Development of Protein Binder from Tannery Waste for Leather Finishing

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Development of Protein Binder from Tannery Waste for

Thiruppathi Venkatachalama,b, Gladstone Christopher Jayakumara,b*, Balaraman Madhana,b

a Department of Leather Technology, Alagappa College of Technology (Housed at CSIR- Central Leather Research Institute), Anna University, Chennai-600020, India

b Biochemistry and Biotechnology Laboratory, Council of Scientific and Industrial Research- Central Leather Research Institute (CSIR-CLRI), Chennai-600020, India.

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Leather Finishing

Abstract

The leather sector constitutes a cornerstone of the global fashion industry; however, the management of solid waste remains a critical barrier to environmental sustainability. Specifically, tannery hair waste—a keratin-rich byproduct of enzymatic dehairing— represents a significant volume of biomass often destined for landfill. Concurrently, the industry relies heavily on commercial casein binders for glaze finishing, a practice constrained by high costs and supply chain sustainability issues. In alignment with the “waste-to-wealth” paradigm, this study engineers a high-value keratin hydrolysate binder derived directly from hair waste to functionally replace casein from leather finishing system.

The extraction process was optimized to maximize protein recovery, and the resulting hydrolysate was characterized using nuclear magnetic resonance (NMR) and fourier transform infrared spectroscopy (FTIR), confirming the structural integrity of the polypeptide chains. Thermal stability was analysed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), which confirms the compatibility of keratin hydrolysate for hightemperature finishing processes. Comparative benchmarks revealed that keratin-finished leathers met all standard industry norms for grain distension, finish adhesion, and rub fastness. Notably, binder significantly outperformed commercial casein in aesthetic and functional metrics, demonstrating

Corresponding author email : venkatachalamvkvk@gmail.com

superior gloss intensity, enhanced hydrophobicity, and water vapor permeability. By substituting casein with a waste-derived alternative, this research successfully demonstrates a process circularity in the leather finishing system. This approach not only mitigates the environmental footprint of tannery effluent but also establishes a cost-effective, circular economy model for the leather finishing system.

Keywords: Keratin Hydrolysate; Leather; Finishing; Binder; Cleaner Technologies.

1. Introduction

The growing interest in sustainable leather manufacturing stems from the increasing awareness of environmental impacts from traditional leather production, which generates a high volume of solid wastes such as flesh, hair, leather scraps, chrome shavings, buffing dust, raw trimmings, lime sludge etc. Incineration and landfilling are the common disposal methods followed to dispose these solid wastes which affects the sustainable growth of the leather industry. The conventional unhairing method uses inorganic chemicals which significantly increases the levels of total dissolved solids and chemical oxygen demand in tannery effluents. Hence, exploring effective solid waste management systems is crucial for leather sector.

Hair is made up of keratin which is a complex structure reinforced in to strong disulphide bridges making them challenging to break down.

To achieve glossy appearance in leather, protein finishing is usually done using a glazing machine with thermosetting

binders (casein binder, albumin, etc.). These binders offer good adhesion and strong heat resistance. However, due to their shorter shelf life, higher water sensitivity, depends on food based raw materials, fluctuating market

costs and susceptibility to bacterial attacks, alternatives are often preferred.

Chemicals(mL) K1 K2 K3 K4 Description Water 690 640 590 540 2 cross coats sprayed followed by medium glazing

In the current study, a new finishing formulation was prepared using keratin hydrolysate binder as a substitute for casein binder. The result of this work led to the development of a protein binder, which is extracted from tannery hair waste, that leads to a circular economy approach.

2. Methodology

Hair waste was collected from enzymatically unhaired goat skin. It was washed and hydrolysis was carried out using sodium hydroxide followed by filtration, dialysis and lyophilisation. Finish formulation was prepared with different concentration of keratin hydrolysate (K1, K2, K3 & K4) and sprayed on the crust leather (Table 1 and Table 2).

Figure 1 Extraction of keratin hydrolysate from

tannery hair waste

Table 1 Recipe for protein-based glaze finishing

(basecoat)

Keratin hydrolysate

220 270 320 370

binder (13%)

and then 1 cross coat sprayed and dried

Wax 15 15 15 15 Dye solution 30 30 30 30 Penetrator 30 30 30 30 Oil 15 15 15 15

Table 2 Recipe for protein-based glaze finishing

(Topcoat)

Chemicals(mL) Experiment Description

Water 1:3

1 Cross Coat sprayed

Keratin hydrolysate

140

binder (13%)

Slip 2%

Fixing

1 Cross Coat sprayed,

followed by Glazing BTX 1:1 Water

Ironing @ 100 o C

The formulation was sprayed as a cross-coat on leather

by High-Volume Low-Pressure gun.

3. Results & Discussion

3.1 Characterization of Keratin Hydrolysate

3.1.1 UV-Visible Spectrophotometer

Keratin has a maximum absorption peak at 217 nm. It also had a strong absorption band at 270–280 nm, primarily due to the presence of aromatic amino acids and these peaks may indicate the presence of a K band which may be due to a conjugated system with a double bond because of the presence of amino acids and peptide bonds.

3.1.2. Fourier Transform Infrared Spectroscopy

Alpha helix and beta sheet structure of keratin hydrolysate was confirmed by amide I and amide II band which shows peak around 1640 cm-1 and 1517 cm-1 respectively. Amide III with a weak band at 1235 cm-1 shows N-H

bending

and C-O, C-N stretching. By using FTIR, conformational changes and secondary structure of keratin hydrolysate samples were confirmed.

