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Utilization of Collagen Wastes as Bioretanning Agent and Effects on the Mechanical Properties of Leather

Aykut Sancakli[1,2*] 0000-0003-3611-4942
Ezgi Ismar[1] 0000-0002-4612-416X
Fatih Arican[1] 0000-0001-6884-3555
Oguzhan Polat[1] 0000-0003-0837-2573
Bahri Basaran[2] 0000-0002-0893-6300
Al Mizan[2,3] 0000-0001-8577-9356

[1] Kazlicesme R&D Center and Test Laboratories, Tuzla, Istanbul, Turkiye
[2] Department of Leather Engineering, Faculty of Engineering, Ege University, Bornova, Izmir 35100, Turkiye
[3] Department of Leather Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh

Corresponding Author: Aykut Sancaklı, aykutsancakli@kazlicesme.com.tr

ABSTRACT

A bioretanning agent was developed as an alternative to conventional synthetic retanning agents to pave the way for sustainability in the leather industry. Solid chromium shaving wastes from leather processing produced a proteinic sub-structure for the constitution building block of the bioretanning agent's backbone. The alkaline hydrolysis method was used to obtain the protein hydrolyzate, and the residual chromium content was determined as <80 ppm. The protein hydrolyzates were acquired in different molecular weights, and the hybrid biopolymers were obtained by grafting the hydrolyzates with acrylic acids (AAc) and acrylamides (AAm). To evaluate the properties imparted by the designed bioretanning agent, it was incorporated into the leather in the retanning processes and compared to the control samples fabricated with conventional procedures. As a result, penetration of hybrid biopolymer into the matrix for retanning was achieved easily, and using low and high molecular weight biopolymers have been recorded by 20% and 23% of improvement in the mechanical performance of the leather samples, respectively. Furthermore, the ratio of the hydrolyzate and AAm/AAc was found to be fitted at 1:2 for both. Furthermore, as per the evaluation of the leathers retanned by novel biopolymer, the results were promising in terms of technical viability and revealed that the biopolymer usage could enhance the mechanical performance of the leather while benefiting from the waste-to-wealth approach.

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KEYWORDS

Leather, Collagen, Chrome shaving, Hybrid polymer, Biotanning agent

1. INTRODUCTION

Leather processing is one of the oldest industries globally and uses many chemicals to produce fashionable, durable, and usable leather from putrescible raw skins. Many quality leather-producing technologies and methods are used, such as chromium tanning, chrome-free, and vegetable tanning. However, this industry is still hunting for newer sustainable technologies and eco-friendly chemicals for leather processing. Environmental concerns are pushing researchers to develop eco-friendly products and processes. The leather industry corresponds to contemporary trends in developing innovative eco-benign products and processes as many other potentially polluting industries. The increasing concerns relevant to the environmental impact of the leather industry have driven tanneries to reduce and valorize their wastes through circular economy approaches. Therefore, recent studies were carried out to recycle collagen-containing leather wastes in different industries [1], [2]. Furthermore, the utilization of collagen-containing wastes through the re-production of leather aiming to enhance the performance characteristics of the produced leather could pave the way for environmental sustainability [3], [4]. Hence, developing innovative retanning materials

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is vital for utilizing tannery wastes.

On the other hand, retanning is the process by which the important qualities of leathers like handle, strength, durability, smoothness, and other physicomechanical characteristics, are modified somehow. Most wet-end processes for leather production are carried out using mostly synthetic auxiliaries such as phenolic syntans, urea, dicyandiamide, melamine resins, and the combination of acrylate polymer and copolymers. Since some are poly-condensation products of formaldehyde in the final leathers, free formaldehyde content could be released. Therefore, those synthetic substances are avoided or sometimes used in controlled dosages due to their harmful effects on human health [5]. Some studies regarding the utilization of collagen and keratin have been noted to be prominent in the retanning process internationally [6,7]. Therefore, the leather industry has still been overlaying challenges in the maximum recovery and reuse of collagen-rich wastes. Nowadays, many researchers are trying to offer alternative benefits from those wastes with their inventions instead of being collected for safe disposal in landfills [8]–[10]. In this scope, it is important to valorize the solid wastes such as chromium leather shavings, collagen-containing scraps, leather buffing dust, and trimming wastes which are the highest in proportion in mass balance statistics in leather production. In this context, the chromium shaving wastes is one of the largest solid tanning wastes and also consist of chromium 2,51%, total nitrogen 12,66%, ash 12.37%, fat 0,29%, and moisture 10.24% [11].

