Impact of Flax Seed Protein and Beeswax Emulsion Blend on Leather Finishing– A Novel Eco-Benign Formulation

by

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Abstract

Protein based finishing on leather surface is generally done using casein-based formulation which forms a transparent and breathable film. Other naturally available options such as protein extracted from flax seeds exhibit versatile application in various fields. Thus in this work, the flax seed protein which is found to be 84%, along with bees wax emulsion is explored for the first time as an Eco benign binder and as an alternative for casein based finish. The binders play very important role in leather finishing as it helps in binding the various constituents of finishing such as pigments, wax, and additives to the leather matrix. The prepared Eco benign binder formed a continuous film on the surface of the leather and improved the of physical properties and crack resistance of the leather. The FTIR and particle size analysis were carried out for the characterization of the Eco benign binder. The experimental leathers were tested for tensile strength, elongation at break, lastometer test, colour fastness and cold crack tests. The results of the said tests were satisfied and on par with control leathers.

1. Introduction

The word wax is defined as a material from various natural and synthetic products. However, natural waxes are not single substances, they are a mixture of various long-chain fatty acids and other constituents, depending on their origin. Each type of wax has unique chemical and physical characteristics with numerous applications.[1] Specifically, a wax obtained from honeybees has a wide spectrum of useful applications such as cosmetics and medicinal practices, inhabits a special position among all variety of waxes.[2] The presence of hydrocarbons such as free acids, saturated, unsaturated and hydroxy polyesters makes Beeswax soluble in most organic solvents such as ether, benzene, chloroform, turpentine oil, and fatty oils.[3]

Natural waxes such as beeswax are industrially classified as materials which are hydrophobic, solid at room temperature, congeal above 40°C, melt without decomposing, and are malleable at room temperature (20°C). Beeswax is being used to form thin insulate, non-corrosive, non-allergic protective films on surfaces like metals, fruits and human skins. Beeswax decreases the viscosity and improves the slip casting properties of emulsions.[4-7] Beeswax has been used for finishing various fabrics such as polyester fabrics, cotton, viscose blends and in textile industries because of its hydrophilization action. The process of using beeswax in finishing fabrics endow them with a shining effect.[8,9]

Leather finishing plays a significant role in determining the final quality of the leather products. Moreover, finishing has unique characteristics that would translate the lower grade crust leathers to high value finished leathers. Though bio-based finishing systems have evolved to attain sustainability in leather manufacture, there is wide scope of improvement to achieve self-sustained bio-finishing systems.[10,11]

The proteins extracted from natural resources are utilized as binders in leather finishing. Extracted proteins are obtained from various sources such as from shaving waste.[12,13] Casein obtained from bovine milk, caprolactam-modified casein,[14] waterborne PU chitosan- poly vinyl alcohol-based product,[15] gelatin, extracted from leather solid waste[16] and the leather shaving scraps were explored as protein binder for leather finishing. Flaxseed meal is one of the industrial by products formed as a result of oil extraction from flaxseeds. Since this flaxseed meal is rich in protein content, we have attempted to extract the protein from this waste for its utilization in leather finishing. Thus, in the present study, the application of wax emulsion blends along with protein extracted from flax seeds has been explored as Eco begin binder.

2. Material and Methods

Beeswax, Polysorbate 80 (Tween 80) extra pure and Sorbitan Monostearate (Span 60) extra pure was purchased from Sisco Research Laboratories Pvt. Ltd (SRL). Flax seed meal was purchased from local market of Chennai.

2.1 Preparation of Bees Wax Emulsion

Ten grams of beeswax melted at 80°C followed by addition of non-ionic surfactant such as Tween 80 (7.5g) and Span 60 (5g) with constant stirring and heating.[17] This was then made to 100 mL with distilled water resulting in the formation of a white colored emulsion

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Table I

Different ratios of Bees wax emulsion and flax seed protein extract to get stable emulsion

S. No.	Bees Wax emulsion in ml (10% solution)	Flax seed protein extract in ml (10% solution)	Observation
	10	40	Stable emulsion
	20	30	Stable emulsion
	30	20	Stable emulsion
	40	10	Stable emulsion

which was utilized as such for leather application along with flax seed protein.

