Chemically Modified Castor Oil for Softening of Leather–A Novel Approach

by

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Abstract

Fatliquoring is an important step of post tanning process of leather manufacturing where incorporation of self-emulsified oil (lubricant) makes the leather soft. There are several methods which introduce polarity into oil and provide the path where reactive species of modified oil can interact with water which leads to form a fatliquor. The aim of this work is to introduce an extra polarity into the fatty acid moiety through chemical modification of castor oil by carbene intermediate. The spectroscopic characterisation such as FTIR, ^{1}H-NMR and ^{13}C-NMR of fatliquor have been carried out. Particle size analysis of fatliquor has also been done. The experimental leathers have been tested for physical strength characterisation such as tensile and tear strength verses control and found to have better properties than control. SEM analysis for morphological study of experimental leather were also carried out which clearly indicates the uniform dispersion of fiber bundles due to the fine distribution of the novel and self-emulsifying fatliquor throughout the matrix.

Introduction

Leather making is a multistep process, which includes tanning, post tanning and finishing steps.[1] In the post tanning process, softening of fibers is an important parameter, which is carried out by the application of fatliquor.[2] Fatliquor is an emulsion prepared by chemical modification of oils or using surfactants/emulsifiers. The proficiency of the fatliquor depends upon its penetration into the pores of the leather fibers.[3,4]

The objective of the chemical modification is to introduce some polarity or functionality into the fatty acid chain of oil. Several oils from synthetic and natural sources such as jatropha oil, castor oil, karanja oil, Neatsfoot oil, flax and soya oil, citrullus colocynthis oil etc., are used for the preparation of fatliquors.[5,6,7,8] With reference to chemical modification of oil, there are only a few known methods which are being carried out for the fatliquor preparation such as transesterification, sulfation, sulphitation, epoxidation and sulfo chlorination.[9,10,11,12] Chemically modified castor oil is used for the lubrication of leather.[13] Turkey red oil is the best example of sulphated castor oil which is commonly used to fatliquor leather.[14] Other methods like transesterification, sulfitation, and epoxidation of castor oil have also been done and explored for the fatliquor preparation. Researchers are always searching for better modification options where cost, time and efforts can be minimised for the making of fatliquors.[15]

The unsaturation which is present in the fatty acids of oils can be exploited for the development of many reactive sites where new opportunities may arise and new products may be formed.[16] Carbene generation and its in-situ reaction with double bonds is another way to explore novel fatliquor preparations. Carbenes are defined as species containing divalent carbon, and they may display either electrophilic or nucleophilic reactivity depending on whether the two unshared electrons on the carbon center are unpaired (triplet carbene) or paired (singlet carbene). When alkenes react with carbenes, three-membered rings are formed. The insertion of a carbene into a π-bond is the most common way for preparing cyclopropanes. The mechanism for a carbene reaction is a concerted process in which all bonds are broken and formed at one time.[17,18]

Carbene can be prepared through many chemical reactions starting from unsaturation.[19] However, oils with multiple double bonds may raise the interest for the development of a variety of fatliquors. Ricinoleic acid present in the castor oil has unsaturation and adjacent polar hydroxyl groups on its backbone. They make it readily available for chemical modification. The uniqueness of castor oil having hydroxyl group in its fatty acid skeleton which is rich in ricinoleic acid (~90%) facilitates the preparation of fatliquor. Consequently, the aim of this study is to add polar moieties to the double bonds which are present in the fatty acid skeleton of castor oil. The di-chloro-carbene polar elements replace double bonds. Furthermore, this new polar group can interact with water which gives water- soluble and/or a preferred self-emulsifying fatliquor.

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Materials and Methods

Materials

Castor oil was purchased from Sigma Aldrich. Analytical grade sodium hydroxide, chloroform and sulphuric acid were used for the preparation of fatliquor. All the chemicals used for leather processing were of commercial grade.

Preparation of novel fatliquor

Castor oil (23.3 G./0.025 moles) was put in a reaction flask, and its temperature was increased to 60°C. Chloroform (6 ml./0.025 moles) was added dropwise into the heated castor oil and stirred for about 15 minutes. Subsequently, NaOH pellets (2.6 G./0.025 moles) were first dissolved in distilled H_2O [50 ml.] and this solution was then added into the above reaction mixture. The completion of reaction was confirmed by an in-house water miscibility test. Excess sodium hydroxide in the reaction mixture was neutralized dropwise with sulphuric acid to give the resultant fatliquor a pH = 6.