This study was based on the extraction of biopolymer from leather wastes and its modification with acrylic acids (AAc) and acrylamides (AAm) to produce a potential bioretanning agent. In addition, the synthesized grafted retanning agents were used in the leather retanning process, and the tanned leathers were checked for different physicomechanical strength properties.

2. MATERIAL AND METHOD

2.1 Material

Wet blue shavings were collected from Iskefe Tanning Corp., Istanbul, Turkey. Shavings were ground and sieved to remove foreign substances and other impurities. The ground shavings were conditioned in a climatic cabin maintaining a standard moisture content of 55%, a temperature of 23±2°C, and a conditioning time of 24 h. After proper conditioning, the wastes were used as the raw material to prepare bio-based retanning agents. In addition, analytical grade hydrochloric acid (37%, ACS), sodium hydroxide (≥97.0%, pellets), acrylic acid (50%), acrylamide (≥99.9%), sodium dodecyl sulfate (SDS) (≥99.0%, ACS), and hydrogen peroxide 30 % (w/w) were collected from the Sigma-Aldrich (St. Louis, MO, USA).

2.2 Method

2.2.1. Collagen hydrolysis for low and high molecular weight fragment

The raw materials of the conditioned shavings were soaked in distilled water for 30 minutes, where the shavings to water ratio were 1:10. Then, the prepared shaving solution was hydrolyzed under different reaction conditions such as NaOH and CaO processes to reach varying molecular sizes [12]. Finally, NaOH and CaO hydrolysis were carried out, maintaining the heating temperature of 100°C. In low-temperature alkaline hydrolysis, protein extraction efficiency from chromium shaving waste and the solubility of chromium in water remains limited. However, at temperatures above 80°C and under 6-hour reaction conditions, the crosslinks between collagen and Cr(III) are broken, and a solution with low residual chromium content can be obtained in high yield [13, 14, 15]. The detailed experimental methodology is shown in Fig 1.

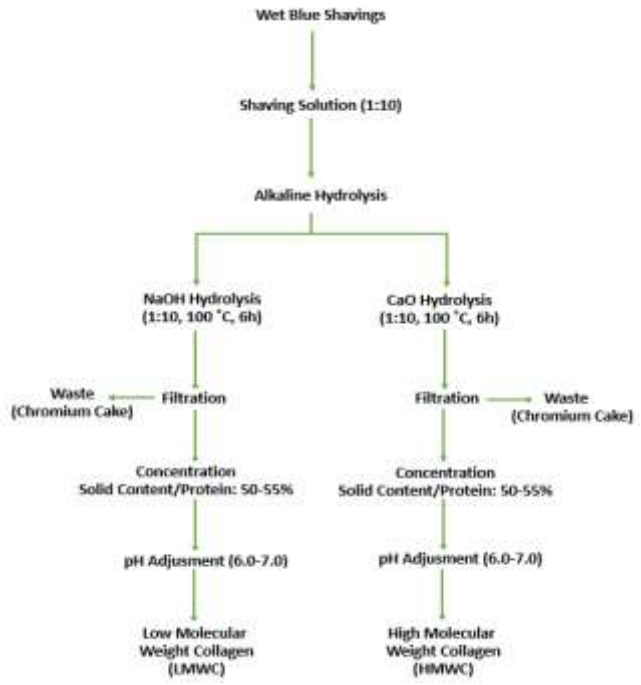

Figure 1. Experimental methodology for optimization of collagen extraction

The alkali treatment of collagen breaks the peptide bonds of the shaving leather wastes. Low molecular weight collagen (LMWC) could be attained through NaOH's higher alkali hydrolysis conditions, whereas high molecular weight collagen (HMWC) hydrolysate was obtained through the CaO treatment (Fig. 1). In this stage, chromium cake wastes were removed from the solution via filtration, and then the solution's value of the solid content (total protein) was increased from 12% to 50-55% by evaporation of the water. Collagens are obtainable through the alkali reaction, which disrupts the triple helix structure and part of the peptide

bonds resulting in lower molecular weight and higher molecular weight polypeptide solution [16].

