Studies on the Physico-chemical Behavior of Synthetic Tanning Agents in Non-aqueous Medium

by

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Abstract

Green labelling is a high priority issue in the modern society that has lead to several green technology initiatives in day-to-day applications. Among the several industry sectors, leather industry, is known to contribute to environmental pollution. Though, there are several alternate cleaner technologies available, till date no drastic shift in methodologies of clean technology has been implemented. In our efforts to use 'green' methodologies, in the present investigation, we have chosen green solvents like ethanol and heptane as possible carrier medium for synthetic tanning agents in leather processing. These tanning agents are performance chemicals that impart special properties to leather depending on end applications. In this study, tunable interfacial properties that arise between the solvated syntans and different solvents + water mixtures have been employed judiciously. Representative class of synthetic tanning agents have been chosen for the evaluation. The interfacial properties of liquid/liquid (solution) have been examined to understand the influence of solvents in the post tanning applications in leather making. Physical characteristics like tensile and tear strength have been determined for experimental leathers. Results show that syntans in ethanol and heptane medium form uniform dispersion and act as diffusing vehicle. The results suggest that the bound and unbound water in the leather matrix can form interfacial tension gradient with the solvent enabling effective diffusion of the chemicals even with non-polar solvents like heptane. Physical strength characteristics of experimental leather have met standard norms. The results have demonstrated an insight into the fundamental behavior of syntans in non-aqueous medium and provide clues for real time application in leather processing.

Introduction

It is well known fact that, tanning industry generates high levels of solid and liquid waste. Recently stringent regulations have been enforced on the industry to reduce the pollution load. As a consequence, leather technologists have been focusing on various technologies to reduce pollution load in both pretanning and tanning operations.[1] There are several alternate technologies that have been adopted to reduce the pollution load in pretanning and tanning operations.[2,3] However, there is wide gap in developing clean technology leather process for wet end finishing.[4] Till date, there has not been enough research to combat the pollution generated in post tanning process. In general, post tanning mainly involves retanning, dyeing and fat liquoring to incorporate desired properties in the final leathers. Retanning is mainly composed of synthetic tanning agents. Majority of synthetic tanning agents are phenolic-formaldehyde, melamine, acrylic and protein based products.[5] The residual content in the post tan liquor is a serious concern during effluent treatment. Though, there are several methods adopted to treat the effluent liquor there is no alternate process to obtain complete exhaustion of retanning agents.[6] In the conventional wet end finishing process, aqueous medium primarily helps to diffuse the chemical agents inside the leather matrix. The complex nature of the synthetic tanning agent makes the diffusion through the leather more complex. The residual compound in the liquor therefore makes it cumbersome during the effluent treatment process. Research has focused on developing eco-friendly synthetic tanning agents to overcome this problem. However, there is a lacuna in technologies to achieve complete exhaustion of retanning agents. Special problems arise specially in post-tanning operations when

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wastewaters containing chemicals are present. Since these wastewaters are produced in large quantities, a high economically unviable operation is required to convert them to a problem-free dischargeable form. Recently attempts have been made to reduce the quantities of wastewaters discharged by increasing the concentration of the chemicals and decreasing the float used in the conventional methods and by eliminating rinsing processes between the individual processing steps.[7] In certain cases, special solvents are employed in combination with active treating agents like chloroformate, to increase the softness and flexibility of the leather. There are studies on the collagen stabilization in various solvent medium.[8-9] Water immiscible organic solvents are used as a single phase lubricating composition along with water insoluble, oil soluble, lubricant for leather lubrication.[10] From our research group, a tool has been explored in the view of identifying non-aqueous medium for leather making alternate to water medium.[11] The tool is based on the cumulative score of GSK's selection guide which shortlisted 41 solvents from 110. Further, screening has been carried out using toxicity parameter that narrow down to 16 from 41. Based on the selection criteria, ethanol is one among the selected solvents for post tanning studies. Moreover, this research has been carried out primarily to understand the post tanning process in non-aqueous medium. In view of understanding the effect of non-polar solvents in post tanning, heptane has been chosen. In the present study, studies have been carried out to understand the behavior of different class of syntans in commercially polar and non-polar green solvents in retanning.

