Advanced Functional Materials for Sustainable Lubrication of Leather

Bindia Sahu*[1,2,4], Akash Bhalla[3]

1. Inorganic and Physical Chemistry, Central Leather Research Institute, Council of Scientific and Research, Adyar, Chennai 600020, India

2. Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India

3. Leather Process Technology Department, CLRI Regional Centre – Jalandhar- 144002

4. Department of Leather Technology, AC Tech Campus, Anna University, Chennai,600025, Tamilnadu, India

Corresponding author -bindia@clri.res.in, bindiya1480@gmail.com (Bindia Sahu)

ABSTRACT

The tanning, post-tanning, and finishing stages are critical for effective leather processing. Post-tanning encompasses several essential steps, including retanning, fatliquoring, and dyeing of leather. Fatliquoring agents play a vital role in lubricating the skin fibers, preventing them from sticking together. The percentage of fatliquoring agents typically varies between 6-25%, depending on the specific requirements of the leather products being produced. The innovative use of host-guest assemblies, formed from beta-cyclodextrin containing seven glucose units combined with unsaturated fatty acid such as oleic acid obtained from fat has been explored as a fatliquoring agent. Furthermore, this eco-friendly process contributes positively to environmental sustainability by supporting plant growth and reducing pollution. With the potential for minimal chemical modifications, this method paving the way for more sustainable leather processing techniques that align with contemporary environmental standards.

Key words- Leather, Post-tanning, Cyclodextrin, Fatty acid

Introduction

The process of making leather begins with a series of wet-end steps, which include trimming, sorting, soaking, fleshing, unhairing, baiting, pickling, tanning, wringing, splitting, shaving, retanning, coloring, fatliquoring, and finally, setting out the leather [1,2]. Once the wet-end procedures are done, several dry processes follow, including drying, conditioning, staking, buffing, finishing, plating, measuring, and grading [3].

After the initial tanning phase, leather is often subjected to retanning, coloring, and fatliquoring. These three processes are commonly grouped together because they can be performed in sequence within the same retanning drum, providing flexibility in the order of operations [4]. Achieving even tanning of the skin fibers is crucial, as the fibers can display various structural patterns. Effective tanning enhances several characteristics of the leather, including fullness, tightness, and smoothness of the grain, as well as flexibility and resistance to water and perspiration [5].

Retanning may utilize a variety of materials, including natural extracts from plants and vegetables, as well as synthetic agents known as "syntans," used either alone or in combination [6]. Following tanning, the leather undergoes fatliquoring, a process where oil is applied in emulsion form. This step is essential for lubricating the leather fibers, resulting in increased softness [7]. Fatliquors are primarily derived from oils through various chemical modifications, incorporating surfactants and utilizing the Pickering emulsion method [8].

Research into the chemical modifications of oils for fatliquor production has been extensive. Various techniques, such as transesterification, sulfation, sulfitation, epoxidation, phosphorylation, and sulfochlorination, have been studied [9]. Non-ionic surfactants are commonly used to create emulsions from natural fats and oils. Moreover, the Pickering emulsion technique employs solid particles—such as polysaccharides, proteins, lipids, and safe inorganic materials like silica, calcium carbonate, and hydroxyapatite—to stabilize these emulsions [10].

Fatty acids, their esters, monoglycerides, and other long-chain apolar alkane-containing molecules, are generally effective guest molecules for forming inclusion compounds with cyclodextrins (CDs), which act as the host. The stability of these complexes typically decreases in the following order: fatty acids > monoglycerides > diglycerides > triglycerides. Additionally, the solubility of the lipid/CD complexes is influenced by this trend in stability [11].

The innovative use of host-guest assemblies, formed from cyclodextrin—composed of six, seven, or eight α-1,4-linked glucose units—and unsaturated fatty acids, such as mono- and polyunsaturated fatty acids plays as a fatliquoring agent. Specifically, an optimized formulation utilizing beta-cyclodextrin containing seven glucose units combined with unsaturated fatty acid such as oleic acid obtained from fat has been explored.

Materials and methods

Materials

Indian goat skins were procured from the local slaughter house, Chennai, India. Cyclodextrin from sigma Aldrich, Chennai, Oleic acid and all other leather chemicals were of commercial grade.

Preparation of Cyclodextrin and fatty acid inclusion compound

OA/β-CD inclusion complex was prepared by the co-precipitation method [12].

Characterization of the inclusion compound

FTIR

The identification and confirmation of functionality, were carried out by FTIR analysis using Perkin Elmer at the Centre for Analysis, Testing, Evaluation and Reporting Services (CATERS), CSIR-Central Leather Research Institute. This method was used to characterize, inclusion compound made up of BCD and Oleic acid, BCD and Oleic acid separately.