Characterization

Particle size analysis of fatliquor

The leather matrix has interspaces with small size gaps. It is mandatory for the emulsion to penetrate the fiber structure and fill those spaces. If the particle size of the emulsion matches the pore size of the matrix, proper lubrication can be done. Particle size analysis of our prepared fatliquor has been done by Zeta potential analyser (Zeta sizer 3000, Malvean instruments HSA:2004) in polymer science and technology lab at CSIR-CLRI.

Spectroscopic analysis of fatliquor

The complete analysis of the chemical reaction has been done by spectroscopic analyses including Fourier Transform Infrared (FTIR) and nuclear magnetic resonance (NMR). NMR spectrometer ASCEND-CV series (400 MHz solid state) was used and Perkin Elmer, FTIR spectrophotometer used for FTIR data. The spectroscopic testing has been done at CSIR-CLRI.

Application of novel fatliquor in leather manufacturing

Cow wet blue [5 sides] was acquired from CLRI – Pilot tannery and their thickness adjusted to 1.1 mm. The tanned leathers were cut along the backbone and marked. The left sides were treated with conventional fatliquor (control) whereas the right sides were treated with the novel fatliquor (Experiment). The detailed process recipe is given in Table I.

Scanning Electron Microscopic (SEM) analysis

The resultant crust leather obtained from both control and experimental process was subjected to scanning electron microscopic analysis. All specimens were coated with gold using a Palaron range CA7620- sputtering coater. The Phenom tabletop scanning electron microscope was used to analyse the surface and cross-sectional morphology of the specimens.

Physical strength characteristics and organoleptic properties of leather

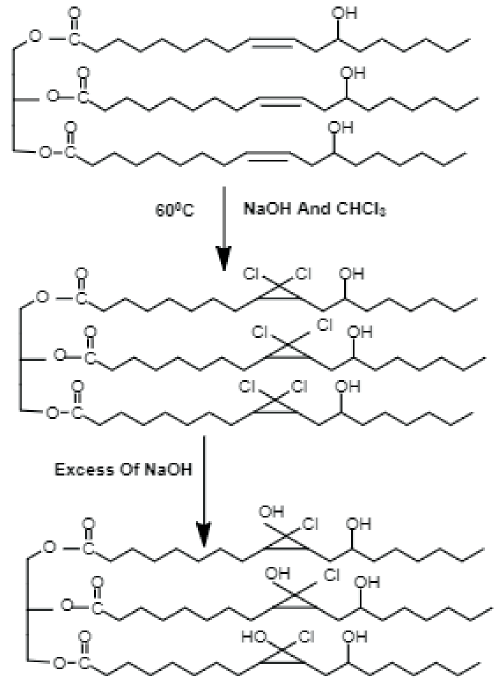
We tested the physical strength of the crust. The tests used tensile strength, percent elongation at break,[20] tear strength, grain crack load[21] and distension at grain crack of crust leather obtained from control and experimental processes. The test specimens for physical testing as mentioned above were obtained per IULTCS standard methods and conditioned for 24 hours at 25±1°C and 65±2% RH. The results are shown in Table II. The crust leathers were also evaluated for various organoleptic properties such as softness, grain smoothness, fullness, grain flatness and overall appearance by hand and visual examination by CLRI-experienced tanners. Performance have been rated on a scale of 1-10, where higher points indicate better properties (Table III).

