color index measurements of (a) normal light and (b) hot light for leathers tanned with F90-mimosa (GM) and F90-mimosa-collagen hydrolysate (GMC)

CONCLUSIONS

The application of collagen hydrolysate as an antioxidant in the F90-mimosa-tanned leather improved the lightfastness and the physical-mechanical properties. The morpho-logical changes also occurred after the addition of the antioxidant. Possibly, the cross-linking between collagen hydrolysate, F90, and mimosa occurred as expected. As an antioxidant, collagen hydrolysate may be applied as an effective stabilizer in the photofading process of leather and for industrial applications, the enhanced lightfastness observed in GMC-treated leather suggests its potential for high-end applications such as automotive or outdoor leather goods where prolonged exposure to sunlight is expected. The darkening effect observed in sample GMC after the introduction of collagen hydrolysate could be of advantage for leather intended to be resistant to UV light however, this effect is of disadvantage if the material was intended to maintain the color of the dye used (lighter color). Hence, to maintain the color of the dye used after the application of collagen hydrolysate while improving the lightfastness of the material, further study needs to be carried out.

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