Application on leather

The prepared inclusion compound was applied on wet blue of goat skin in following the manner as indicated by table 1.

Table 1-Process recipe for fatliquoring

Process	Materials	Amount (%)	Time	Remarks
Neutralization	Water Neutralizing syntan Sodium bicarbonate + Water	100 0.5 0.2 10	30 min 2 × 10 min + 30 min	pH:5.0-5.2, Drained and wash twice
Retanning	Water Melamine syntan + Phenolic syntan + Tara powder	50 5 5 4	60 min	
Fatliquoring	Water	50	2 × 15 min + 60 min	
Control	Comercial fatliquor	10		
Experimental process	Experimental fatliquor	10		
Fixing	Formic acid + water	2 + 10	3 × 10 min + 60 min	Check exhaustion and pile

Results and Discussion

FTIR-

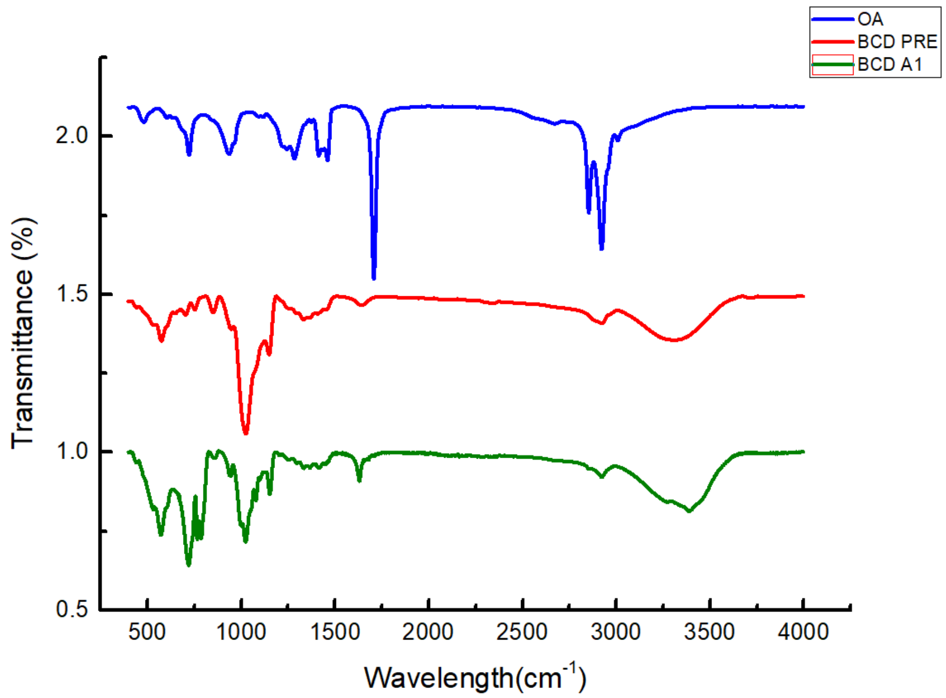

Fig-1 FTIR of Oleic acid (OA), β-CD and Inclusion compound (BCD A1)

Characteristic peaks for pure Oleic acid (OA) at 2853 and 2822 cm^{-1} were attributed to symmetric stretching vibrations of C-H in CH_2. 1707 cm^{-1} due to C=O stretching vibration, 1460 cm^{-1} due to C-O stretching vibration and 935 cm^{-1} was attributed to the O-H out-of-plane bending vibration. Characteristic peaks for pure β-CD at 3287 (O-H stretching vibration), 2923 (C-H stretching vibration), 1642 (O-H bending vibration), 1151(C-O stretching vibration) and 1020 cm^{-1} (C-O symmetric stretching vibration) were reported. In the spectrum of OA/β-CD inclusion complex (BCD A1), bands for OA were disappeared by strong and broad β-CD bands, and the characteristic peaks for OA at 2853, 1707 and 1460 cm^{-1} disappeared, suggesting that the carboxyl group of Oleic acid was probably entered into the cavity of β-CD and the vibrations of carboxyl group were restricted after the formation of inclusion complex.

Plausible mechanism of inclusion compound with collagen

The core process involves the hydrophobic tail of oleic acid inserting into the hydrophobic cavity of the cyclodextrin molecule. This is a non-covalent, reversible physical interaction driven by hydrophobic effects. β-CD is most suitable for fatty acids like oleic acid due to its cavity size (~7 Å). The interior cavity of cyclodextrin is relatively hydrophobic, favouring the encapsulation of hydrophobic molecules or parts of molecules like oleic acid's hydrocarbon chain. This interaction is reversible, governed by an equilibrium that can be influenced by environmental factors, leading to enhanced solubility, stability, and controlled delivery of oleic acid. The polar carboxyl group (-COOH) tends to stay near the aqueous exterior or at the cavity entrance, possibly forming peptide bond with amino groups on the collagen molecule.