Materials and Methods

Materials

Three syntans were used in this study, acrylic, phenolic and aldehyde based syntans. The stock solutions of each syntans (2, 6 and 8%) were prepared. Each stock solution of syntans mixed with various compositions of ethanol and heptane (50:50, 30:70, and 20:80) were used for retanning trials.

Physicochemical Characterization of Solvents and their Interfacial Behavior with Syntans

A custom built spinning drop tension meter (modified from a NIMA tensiometer) has been used to determine the interfacial tension. All measurements have been repeated at least thrice. The prepared solution with the respective syntans (2 mL) has been introduced into a capillary tube with a syringe making sure that no bubble was present. The capillary tube has been sealed by a lid with a small central hole, and the solvent (either ethanol or heptane 5 mL) has been injected into the capillary tube by using a microsyringe to form a suspended droplet. The tube has been placed horizontally in the thermostat bath, the rotation speed was set to be 5000 rpm, and the temperature was set to be 303 K. The drop has been viewed through a microscope.

After an equilibration time of about 15 min., the drop size (diameter and length) has been recorded to calculate the interfacial tension, which was determined by the following equation:

Interfacial tension $\gamma = 3.426X10^{-7} (\rho_h - \rho_d)\, \omega^2.D^3$

ρ_h is the density of the syntan solution, ρd is the density of solvent (ethanol or heptane)

ω is the angular velocity of the droplet, and D is the minor axis length of the droplet. An Anton Paar DMA 5000 M densitometer has been used to measure the densities of the different solutions.

Post Tanning Process

Conventional chrome tanned leathers have been shaved to a uniform thickness of 1.1-1.2 mm and neutralized to pH 4.5-5.0 through conventional method. After, neutralization, leathers are completely drained and washed with solvents (ethanol and heptane) prior to retanning in solvent medium. Different combinations of solvent medium (20-100%) have been used as the medium for retanning. Representative classes of syntans of phenolic, acrylic and aldehyde base of commercial grade have been selected as follows Basyntan DI (DI), Relugan RE (RE) and Relugan GT-50 (GT50) respectively. After retanning, leathers are fixed using formic acid and piled overnight. After 24 h, leathers were set, hooked to dry, staked and buffed.

Physical Testing of Leather Samples

The samples for physical testing are obtained as per IULTCS methods. The samples have been conditioned at 80°F and 65% R.H. for 48 h (IUP 2, 2000).[12] Physical properties such as tensile strength have been investigated as per standard procedures (IUP 6 2000).[13] Each value reported is an average of four (2 along and 2 across the backbone) measurements.

Evaluation of Organoleptic Properties

Crust leathers have been assessed for grain smoothness, fullness and general appearance by tactile evaluation. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property.[14]

Results and Discussions

Figure 1(a) and 1 (b) show the interfacial tension plots of the different syntans RE, GT and DI used in mixtures of water with ethanol and heptane. It is seen that the interfacial tension decreases with increasing concentrations of the solvent for a constant concentration of the syntan. Among the syntans, RE shows maximum decrease in interfacial tension in the presence of ethanol while DI shows a decrease in Heptane. From the plots, it is seen that the minimum in interfacial tension is reached for almost the same % of the mixed solvent (that is about 50%) with water.

It is well established that salts can change the solution properties of surfactants, which may be, present in the different syntan systems used. This in turn might affect the interfacial tension of water with ethanol/heptane systems and such changes for water + n-heptane + surfactant system where a synergistic effect of surfactant and salt mixture on interfacial tension reduction between crude oil and water in enhanced oil recovery have been reported.[15,16] In the presence of syntan containing some charged species, and if there are some surfactant molecules present, the intermolecular spaces between the alkyl chains may be compressed due to the heptane inserting itself and thereby altering the electrical potential at the interface which in turn may organize the syntans in the form of some micellar like aggregates that then diffuse better into the leather matrix. Moreover, the formation of micellar in the presence of heptane would be few angstroms owing to its chain length which, might retards the formation of larger aggregates due to the size limitation of the solvent itself. Such a possible mechanism where favorable interfacial tension helps in better diffusion of the syntan is shown in Figure 2.