2.2.2. Grafting of collagen with AAc and AAm monomers

LMWC and HMWC were grafted with monomers such as AAc and AAm by the emulsion polymerization method. Collagen with AAm and AAc and collagen with AAc were grafted by taking the ratios following collagen:AAm 1:1, 1:2, 1:3 and collagen:AAc 1:1, 1:2, 1:3 (Table 1).

Collagen, AAm, AAc, and SDS were dissolved in distilled water. This reaction mixture was taken into a beaker fitted with a mechanical stirrer. Beaker was put in a temperature-controlled water bath at 60°C. The initiator was added dropwise while the water bath temperature was raised to 80 °C, and the top of the beaker was closed with a cap and parafilm. Stirring was continued until the reaction mixture became viscous [17]. The flask was then removed from the bath and allowed to cool at room temperature. The solutions were stored in closed bottles. The film-forming capability was observed, and the mechanical properties were analyzed by pouring the samples at room temperature into molds in equal volumes.

2.2.3. Applications of bioretanning agents in leather production

Synthesized biopolymers were tested on conventionally chrome-tanned bovine leather as a retanning agent. First, the leathers were divided into two parts along the backbone line. Then, one part was retanned with a synthesized bioretanning agent, and the other was retanned with the control sample. Generally, leather retanning processes using acrylics resins are performed as 10-12% of polymeric retanning agents. Therefore, control and experimental applications are done with the same amount of samples. Finally, applying the developed retanning agent in leather processing was carried out by following the recipe mentioned in table 2.

Table 1. Formulation ratios of LMWC-HMWC /AAm and LMWC-HMWC/AAc monomers

Sample Name	Protein Molecular Weight	Monomer Type	Protein Monomer Ratio	Initiator (%)	SDS Ratio (%)	Water (%)
LM1	Low	AAm	1:1	0.15	0.4	80
LM2	Low	AAm	1:2	0.30	0.4	80
LM3	Low	AAm	1:3	0.15	0.4	90
LM4	Low	AAc	1:1	0.15	0.2	80
LM5	Low	AAc	1:2	0.3	0.2	80
LM6	Low	AAc	1:3	0.5	0.2	80
HM1	High	AAm	1:1	0.05	0.4	90
HM2	High	AAm	1:2	0.05	0.04	75
HM3	High	AAm	1:3	0.75	3	80
HM4	High	AAc	1:1	0.1	0.02	80
HM5	High	AAc	1:2	0.05	0.02	80
HM6	High	AAc	1:3	0.05	0.02	60

Table 2. Formulation of the retanning process of leather

Process	Chemicals	Control
Washing	200% Water 45 °C	10 mins
Neutralization	100% Water 35 °C 4% Bioretanning Agent 1.5% Sodium Formate 0.5% Sodium Bicarbonate	60 mins pH 5.0-5.5
Draining & Washing	200% Water 45 °C	10 mins
Retanning	80% Water 25 °C 4% Bioretanning Agent 15% Tannins 3% Dyes 0.2% Formic Acid	60 mins 20 mins pH 4.2-4.4
Fat-liquoring	100% Water 55 °C 4% Bioretanning Agent 10% Fat-liquor 2% Formic Acid	10 mins 15 mins 30 mins 30 mins pH 3.8-4.0
Draining & Washing	300% Water 45 °C	10 mins

2.2.4. Characterization Analysis

Molecular weight analysis was performed via Agilent Technologies 1260 Series gel permeation chromatography (GPC) system. The optimum work conditions for the GPC were maintained one $mLmin^{-1}$ flow rate of the mobile phase; 100 µL injection volume of the sample; 35°C temperature for the detectors and the column. The weight average molecular weight (Mw) and number average molecular weight (Mn) calculations were performed using Agilent GPC/SEC Software (Version 1.1, Agilent Technologies, USA).