Table I
Process recipe for upper leather making

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 process	Conventional fatliquor	10		
Experimental process	Novel fatliquor	10		
Fixing	Formic acid + water	2 + 10	3 × 10 min + 60 min	Check exhaustion and pile

Table II
Physical strength characteristics of crust leathers treated with conventional and novel fatliquor

S. No.	Characteristics	Control process	Experimental process
1.	Tensile strength (N/mm^2)	19±1	21±1
2.	Elongation at break (%)	56±2.5	41±3
3.	Tear strength (N)	121±2	112±2
4.	Load at grain crack (kg)	37±3	36±2.5
5.	Distension at grain crack (mm)	8.2±0.5	8.6±0.5



Plausible Reaction Scheme 1

Results and Discussions

Preparation of novel fatliquor

Carbenes are highly reactive species and therefore must be produced in-situ. Exploration of carbene chemistry in synthesis of various organic molecules is emerging. However, application of carbene chemistry in the preparation of leather chemicals has not been attempted so far. In the present work, a novel carbene derivative of castor oil has been prepared for softening the leather matrix. Chloroform and NaOH generate carbene which adds to the double bonds in the ricinoleic acid component of castor oil. In a consecutive reaction, the excess hydroxyl ions from NaOH replace chlorine atoms in the intermediate dichloro-cyclopropane to form geminal chlorohydrins. This chlorohydrin is formed by a nucleophilic aliphatic substitution reaction. The overall synthesis of the plausible gem-chlorohydrin product is shown in Reaction Scheme 1. The product on completion of the reaction contains a lot of froth due to the excess NaOH. In order to separate the product from this froth, the contents of the conical flask are emptied into a separating funnel and allowed to settle for an hour. After that the required product can be extracted from the funnel slowly into a beaker. The final pH value of the product was adjusted to pH=6.0. This novel self-emulsifying fatliquor is stable at room temperature.

Particle Size Analysis

The particle size of the experimental fatliquor and the control from Figure 1(a) and 1(b) was (315.9 dnm) and the control (195.3 dnm) respectively. The particles of the experimental emulsion were suitable for their (good) penetration in the fibrils of the leather matrix.