2.2 Extraction of protein from flax seeds

Initially, the flax seed meal was treated with a solution of hexane to remove any residual oil/fatty matter present in them following the Soxhlet method.[18] The de-oiled flax seed (10 g) was then hydrolyzed in aqueous conditions maintained at a pH of 9.0 using 0.5 N NaOH solution for 12 hours at 70°C. The pH of the solution was then reduced to 4.0 using 1N HCl solution leading to the precipitation of hydrolyzed protein which was then separated by centrifugation and lyophilized. The protein content of the extract was found to be at 84% as confirmed by Lowry's method.

2.3 Formulation of Bees wax emulsion and flax seed protein

Different ratios of Bees wax emulsion and flax seed protein extract were mixed together as shown in Table I. The ratio of 40 ml of Bees wax emulsion with 10ml of flax seed protein extract was optimized. The emulsion was stirred vigorously in a homogenizer under high-speed rpm for a few minutes. As far as their stability is concerned after cooling, it was kept for 10 days for observation.

Since all compositions were stable the composition 40:10 where minimum protein extract and maximum Bees wax emulsion has been used taken for consideration to explore protein's binding capacity.

3. Physiochemical Characterization of the emulsion

3.1 FTIR

FT-IR spectra of the binder was recorded using Perkin Elmer, Spectrum Two FT-IR spectrometer over a range of 4000 cm^{-1} to 400 cm^{-1}.

3.2 Zeta Potential and Particle Size Analysis

Zeta is used to determine the surface charge of the particle by the electrostatic repulsion from the adjacent dispersed particles. Zeta potential is used to control the colloidal suspensions/emulsions to understand the behavior of their structural components. The Particle size directly affects the physical stability of emulsions (smaller dispersed particles). The size and distribution of particles were determined by Zeta sizer 3000, Malvern instruments HSA:2004.

3.3 Application of emulsion as finishing material

Experiment Set 1: Application of emulsion/protein binder with water with the ratio of 1:10

Experiment Set 2: Application of sprayed emulsion/protein binder with 10/20/30 part of pigments in base coat

In the case of the control experiments, commercially available season wax procured from M/s Alpa chemicals was used in place of

Table II

Application of emulsion on leather

Experiment	Components	In Percentage (w/w)	Remarks
Set-1	Emulsion	10	4 cross coats Plain Plate at 90° C, 50 atm pressure
	Water	100	
Set-2	Water	Made to 100	4 cross coats, ageing for 2 hours Plain Plate at 90°C and 50 atm pressure
	Emulsion	10	
	Wax	1	
	IPA	2	
	Pigment	1/2/3	
	Formaldehyde free fixing	Top coat	1 cross coat, ageing for 12 hours

the beeswax for the leather coating trials with an offer of 2% (w/w) i.e. 20 parts. The season wax used was anionic in nature with a solid content of 11.5 ± 0.5% and the pH of 10% solution at 7.5 ± 0.5.

3.4 Optical Microscopy Imaging

Optical or light microscopy involves passing visible light transmitted through or reflected from the sample through a single lens or multiple lenses to allow a magnified view of the sample. The images were taken at CARE lab CSIR-CLRI.

3.5 Physicochemical characterization

The leathers were subjected for physicochemical characterization such as, tensile strength (IUP 6), elongation at break (IUP 6) lastometer test (ISO-3379, 2015), color fastness (ISO-105,2014), flexing resistance (ISO 17694:2016), resistance to abrasive action (ISO 17704:2019), cold crack test (ISO-17233, 2017) and finish film adhesion test (SATRA TM 408:1993) as per the standard processes.[19-23]

4. Result and Discussion

4.1 FTIR Spectra

FTIR provides information about the functionality of the material, and it is influenced by other factors. Figure 1a represents the FTIR spectra of the beeswax, the peak at 2916 cm^{-1} represents the asymmetric stretching vibrations of the hydrocarbons. The peak at 2849 cm^{-1} represents the CH_2 symmetric stretching vibrations of hydrocarbons. These two peaks represent the long chain of the SP^3 carbons from the fatty esters. The peak at 1636 cm^{-1} represents the C=O stretching vibrations of ester. The broad peak at 3341 cm^{-1} represents the hydrogen bonding present in the emulsion due to O-H stretching.