Particle size determination was performed with Anton Paar instrument type PSA 1190 LD particle size analyzer for powder form of the samples were placed into the device and collecting data accordingly. Agilent 600-IR Series Fourier transforms infrared spectroscopy (FTIR) was used to determine the chemical structure of the samples in the range of 4000 – 650 cm^{-1}.

Mechanical properties of the leathers produced with bioretanning agents were measured with the tensile testing machine (Shimadzu AGX). In this scope, Tensile strength and elongation (ISO 3376), single edge tear resistance (ISO 3377-1), and double edge tear resistance (ISO 3377-2) were measured, respectively.

The morphological properties of the samples were determined by scanning electron microscopy (SEM) (EVO® LS 10, ZEISS, Germany). All samples were coated with gold before the characterization.

3. RESULTS AND DISCUSSION

3.1. Molecular weights of extracted collagens

Collagen molecular weights were determined by gel permeation chromatography (GPC). The weight average molecular weight (Mw) and several average molecular weights (Mn) were presented in Table 3. The collagen protein was extracted at different molecular weights to determine the molecular size effect on the samples. For the extracted proteins, the Mw was calculated as 1.243 g/mol and 30.028 g/mol for the low- and high-Mw protein samples, respectively.

Table 3. Molecular weights of the low and high collagen

Sample	Mw (g/mol)	Mn (g/mol)
LMWC	1.243	1.228
HMWC	30.028	28.000

3.2. Film formation and tensile strength of the film-forming agent

The grafted samples' film-forming properties and mechanical strength were observed before selecting the best retanning agents for leather applications (Fig. 2). Products with acrylic resins used in the leather retanning show film-forming properties. In this context, the film-forming behaviors of the developed samples and their mechanical properties were compared. In this study, some synthesized biopolymers could not form the film because of different ratios of the protein and monomer; thus, they were directly eliminated. Harder films were obtained by increasing the monomer and initiator of the films obtained at the end of the graft polymerization reaction using collagen and acrylic monomer. Also, the formulation contains a higher amount of protein, for which the films were weak and not durable. Besides, the film structure could not be reached in the reaction experiments using high amounts of SDS [17].

Figure 2. Film formation of synthesized bioretanning material

The results presented in Table 4 showed that the highest elongation was found in the LM5 and HM2. In addition, the highest tensile strength was found in the samples LM6 and HM4. However, these sample films were too hard and fragile. Thus, according to the results, HM2 and LM5 were selected as application samples for the leather retanning process due to their highest elongation, tensile strength, and physical appearance.

Table 4. Tensile strength and elongation of the casted films

Sample Name	Film Formation	Tensile Strength N/mm^2	Elongation %
LM1	✓	0.68	189.61
LM2	✓	0.35	200.08
LM3	✓	1.60	158.85
LM4	✓	1.54	165.19
LM5	✓	1.01	250.42
LM6	✓	1.89	120.03
HM1	✓	0.64	170.50
HM2	✓	1.75	244.81
HM3	✓	1.28	148.04
HM4	✓	2.13	98.97
HM5	✓	0.82	170.66
HM6	✓	1.89	219.07

3.3. Particle size distribution of retanning agents

The particle size distribution of the selected samples is shown in Fig. 3. The particle size was measured as 226.54 ± 11.2 µm for LM5 and 542.47 ± 5.99 µm for HM2 after the Grafting of the low- and high-molecular-weight collagens. Molecular weight ratios and particle size of bioretanning agents play an important role in tanning power and shrinkage temperature [18]. The result signifies that the sample having a lower particle size will facilitate retanning properties because the lower particle size increases the surface area of the materials and enhances reaction capability and binding power with the collagen [18,19].