3.1.3 Nuclear Magnetic Resonance Spectroscopy

Strong peak around 174 ppm was ascribed to carbonyl carbon(C=O) confirms the presence of peptide backbone. Peak around 53 ppm indicates -carbon, and at 24 ppm, -carbon was confirmed. The signals observed in the region of 20–30 ppm correspond to the methyl and methylene carbons of aliphatic amino acids such as alanine, valine, leucine, and isoleucine.

α

β

3.1.4 Thermogravimetric Analysis

Initial weight loss of 10-15% was observed around 95°C to 130°C due to loss of water. Degradation occurs at the temperature range of 200-380°C, and 50 % weight loss was observed at 380°C.

3.1.5 Differential Scanning Calorimetry

From the thermal characterization studies, the first peak around 120°C indicates loss of water and the peak around 240°C indicates the thermal decomposition of keratin hydrolysate.

3.2 Characterization of Keratin Hydrolysate Binder Finished Leather

3.2.1 Adhesion Properties of Keratin Hydrolysate Binder Finished Leather

Adhesion is crucial in the finishing process as it reflects the interaction between the leather surface and the finishing chemicals. An optimal concentration of binder is important for achieving strong adhesion. At the concentration of 1.5 % - 2.0 %, the binder forms a cohesive layer that effectively binds the finish to the leather. This not only enhances adhesion but also improves the overall performance of the leather, providing resistance to wear, water, and other environmental factors. The optimal binder concentration allows for adequate film formation, ensuring that the finish adheres uniformly across the leather surface.

At lower concentration (0.5%), binder leads to weak adhesion, whereas a higher concentration (> 2%) of binder leads to a brittle finish that is prone to cracking, poor breathability and delamination over time. Keratin hydrolysate-based binder shows better adhesion strength. Experiments with different concentrations of keratin hydrolysate (K1, K2, and K3) meet the minimum test requirements.

3.2.2 Colour Fastness to Rubbing of Keratin Hydrolysate Binder Finished Leather

Sample K1, K2 and K3 showed a grey scale rating of 4/ 5, which demonstrates the strong binding of binder towards the leather matrix whereas when the concentration of the binder is greater than 1.5 %, there is a reduction in fastness property of 4/5 to 4.

3.2.3 Water Vapour Permeability of Keratin Hydrolysate Binder Finished Leather

Water vapour permeability of the leather changes after finishing process based on types of finishing system. By comparing the values of water vapour permeability of samples K1, K2, K3 and K4, sample K4 has the lowest water vapour permeability. In general, the higher concentration (2%) of keratin hydrolysate solution affects the water vapour permeability of finished leather. The findings confirm that, binder concentration of (d 1.5%) doesn’t affect the natural breathability of the leather.

≤

3.2.4 Determination of Distension of Grain of Keratin Hydrolysate Binder Finished Leather

Thermosetting binders, like casein or keratin, typically result in better grain crack resistance due to their stable structures at high temperatures, allowing the leather to be processed (e.g., ironed or pressed) without compromising its mechanical properties. Thermoplastic binders, on the other hand, may soften under heat, which could reduce their effectiveness in maintaining grain integrity during distension. Experiments with different concentrations of keratin hydrolysate (K1, K2 & K3), passing minimum test requirements for shoe upper leather as per Indian standard IS: 578, 1985.

Determination of Gloss Value of Keratin Hydrolysate Binder Finished Leather

Similar to casein binders, keratin hydrolysate binders also belong to the category of thermosetting binders, which means their structure remain stable at particular temperatures. Because of this, finished leather is nonsticky, enhances gloss and can be treated with higher temperature. The higher gloss values (minimum 11.68

- maximum 16.57 at 60°) were obtained when the binder concentration ranged from 0.5% to 2%. In this instance, the surface gloss is elevated because there is minimal light scattering at this concentration. It is evident from the results that gloss values increase as the concentration of keratin hydrolysate increases which confirms the leather show semi-gloss finish. But based on the other properties (Distension of grain, water vapour permeability and fastness), 1.5% (K3) was chosen as an optimum concentration for leather finishing.

Contact Angle of Keratin Hydrolysate Binder Finished Leather

Extracted keratin hydrolysate solution, commercial finish formulation and formulation along with keratin hydrolysate binder (K3), each 5 µL, were dropped in the crust leather. The contact angle of the commercial finish formulation was 26.74°, whereas the keratin hydrolysate-based formulation shows an increase in contact angle of 52.60°. Experimental leather shows a slight decrease in hydrophilicity because of the presence of keratin hydrolysate binder, which coats with fibre bundles, as a result, surface energy gets reduced, leading to decreased hydrophilicity.

4. Conclusion

Reducing chemical usage and utilizing solid wastes effectively are complex and challenging aspects of transitioning the leather industry towards cleaner production. By using chemical reduction method, Keratin hydrolysate was extracted, which is easier to process, and suitable for inhouse production. Conventionally, casein binder was used for glaze finishing process, which was

replaced by the keratin hydrolysate binder. The production of byproduct (keratin hydrolysate) and its use as a finishing agent in the same leather-making process leads to waste reduction and also decreases reliance on food derived binders. Further research and development in application techniques will pave the way for a greener and more sustainable leather industry.

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