In Figure 1b. The presence of peak at 3291 cm^{-1} corresponds to N-H stretching of protein molecules. The peak at 2849 cm^{-1} represents the CH_2 symmetric stretching vibrations of hydrocarbon. The peaks between 1740 and 1450 cm^{-1}, shown by the protein amide I (C=O stretching) and amide II (NH bending) respectively.

4.2 Particle size analysis

The Figure 2a indicates the zeta potential value obtained for the binder is -0.00652 mV (considered to be zero). The very less negative value indicates that the dispersed particles in the suspension have a minimal negative charge and are predominantly non-ionic in nature. Figure 2b represents the size distribution of the particles. The scattered intensity for each particle size is approximately 530 nm which is indicated as a sharp intensified peak.

4.3 Physical characterization

The three experimental leathers with different pigment percentages (1/2/3) used for finishing with the same ratio of emulsion were used for the following tests. In case of the control, the commercially available casein-based protein binder was used along with the season wax and compared to the experimental process. It was found that the formed film was very much resistant to cold temperatures, no cracks were observed as shown in Table III. The experiment (E2) and the control leathers were also assessed for the flexing resistance test following the Bally method in both wet and dry conditions. It was found that the experimental leather showed no signs of cracking until 60,000 cycles while a slight creasing was observed after the leather was subjected to 1,00,000 cycles in dry conditions. In case of flexing resistance at wet condition, it was found that there was no effect till 30,000 cycles and a little creasing up to 50,000 cycles which were on par with that of the control leather coated with conventional protein binder. The abrasion resistance test conducted following the Martindale method showed that the experimental leather (E2) showed no effect up to 3200 revolutions while a slight abrasion at 12800 revolutions and moderate abrasion at 25600 revolutions for dry test. In case of wet abrasion, there was no