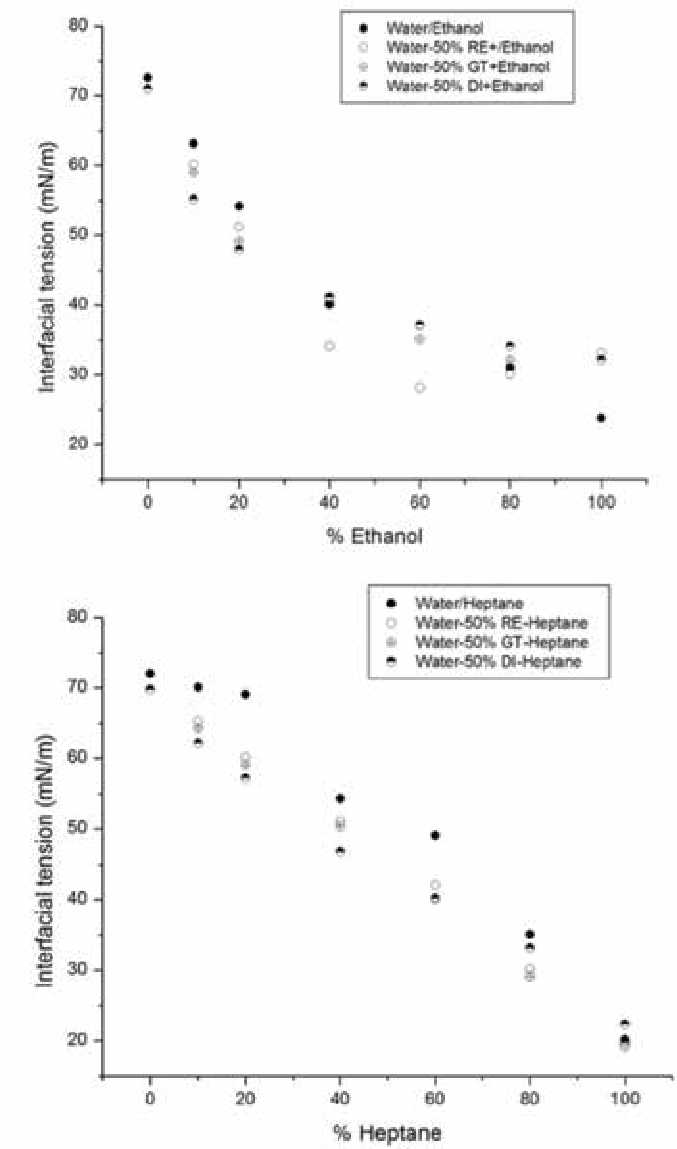

Figure 1. (a) Interfacial tension plots of the different syntans in ethanol-water system (b) Interfacial tension plots of the different syntans in heptane-water system.

In the case of ethanol, a similar phenomenon may occur. But here the process may be like annealing and increasing the fluidity of the chains rather than the neutralization of the electric potential. It has been observed that in case of actual tanning process, the available water in the leather matrix itself acts as a solvent which in turn can form interfacial gradient with the solvent being used and depending on the lowering of the interfacial tension push the syntan effectively across the matrix, thus enabling effective diffusion of the chemicals even with non-polar solvents like Heptane.

Application Studies

Based on the interfacial tension experiments (seen in Figure 1) it is observed that syntans in solvents medium can effectively act as a diffusing medium for leather chemicals. Moreover, from the various research studies that green solvents like ethanol is compatible with collagen. Fundamental research on collagen interaction with solvent has shown that this can be an effective alternate tanning medium for leather processes. Hence, a pragmatic approach is attempted in the present study to explore the post tanning application for representative syntans like glutaraldehyde, acrylic and phenolic-based syntans effect in solvent medium. Physical strength and organoleptic properties are assessed for the various trials to check the efficiency of chemical diffusion and effect of solvent in crust leather properties.

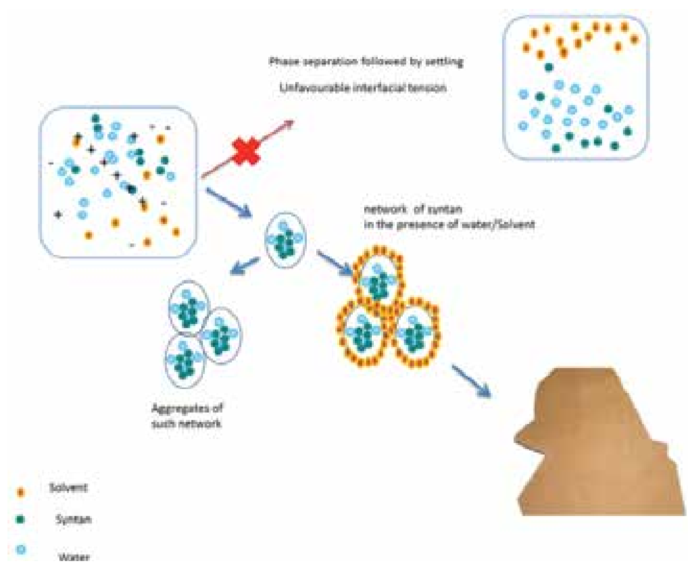

Figure 2. Scheme for optimal interfacial tension leading to effective diffusion of syntan.