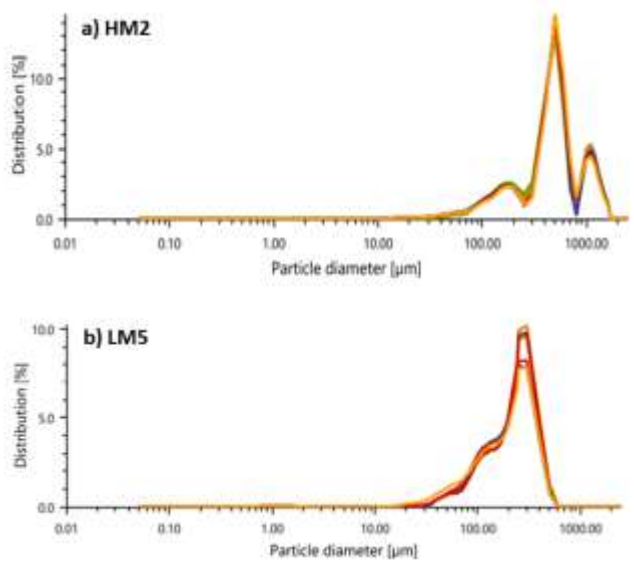

Figure 3. Particle size distribution of a) HM2 and b) LM5

3.4. FTIR spectrum of bioretanning agents

The FTIR graph of the synthesized bioretanning agent is delineated in Fig. 4. Characteristic peaks of the protein structure such as amide I, II, and III were recorded. For amides, I, II, and III peaks were recorded at around 1713, 1634, and 1335 cm^{-1}, which signifies that the material contains protein and comes from C=O stretching and NH_2 bonds, respectively [20-22]. The peak at 1136 cm^{-1} is related to C-O stretching. Peak around 2850 cm^{-1} is stretching peak from COOH structure. For polymeric structure, characteristic peaks were also detected. The band observed at 1634 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of substrate backbone [23]. The band around 1407 cm^{-1} is related to the carboxylate anion, which is due to the symmetric stretching mode of the carboxylate anion [23-24]. The groups in the synthesized bioretanning agent confirmed the proper crosslinking of the LMWC and HMWC with the concerned amide and made it a potential retanning agent.

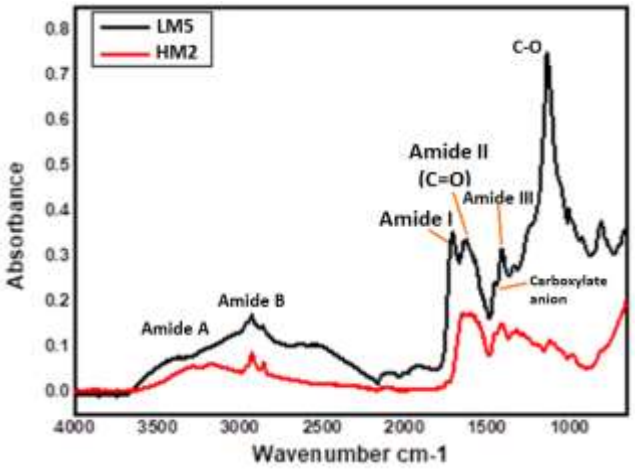

Figure 4. FTIR spectra of low and high molecular weight bioretanning agents

3.5. Application in leather and mechanical properties

The mechanical characteristics of the experimental samples were compared to control samples which were retanned using conventional retanning agents. Mechanical characterization showed that applying a bioretanning agent improves the leather samples' mechanical strength while improving the leathers' elongation. Fig. 5 compares the mechanical test results for the control and experimental samples.

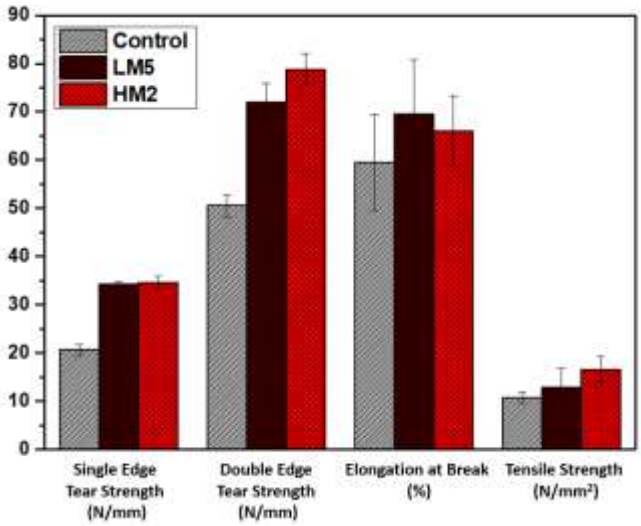

Figure 5. Results of mechanical characteristics of leather by application of retanning agents.