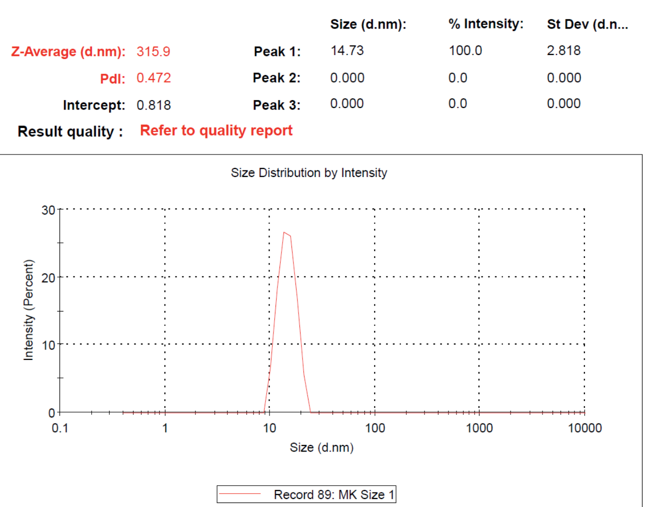


Figure 1a. Particle size distribution of novel fatliquor

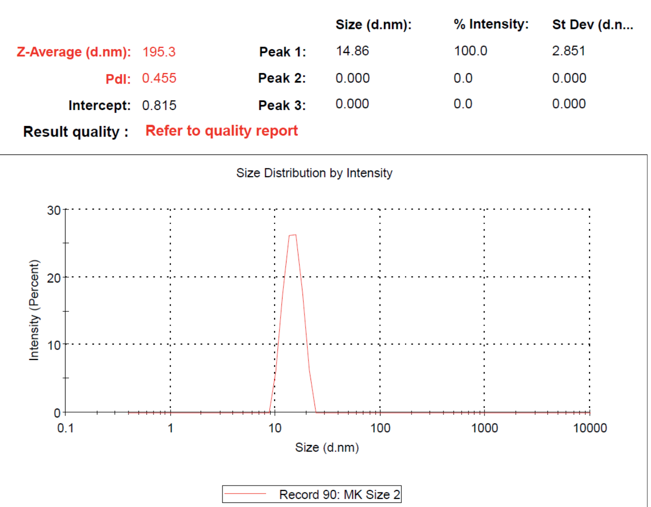


Figure 1b. Particle size distribution of control

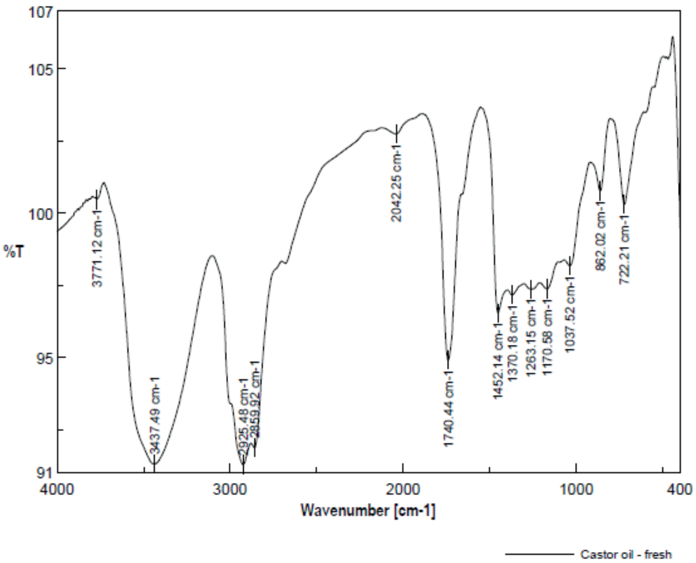


Figure 2a. FTIR spectra of castor oil

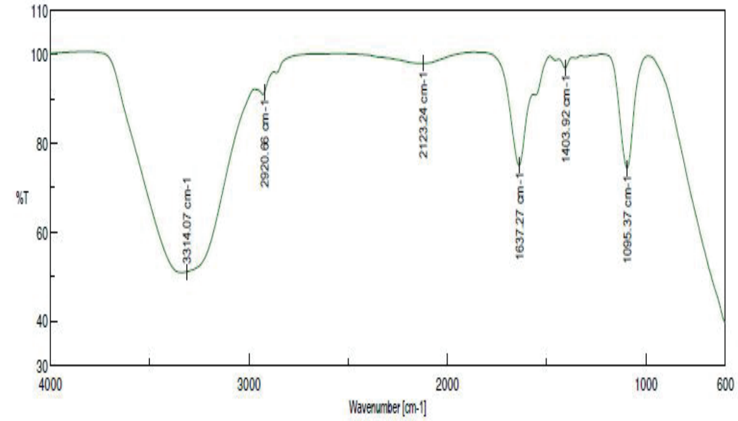


Figure 2b. FTIR spectra of novel fatliquor

FTIR Analysis

The spectroscopic analysis of functionality of fatliquor (control and experimental) have been characterised by FTIR which is shown in the Figure 2(a) and 2(b). The C-H symmetric and asymmetric stretching vibrations of CH_2 groups have been detected at 2923 and 2853 cm^{-1}.

The intense band at 1742 cm^{-1} is due to CO stretching and the absorption bands at 1462 and 1364 cm^{-1} are attributed to CH_2 bending and C-H bending vibration, respectively. The peak at 1655 cm^{-1} represents CH=CH stretching and at 3008 cm^{-1} for =C-H stretching.

Comparing the FTIR of castor oil and the sample, its clearly indicates that the peaks at 3008 cm^{-1} completely vanish in the sample. This peak specifically implies the presence of unsaturation (double bond) in the castor oil. Hence, the attack of carbene onto the double bond of ricinoleic acid thereby removing the unsaturation in the compound. The presence of a peak at 3384 cm^{-1} in castor oil implies the OH group present in ricinoleic acid. The presence of such a big bulge at 3314.07 cm^{-1} implies the presence of intramolecular hydrogen bonding. The presence of a peak at 1095 cm^{-1} corresponds to cyclopropane ring.

NMR

Figure 3(a) and 3(b) shows the ^{1}H-NMR spectra of the castor oil and modified castor oil through carbene intermediate. The δ value at 0.88 ppm corresponds to the terminal methyl group. The δ values from 1.2 to 2.3 shows the signal for the methylene protons associated with long fatty acid chain.