Syntans in Solvent Medium

Glutaraldehyde syntan is used in the leather manufacture as an auxiliary chemical agent to enhance the softness, fullness and to replace the mineral tanning chemicals. Moreover, the crosslinking effect of aldehydes results in high crosslinking and would benefit the shrinkage properties to leather. In the present study, chrome tanned leathers are treated with 8% of Relugan GT50, Relugan RE and Basyntan DI in the ethanol and heptane medium as a float with different concentration.

After retanning, 10% vegetable based fatliquor is used for lubrication and fixed using formic acid. The crust leathers are evaluated for physical strength and organoleptic properties to understand the efficiency of diffusion and interaction of chemicals within the leather substrate. Furthermore, the inherent bound and unbound water in the leather substrate would play a vital role in the diffusion processes, as observed in the interfacial results. As seen from Figure 3, it is observed that tensile strength of ethanol-retanned leathers are in the range of 270 -210 Kg/cm^2. From the result it is inferred that, at 20% ethanol concentration, the tensile strength found to be 210 Kg/cm^2 whereas at 100% ethanol concentration, it is found to be 270 Kg/cm^2. This result reiterates the elongation of the leathers, from 60 to 80% with increased ethanol concentration.

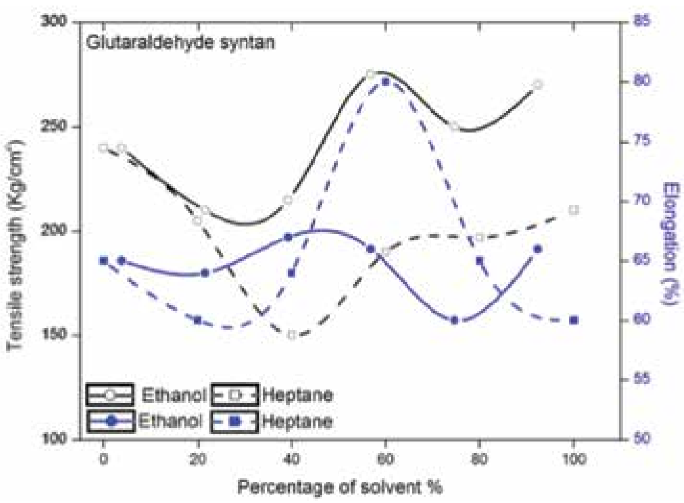

Figure 3. Physical strength characteristics of retanned leathers (aldehyde syntan).

Tensile strength and elongation of Acrylic syntan is present in the Figure 4. From the results, it is seen that tensile strength of ethanol medium leathers in the range of 300-200 Kg/cm^2 which shows a decrease trend with increase in the ethanol concentration.

This is probably due to the diffusion of acrylic syntan in ethanol medium is considerably reduced resulting in reduction in strength properties. However, heptane retanned acrylic leathers are found in the range of 170-210 Kg/cm^2. The major properties obtained using acrylic syntan are grain tightness and compactness for the final texture. However, more than strength properties, organoleptic properties are detrimental parameter to evaluate the efficiency of acrylic syntan in the solvent medium.