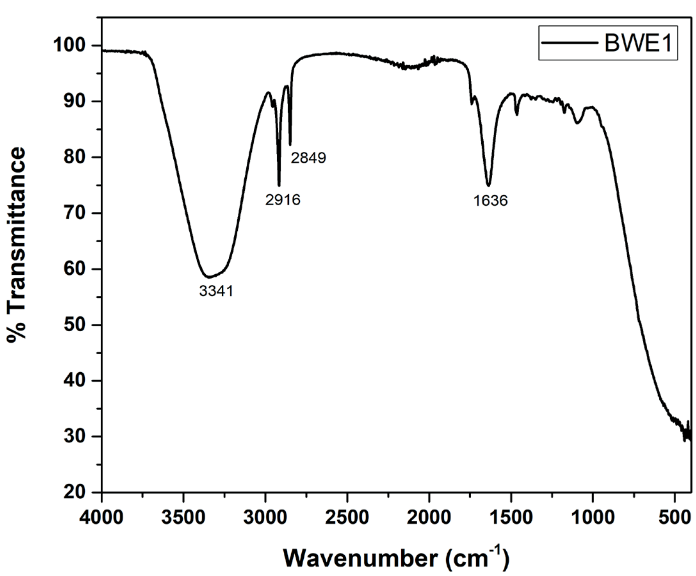

Figure1a. Represents the FTIR spectra of Beeswax emulsion

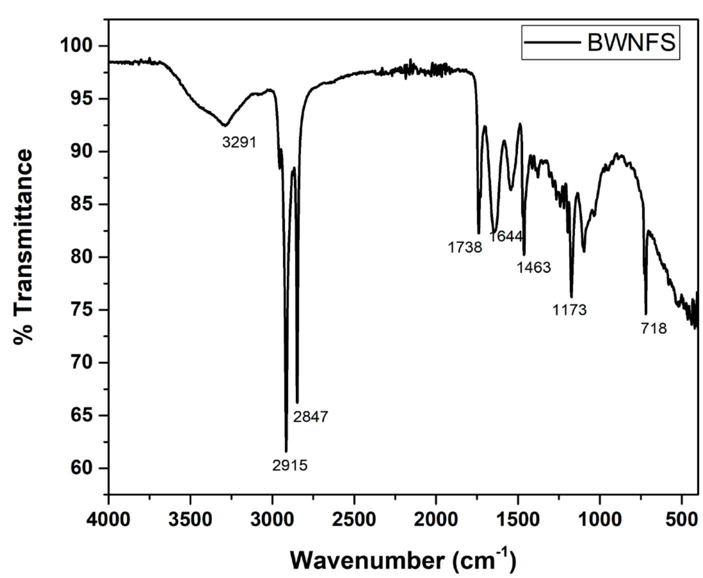

Figure 1b. Represents the FTIR spectra of Beeswax emulsion with protein

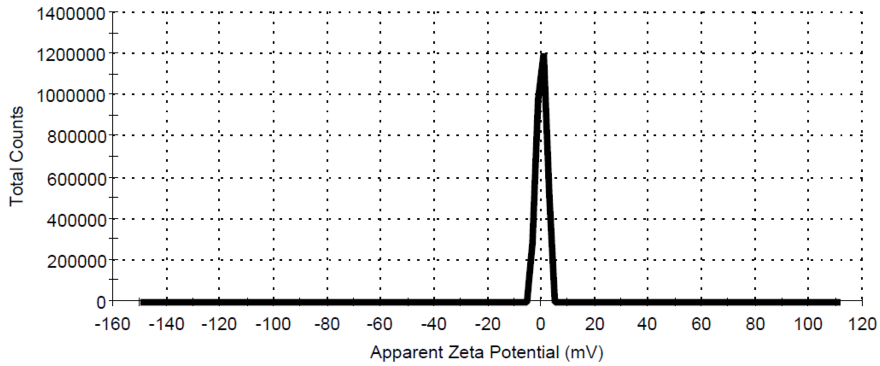

Figure 2a. Represents the Zeta potential distribution of the emulsion

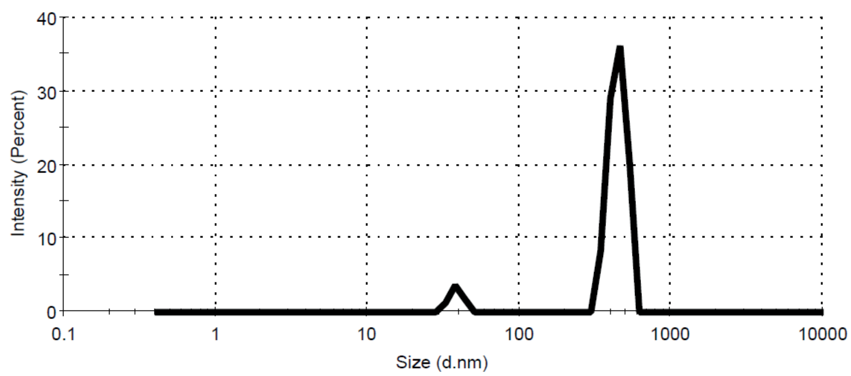

Figure 2b. Represents the Size distribution by the intensity of the emulsion

effect at 1600 revolutions but moderate to severe abrasions at 3200 revolutions and hole formation was observed at 6400 revolutions. Additionally, the rub fastness test showed that the pigment holding capacity of the prepared flax seed protein and beeswax emulsion was on par with the control process. The physical characteristics of experimental leathers were also on par with the control leathers where commercial binder was used in the finish. The results indicate better compatibility of binder with the different ratios of pigments. Finally, the finish film adhesion test was done to assesses whether the film has strong bonding to the surface of the leather. It was found that the average peel strength of the experimental leather was at 3.48 N/cm which is higher than the required strength of 2 N/cm as per ISO 11644 norms confirming that the finish film has better binding to the leather surface.