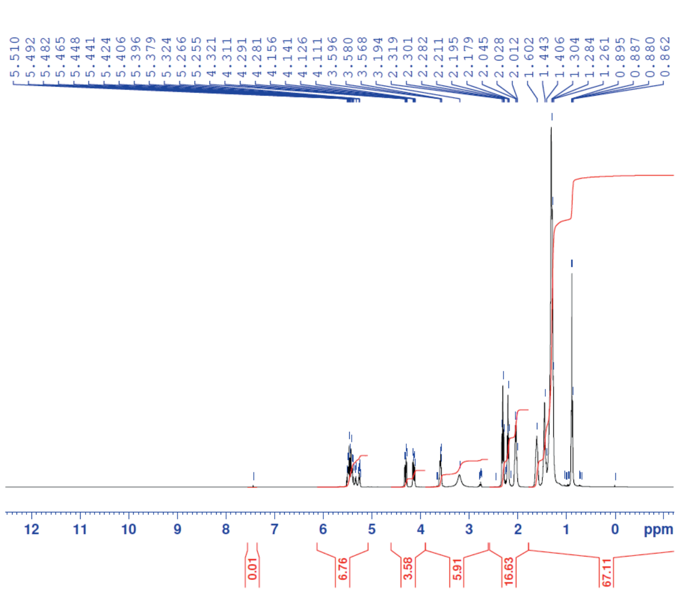


Figure 3a. NMR spectra of castor oil

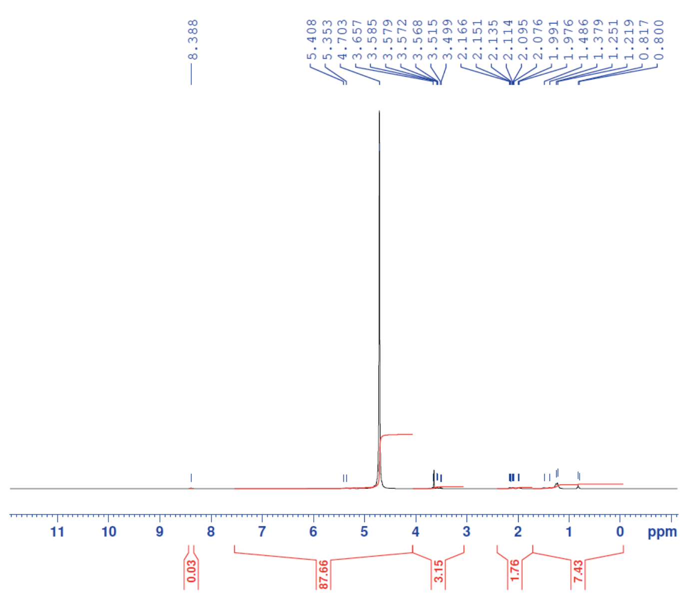


Figure 3b. NMR spectra of novel fatliquor

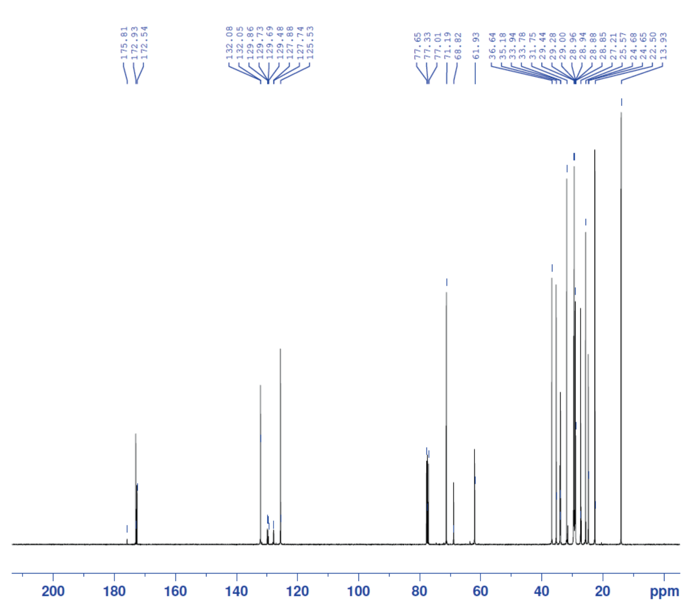


Figure 4a. ^{13}C-NMR spectra of castor oil

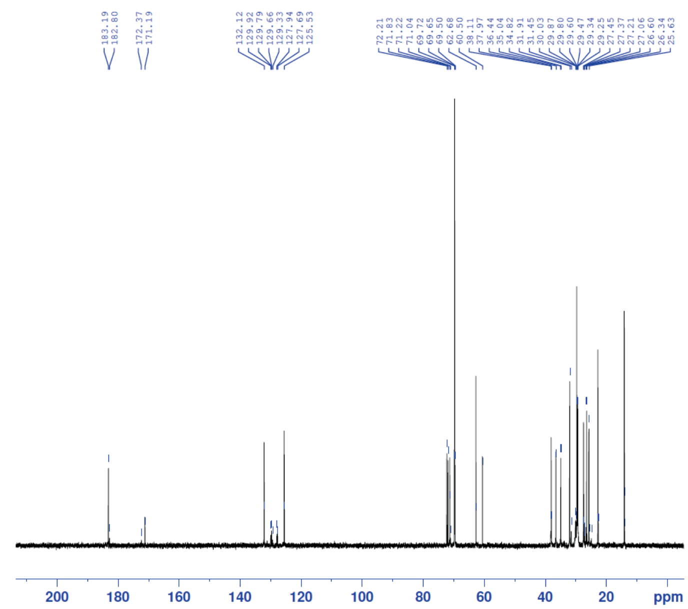


Figure 4b. ^{13}C-NMR spectra of novel fatliquor

Signal at δ 4.1 to 4.3 indicates protons linked with glyceride group. From Figure 3(a) it has been observed that the peaks which are present in the region δ 5.2 to 5.5 of the spectrum of castor oil (fig 3a) indicates the presence of unsaturated protons which are deshielded by the presence of hydroxyl group present in the castor oil. The disappearance of the strong signal in the region δ 5.2 to 5.5 (fig.3 b) indicates the disappearance of the unsaturation.

^{13}C-NMR

^{13}C-NMR spectra of castor oils and experimental fatliquor have recorded in $CDCl_3$ and represented by Figure 4(a) and (b), in the Figure 4(a) the signals at δ 132.08 and δ 125.53 ppm corresponds to unsaturated carbon present at ricinoleic acid which is a major fatty acid component (approx.95%) of castor oil. The peak at δ 71.9 ppm corresponds to carbon atom linked with hydroxyl group and peaks at δ 36.64 and δ 35.19 ppm indicates the carbon atom directly linked with hydroxyl carbon atom. Figure 4 (b) shows all peaks with additional peak at δ 183.19 ppm corresponds to cyclopropane carbon which indicates the conversion of unsaturation present in the castor oil to the three-member cyclic structure.

Physical Strength Characteristics and Organoleptic Properties of Leather

In order to study the effect of the novel fatliquor on leather properties, the matched pair crust leathers of both control and experimental leathers were subjected to various physical strength measurements. The physical strength parameters for control and experimental crust leathers are given in Table II. It is evident from Table II, that there is no significant difference in tensile strength, load at grain crack and distension at grain crack. Whereas tear strength of experimental leather was slightly lower than the control leather. The analysis of bulk properties results reveal that the softness and grain smoothness were (8.5/10) for the experimental leather and (8.0/10) for the control leather, respectively. The overall appearance and other characteristics are on par with control leather.

