NANO-BIO ALDEHYDE SYSTEM FOR LEATHER MANUFACTURE

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Abstract. Development of eco-friendly chemicals from natural renewable resources are widely explored owing to their eco-acceptability and sustainability. Exploring biopolymers is the need of the hour to combat the ustainability in leather processing. Currently, the use of biopolymers is undergoing intense study since it enables a more sustainable leather manufacturing. Finishing is an imperative step that enhances the aesthetic appeal of the final leather during which protein finishing systems known for its glazing properties are applied. Commonly used cross-linkers such as formaldehyde and glutaraldehyde are restricted owing to biocompatibility issues. However, the use of crosslinker is inevitable for protein finish system. In the present research, nano-bio polyaldehyde (NBP) system is established through selective oxidation of starch ; the size of the system is fine-tuned in the nano range for effective and efficient crosslinking through emulsion technique. From the characterization studies, the architectural design of NBP is ascertained as a good crosslinking agent for leather finishing chemicals. A particle size of the NBP system is found to be in the range of 80-110 nm. The leather samples showed an improved hydrophobicity nature and also enhanced wet, rub fastness, color fastness, and adhesion strength. The study provides an insight on tunability of known biopolymers for developing sustainable technology.

1 Introduction

Nowadays, nanotechnology holds enough promise to be one of the major drivers of technology. Indeed, using nanoparticles can potentially help achieve higher performance materials, intelligent systems and new production methods. With the rapid discoveries made in the nanotechnology field, shortly enough, nanoparticles will be ubiquitous and used to their full potential. In the past few decades, the leather industry has gained a negative image due to its use of highly polluting chemicals and the discharge of toxic tannery effluents. Thus, recently research has been focused on manufacturing sustainable leather with the use of nanoparticles. Nanotechnologies are considered in leather manufacturing process since they can offer cost-effective improvements to the quality of finished leather. The enhancement of the properties of the leather is owed to the increased surface area to volume ratio. During leather finishing processes, the reactions occur at the surface of the chemical or the material; hence, for the same volume, the greater the surface, the greater the reactivity. And nanotechnology allows just that, as particles get smaller, the surface area to the volume ratio increases effectively.

The previously mentioned advantageous property of nanoparticles can be put to use (effective) during coating processes for leather goods such as garments, furniture, car seats or even for footwear leather. Moreover, this would allow for a more eco-friendly, biologically safe finishing process requiring lower maintenance and cleaning. The improved chemical bonding between the nanoparticles and leather surface provides for a more durable and high quality leather. Indeed, furniture upholstery needs to be stain resistant and resistant to the effects of continued sunlight exposure. Leather car upholstery needs light fastness, resistance against UV radiation and a high degree of rub fastness properties. These necessary properties for high quality leather can be achieved through incorporation of suitable metal nanoparticle in finishing formulations. Hence, the primary ambition of this project is to attain superior quality of high-performance leather by combining the fields of leather technology and nanotechnology.

The present study aims specifically to develop a leather coating agent incorporating nanoparticles to form a layer that provides the different required properties. There by developing a novel nano-finish formulation for a flexible substrate with multi-function properties like leather. The polyaldehyde nanoparticles embedded in leather coating chemicals will exhibit enhanced wet and dry rub fastness, color fastness and perspiration and color migrations. Additionally, further properties such as resistance, abrasion resistance…etc will also be allotted, allowing leather to be used for high-end leather applications like automobile upholstery, high performance upper leather…etc.

2 Experimental

2.1 Material and methods

Soluble Starch powder (st), Span80, ethanol and Acetic acid was obtained from SRL Chemicals, India. Sodium Periodate ($NaIO_4$), Hydroxylamine hydrochloride, Chloroform, Toluene, All the chemicals used were of analytical reagent grade obtained from SD Fine chemicals(India). All the leather finishing chemicals were procured from TFL, Chrompet, Chennai, India and Stahl India. Pvt. Ltd, Nagalkeni, Chennai, India. Cow crust leather was obtained from Tannery Division, CLRI, and India. All the characterizations were done the CSIR- CLRI, Caters Lab.

2.2 Synthesis of Dialdehyde Starch Nanoparticle

Aqueous soluble starch solution of 1% was heated and hydrolyzed until the solution got clarified. Toluene and Chloroform were mixed in the ratio 3:1 to make as a solvent. 2% Span 80 was prepared by dissolving in the above solvent. The clarified starch solution was mixed with the centrifuged solution in a beaker and placed in a magnetic stirrer. 1.52% of Sodium periodate was added and stirred for 40 minutes, and than 0.05% of cross-linking solution, was added and stirred for 1.5 hours. During this period, the micro-emulsion was broken with Ethanol and washed with dilute hydrochloric acid once. Then again it was washed with acetone and water alternatively. The stirred solution was then subjected to centrifugation. The resultant precipitate was freeze-dried to obtain the final product of dialdehyde starch nanoparticles.

2.2.1 FT-IR

The powder samples were analysed using JASCO FTIR 4100 FTIR spectrometer. The powder samples were directly taken for FTIR analysis. The spectra were recorded between 400-4000 cm^{-1} with average of four scans and 4 cm^{-1}.

2.2.2 SEM Analysis

Morphological features of the dialdehyde starch nanoparticles and starch solution was done using Scanning Electron Microscopy (SEM). The samples were mounted on the sample grid and examined by the microscope at 10.00 kV with a range of magnitudes. SEM analysis provided the morphological details of the various samples.

2.2.3 Preparation of Leather Finishing Formulation

Compact Binder of 7.5 g were taken in beaker and add 1.25g of pigments was added and stirrer for 20 minutes and followed by water and commercial cross linker (AKU) and stirred for 10 minutes than applied on the goat upper leather the same process is followed by the experimental also The above formulation was sprayed by High Volume Low Pressure (HVLP) Spray gun. Then the leather was subjected to 80^{o}C and 80 kg/cm^2 pressure in hydraulic press.