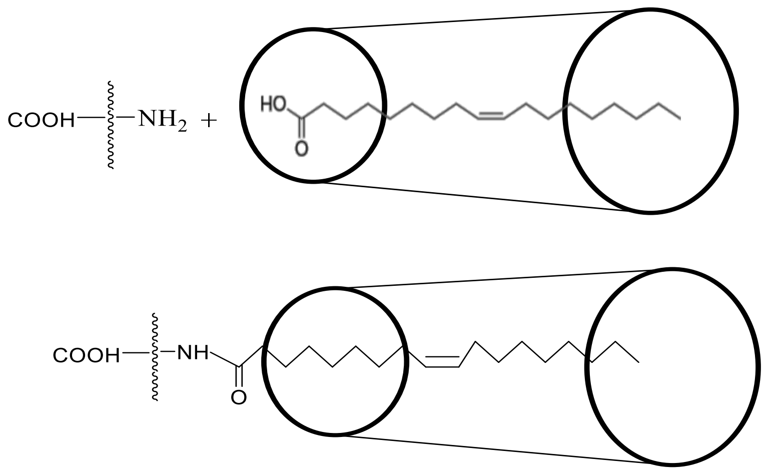

Fig-2 Plausible mechanism of inclusion compound with collagen

Conclusions

The inclusion compound formed by beta-cyclodextrin and oleic acid significantly influences the softness of leather. Beta-cyclodextrin, a cyclic oligosaccharide, possesses a hydrophobic interior cavity capable of encapsulating hydrophobic molecules like oleic acid. When combined, the inclusion complex stabilizes oleic acid within the cyclodextrin cavity, controlling its release and interaction with the leather via peptide linkage. This modulation enhances the leather's flexibility and softness by uniform distribution of oleic acid, ensuring consistent softening effects across the leather surface. Moreover, this complex can improve the durability of the softening effect and reduce the use of harsher chemicals. Overall, the beta-cyclodextrin-oleic acid inclusion compound acts as a controlled-release softening agent, improving tensile and tear strength of experimental leather.

Acknowledgements

The author acknowledges financial support from Sustainable Manufacturing and Environmental Pollution (SMEP) project (GAP 2405). Authors also thank to Janani V, Aparna KT and Department of Leather Technology, AC Tech Campus, Anna University.

References

1. Ahmad, T., Ahmed, S., Ikram, S., Role of Surfactants in Emulsification of Fats and Oils: A Review, Colloids and Surfaces A, 532, 52-60, 2017.
2. Bailey, D.G., Modern Fatliquoring Technology, J. Soc. Leather Technol. Chem., 87, 1-9, 2003.
3. Bindu, R., Joseph, P., Dinesh, S., Syntans: A Versatile Class of Retanning Agents, J. Am. Leather Chem. Assoc., 112, 305-312, 2017.
4. Chen, L., Liu, L., Bai, L., Pickering Emulsions Stabilized by Renewable Materials: A Review, Adv. Colloid Interface Sci., 299, 102578, 2022.
5. Covington, A.D., Tanning Chemistry: The Science of Leather, Royal Society of Chemistry, 1-312, 2009.

6. Dickinson, E., Food Emulsions and Foams: Stabilization by Particles, Curr. Opin. Colloid Interface Sci., 15, 40-49, 2010.

7. Dutta, S.S., Mahapatra, N.N., A Review on Leather Processing: Chemistry and Applications, J. Soc. Leather Technol. Chem., 100, 25-35, 2016.

8. Gonçalves, C., Ferreira, D., Pintado, M., Pickering Emulsions Stabilized by Biobased Particles: A Review, Trends Food Sci. Technol., 86, 88-99, 2019.

9. Gutteridge, C.S., Retanning and Syntans, J. Soc. Leather Technol. Chem., 74, 13-20, 1990.

10. Heidemann, E., Fundamentals of Leather Manufacturing, Eduard Roether KG, 1-230, 1993.

11. Kanth, S.V., Venba, R., Madhan, B., Green Process for Vegetable Tanning Using Acacia Mollissima, J. Am. Leather Chem. Assoc., 104, 1-8, 2009.

12. Rui L., Xiaoli Q., Xiong L., Yonghua W., Jinfeng Z., Host-guest interactions between oleic acid and β-cyclodextrin: A combined experimental and theoretical study, Food Chem. 387, 132910, 2022.