Table III

Organoleptic property evaluation

S. No.	Characteristics	Control process	Experimental process
1.	Softness	8.0/10	8.5/10
2.	Grain smoothness	8.0/10	8.5/10

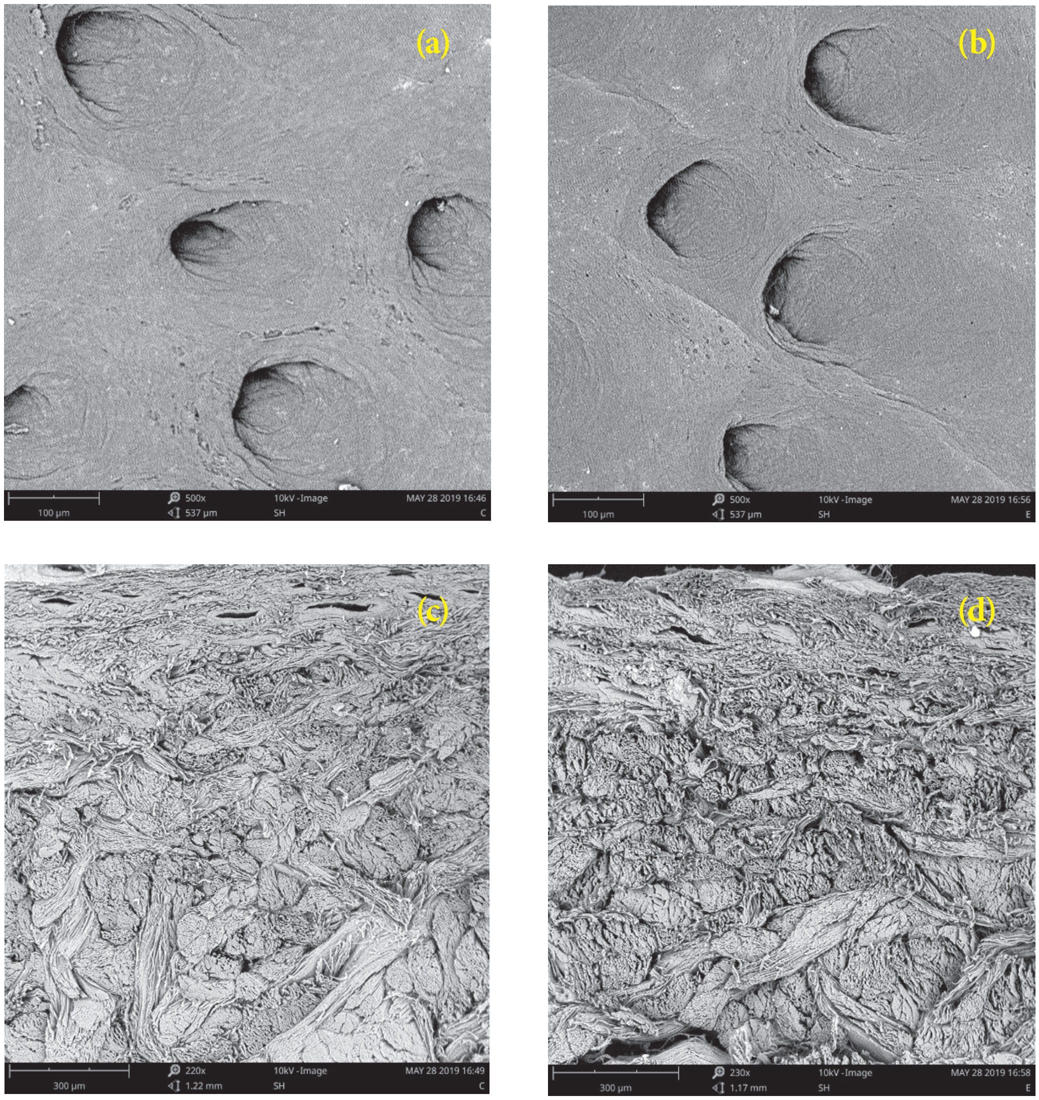


Figure 5. Surface morphology of control and experimental leather **(a)** and **(b)**, respectively. **(c)** and **(d)** cross-sectional view of control and experimental leather, respectively

Scanning Electron Microscopic Analysis

The grain morphology of crust leather from control and experimental process is shown in Figure 4 (a) and (b), respectively. Whereas, Figure. 4 (c) and (d) shows the cross-sectional view of control and experimental process, respectively. It is evident from Figure 4 that the surface characteristics of control and experimental leather are similar. Whereas, it is obvious from cross-sectional micrographs that the fiber splitting of experimental leather is better than control leather. And this clearly indicates the better diffusion and uniform distribution of fatliquor at the fibrillar level.

Conclusion

In the current study, a new approach for the preparation of fatliquor has been reported where, oils with high as well as low number of double bonds can be modified which will be the best part of this work. Any chemical compounds which generate carbene can be used here. The use of castor oil is recommended because of the presence of the polar hydroxyl group which can stabilise the product via hydrogen bonding. This could be a versatile approach for the production of several different kinds of fatliquors.

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