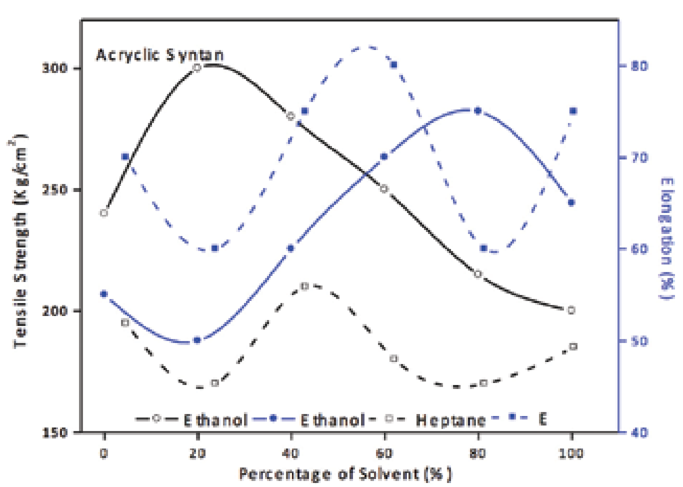

Figure 4. Physical strength characteristics of retanned leathers (acrylic syntan).

The % elongation of acrylic retanned leathers is found to be 50-75%, there has been no obvious trend obtained with acrylic syntan. Most commonly used syntan for chrome-tanning agent is phenolic based syntan. It is one of the high priority performance chemicals in leather manufacture due to their properties like fullness, light fastness, etc. Hence, insight into retanning with phenolic syntan in solvent medium is of profound interest. The tensile strength and %Elongation results are shown in Figure 5. Similar to acrylic syntan, organoleptic assessment would be a preferred choice of evaluation to evaluate the leather. Tensile strength of ethanol medium retanned leathers are (140-210 Kg/cm^2) found to be less compared to heptane retanned

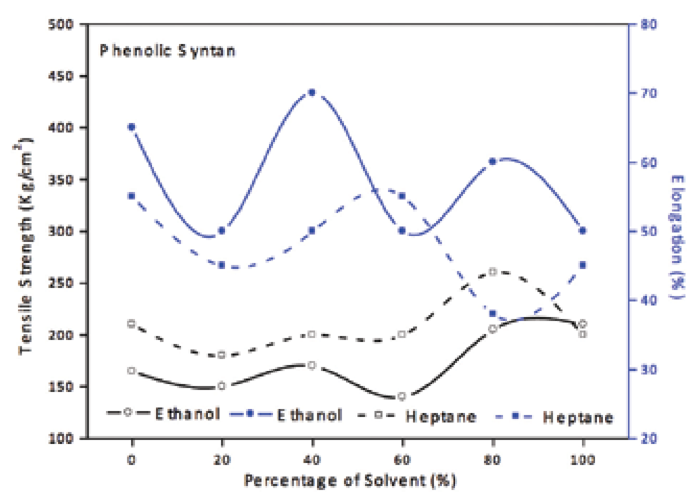

Figure 5. Physical strength characteristics of retanned leathers (phenolic syntan).

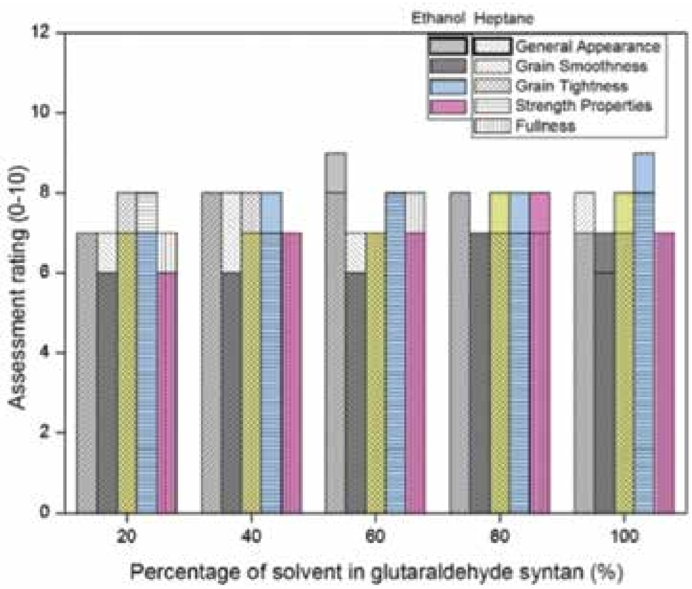

Figure 6. Organoleptic properties of retanned leathers (aldehyde syntan).