4.4 Optical Microscopy Imaging:

The Optical microscopic images of the experimental leathers are shown in Figure 4. The optical images of the experimental leathers E1(10%pigment), E2(20% pigment) and E3(30% pigment) are shown along with the respective control leathers (commercial binder). It

Table III

Represents the Physical characterisation of the finished leather samples

S. No	Sample	Cold Crack	Colour Fastness to Circular Rubbing (Dry and Wet)	
			Dry 512 rub	Wet 256 rub
1.	Control	No crack	4	3/4
2.	E1 (10 parts pigment)	No crack	4	3/4
3.	E2 (20 parts pigment)	No crack	4	3/4
4.	E3 (30 parts pigment)	No crack	3/4	3/4

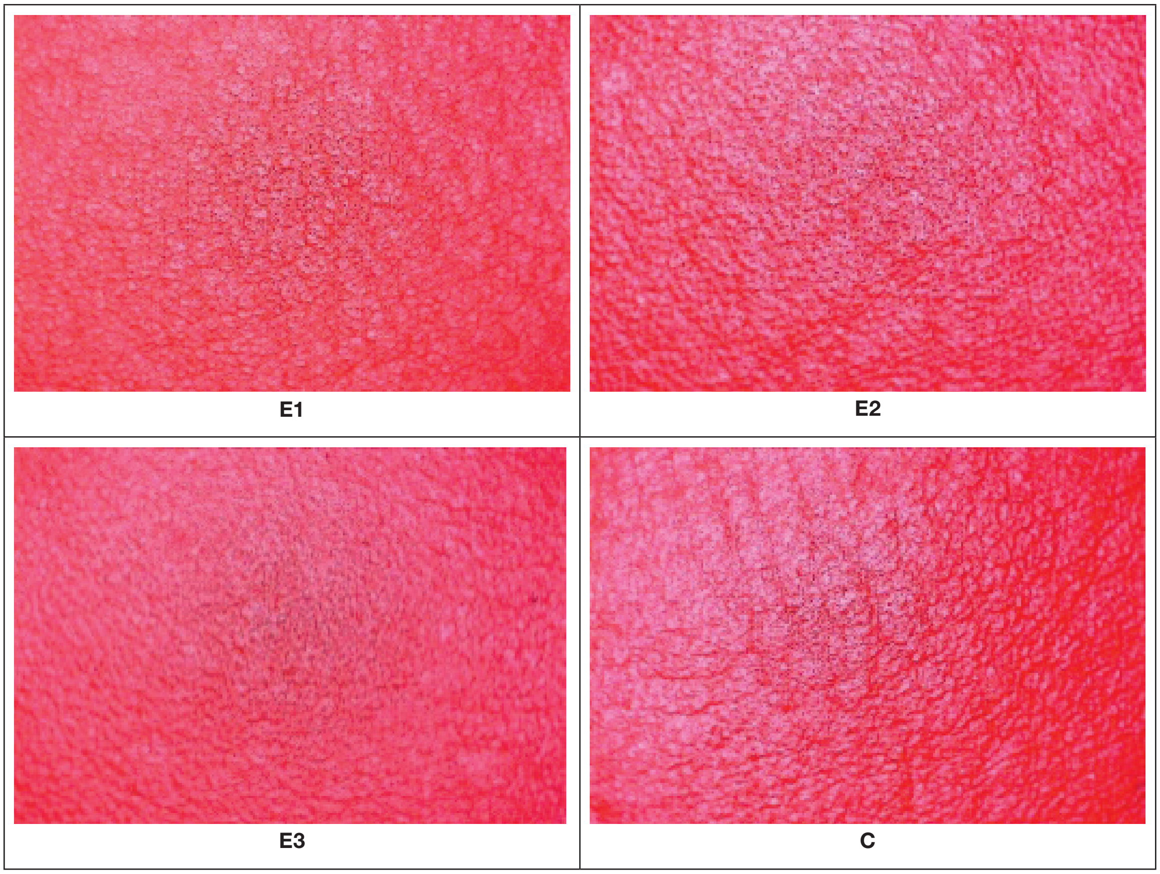

Figure 3. The optical images of the experimental and control leathers

could be seen that the film formed was very transparent and naked similar to the conventional casein-based binders. Additionally, the finish was also friction glazed and found that the prepared eco-benign binder did not crack or peel off at high temperature making this an alternative for development of glaze finished leathers.

Conclusion

The uses of natural compounds as binder in leather finishing is explored and characterised in the present work. The blend of extracted flax seed protein with bees wax emulsion as a binder can be used as Eco benign binder for leather finishing and can be possibly explored as an alternative for casein based finishing systems. The strength, stability and compatibility of the blend with the finishing pigments, confirms its usability in leather finishing.

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