2.3 Physical Properties of formulated leather

The physical properties of finished leather sample from both control and experimental goat upper leather were taken for physical testing measurements**.** The samples were taken from official sampling position by IUP testing method (ref). For all physical strength analysis of leather samples were conditioned at 20±2°C and 65±4% humidity for 48h. The Measurement of Wet, dry rub, color fastness and fastness test carried out according to IUF 450 by veslic C-4500, and the results are given in Table 4.

3 Results and Discussions

3.1 Functional group analysis of ATIR-FTIR

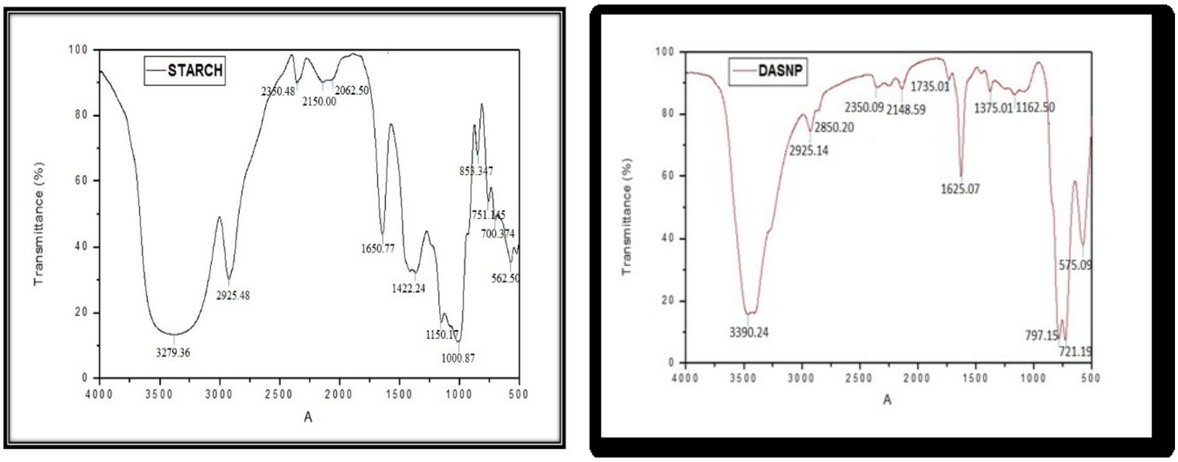

Fig. 2. FT-IR spectra of Starch and DASNP.

The FT-IR peaks of the control-starch and the dialdehyde starch nanoparticles were compared. From the FTIR analysis, the compounds mainly present in Starch were found to be alcohols, phenols and hydrocarbons such as alkanes and alkenes. On conversion of starch to DASNP by periodate oxidation most of the alkanes and alkenes were seen to be converted to alcohols, amines and carbonyl groups. The introduction of carbonyl stretching around 1735cm-1 indicates the formation of dialdehyde derivative. The hydroxy (-OH) stretching was narrowed due to the conversion of hydroxyl to carbonyl.

3.2 Morphology structure (SEM) of Synthesised DASNP

The morphology of the prepared nanoparticles was examined using scanning electron microscopy. Fig. 2 (a) shows that the surface morphology and shapes of the particles are nearly crystalline structure and Fig. 2 (b) shows the surface morphology and shapes are nearly spherical and clearly show a slight aggregation of the particles. The aggregation occurred probably during the process of drying [23, 24].

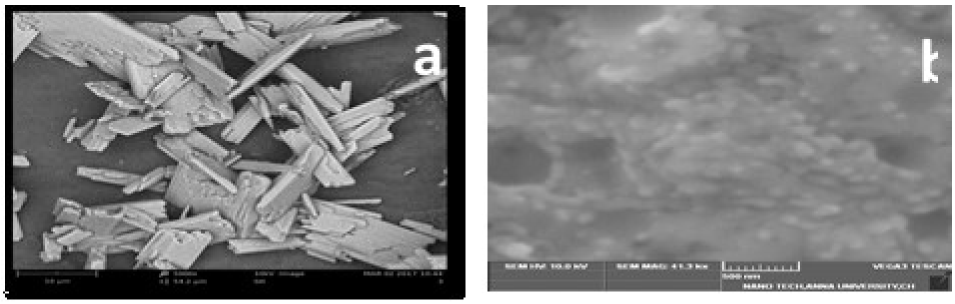

Fig. 3. SEM images of (a) starch and (b) Dialdehyde starch nanoparticles.

3.3 Effect of Physical Properties of Formulated Leather

The goat upper leather finishing formulation prepared as per Table 1 i.e., with water, compact binder, AKU commercial cross linker and pigment was sprayed on the standard goat upper leather crust by HVLP gun at 30 psi. 8 grams of season mix was deposited on one sq.ft of leather by four cross coat spray with intermediate drying. The same formulation as followed by experimental like DASNP. Then the leather was subjected to 80°C and 80 kg/cm2 pressure in hydraulic press and the results are given in Table 1. Measurement of fluxing is carried out by SATRA STM 601/12 12 and the values are given in Table.

S.No	Wet Rub	Dry Rub	Color fastness	Perspiration Resistance	Color Migrations
Control	3/4	3/4	3/4	3/4	3/4
Expt.	4/4	4/4	4/4	4/4	4/4

4 Conclusions

The present study establishes novel nano bioaldehyde system for leather finishing. Finished leather characteristic of NBP system crosslinker is similar commercially used cross-linker. The study provides new insight in using eco-friendly and sustainable chemical as a crosslinker for leather finishing.

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