The highest elongation was found in the LM5, while the highest tensile strength was in sample HM2. Single and double-edge tear strength results also indicate the positive effect of the bioretanning agent depending on collagen's molecular weights when compared to control. The test results showed well above values than the control samples. The applied bioretanning agents could penetrate easily and strongly interact with leather fibers. Though a small difference was found in the fullness and softness, the applied retanning polymer improves leather's physical characteristics and appearance. The improved leather's physical properties by applying acrylic monomers in collagen fibers under suitable conditions may be due to the formation of an interlocking network between the applied acrylic monomers and collagen fibers. The free NH_2 and COOH groups of acrylamide and collagen are found to be more positive for the co-initiation of leather fibers and improve strength, fullness, and softness [12,25].

3.6. Scanning electron microscopy (SEM) of biotanned leather

The influence of developed bioretanning agents on the surface texture of the leather samples was monitored with the scanning electron microscopy technique (SEM). In addition, these samples were compared with control samples in Fig. 6.

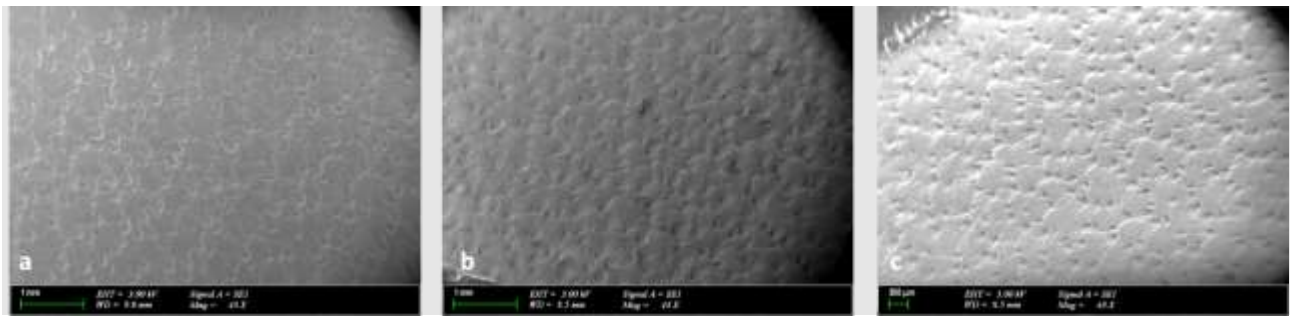

Figure 6. SEM images of a) control sample, b) sample HM2, and c) sample LM5

After the retanning process, the porous structure of the hide becomes smoother and easily examined [26]. The surface of the control sample exhibited a more smooth structure and was eliminated from pores when compared with LM5 and HM2. On the other hand, it is seen that the pores of both the control and other leather samples are filled, which signifies the effectiveness of retaining agents to fill the pores leading to high tensile strength and other physical properties, as shown in fig 5.

4. CONCLUSION

For decades, sustainability in leather processing has been searched, especially for tanning and retanning processes. This study aimed to recover chromium shavings and hydrolysate resue in synthesis bioretanning agents. Accordingly, it gives rise to a sustainable solution to the retanning process for enhanced eco benignity and circular economy, besides enabling the secondary production potential of the synthesized agent. The synthesized agent showed prominent retanning properties compared to the conventional acrylic retanning agents with the improvement of 20-23% physicomechanical properties of the tanned leather. It will also create a waste minimization of 10-15% of the total tannery solid wastes by utilizing it as a retanning agent. In addition, grafting of acrylic acids (AAc) and acrylamides (AAm) with HMWC and LMWC showed the best properties as bioretanning agents at the ratio of 2:1, respectively. Therefore, the developed bioretanning agent could be a potential alternative to conventional synthetic acrylic retanning agents and a plausible way to valorize shaving waste generated from the tannery.

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