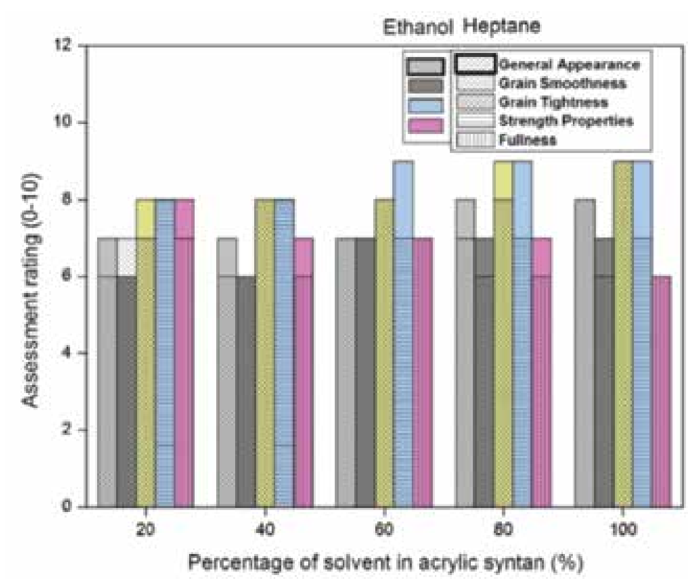

Figure 7. Organoleptic properties of retanned leathers (acrylic syntan).

leathers (180-260 Kg/cm^2).These results are again attributed to the fact that non-polar medium enhancing the diffusion of leather chemicals. Furthermore, the % elongation of ethanol and heptane retanned leathers show a similar behavior. The retanned leathers using Glutaraldehyde, Acrylic and Phenolic are assessed for various organoleptic properties like general appearance, grain smoothness, grain tightness, strength properties and fullness as shown in Figure 6, 7 and 8 respectively. All the experimental retanned leathers have shown agree with the specific properties through hand assessment. The exhaustion of syntans during post tanning process is estimated separately without offering fat liquors and calculated based on the left over

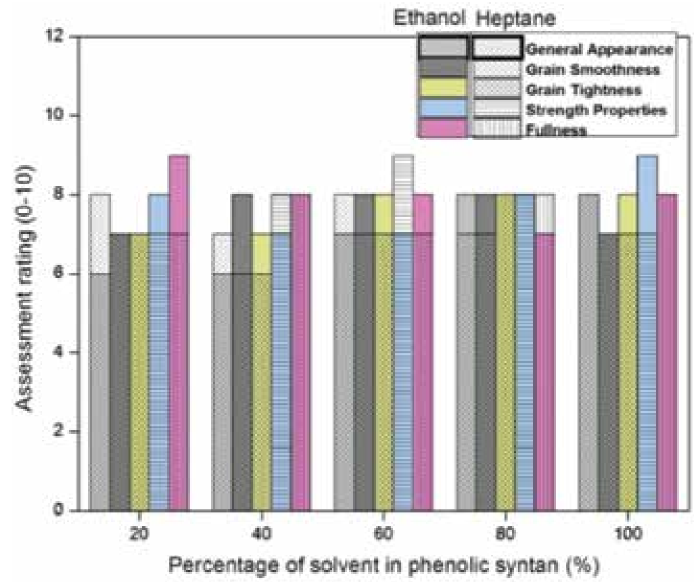

Figure 8. Organoleptic properties of retanned leathers (phenolic syntan).

solid content in the post tan liquor in solvent medium (100%). It is observed that based on the solid content in the effluent liquor, there are about 65-75% exhaustion has been observed.

Conclusions

In the present study, application of retanning in polar and non-polar medium is studied to understand the role of physical properties like interfacial tension, tensile strength and elongation. Hand evaluation is carried out to assess the final properties. Three different syntans, glutaraldehyde, acrylic and phenolic syntans, are used in the study. From the interfacial tension result it is seen that acrylic syntan shows maximum decrease in interfacial tension in the presence of ethanol while phenolic syntan shows the decrease in heptane. This provides a positive insight to use polar and non-polar solvents for the diffusion of leather chemicals. To evaluate, the efficiency of syntan in leather processing, chrome tanned leathers are retanned with syntans with different concentration of solvent. Physical strength of all the retanned leathers have meet the standard norms. Similarly, to assess the performance properties like general appearance, grain smoothness, grain tightness, strength and fullness are carried out using hand evaluation. It can be concluded that depending on the final leather application, choice of solvent and concentration can be selected to attain the maximum benefits. These research findings provide new avenues for effective diffusion and delivery of syntans in non-aqueous medium that considerably cut down the pollution load though recycling of solvent and reduction of chemicals offered.

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