

Development of Nano Bio Aldehyde Tanning Agent for Sustainable Leather Manufacture

by

Yasothai Arjunan,^{a,b,c} Gladstone Christopher Jayakumar,^{b,c} Angayarkanny Subramanian^{a*} and Swarna V. Kanth^{b,c*}

^aDepartment of Chemistry, College of Engineering (CEG), Anna University, Chennai-600025, India.

^bDepartment of Leather Technology, (Housed at CSIR-Central Leather Research Institute),

Alagappa College of Technology, Anna University, Chennai-600025, India

^cCSIR-Central Leather Research Institute, Adyar, Chennai-600020, India.

Abstract

Exploring the application of natural biopolymers in leather manufacture is a need of the hour to achieve sustainability. The present research work explores the possibility of using modified biopolymer nanoparticles as a tanning agent. Starch, a polysaccharide with high functionalization, is converted into Nano Bio Aldehyde (NBA) through periodate oxidation as water-in-oil microemulsion method. The synthesized product was characterized by its physico-chemical nature. The prepared NBA shows an aldehyde content of 85%, which endorses its application as a tanning agent. Experimental leather trials were carried out to assess the tanning efficacy and found that NBA tanned leathers show a shrinkage temperature of 90°C. Physical characteristics of the experimental leathers were found to be 24 N/mm² and 90 N for tensile and tear strength, respectively. The study provides a holistic understanding of modified biopolymer as a nano tanning agent to manufacture leather.

Introduction

The tanning process improves the thermal and enzymatic stability of leather.¹⁻² Among organic tanning systems, aldehyde tanning agents have gained prominence in the global leather industry because of their crosslinking ability.³ Aldehydes, aliphatic aldehydes, aldehydic agents, and dialdehyde polysaccharides have been studied as crosslinkers for stabilizing native collagen.⁴ Polysaccharides such as starch, alginate, and cellulose are modified based on their functionality to increase their crosslinking ability as tanning agents.⁵ Such modified biopolymers show profound changes in properties and enhanced functionalities. Dialdehyde Starch (DAS) as oxidized starch exhibits biocompatibility, biodegradability, alkali-solubility, crosslinking and strong bonding ability.⁶ DAS also has higher reactivity associated with the aldehyde functional groups in each oxidized monomeric unit, which provide the basis for a more effective application of DAS as a tanning agent.⁷ The enzymatic degradation of collagen is significantly reduced by DAS crosslinking with an increase in thermal stability. Functionalized starch-based nanoparticles have recently drawn more attention due to their versatile and multi-functional properties.

The most salient feature is the profuse functional groups and high surface area (surface/volume ratio) ascribed to their submicron sizes allowing higher reactivity and solubility.⁸⁻⁹ The present study focuses on converting SS to NBA (NanoBioaldehyde) for its possible application as a tanning agent in leather manufacture. The tanning properties of NBA are characterized by their morphological, thermal and physical properties, viz., SEM images, shrinkage temperature, tensile strength and tear strength properties. The studies provide an insight into process technology towards developing sustainable leather manufacture using natural biopolymeric agents.

Materials and Methods

Materials

Soluble Starch (SS) powder, Span 80, acetic acid, sodium periodate, chloroform, and toluene were obtained from SRL Chemicals, India. Wet salted goat skins were procured from Slaughterhouse, Chennai, India. The chemicals used for the leather process were of commercial-grade. All other chemicals used were of analytical grade and purchased from SRL Chemicals, India.

Methods

Preparation of Nanobioaldehyde Particles

SS solution (1%) was heated at 70°C with constant stirring (1000 rpm, 30 min) and hydrolyzed using 4 N sulfuric acids (H₂SO₄) until it reached a proper solution and then sonicated for 1 h. 2% Span 80 was dissolved in toluene, and chloroform solvent mixture (3:1 ratio) at 1500 rpm stirring condition and hydrolyzed SS was added dropwise to form micro-emulsion to the solvent mixture. For this micro-emulsion, 1.49g sodium periodate (NaIO₄) was mixed to form a micro-emulsion to the solvent mixture and stirred for about ~2.5 h. The pH was adjusted to ~3-3.5 using 4 N sulfuric acid. The oxidation reaction was carried out in the dark at 27°C for 2.5 h under constant stirring (500 rpm). Five milliliters of 0.25% of sodium tripolyphosphate was added with continuous stirring for about 45 min. As a continual process, the micro-emulsion was treated with ethanol and dilute acetic acid. Finally, acetone and

*Corresponding authors email: swarna@clri.res.in & akilaprince@gmail.com

Manuscript received August 11, 2022, accepted for publication October 23, 2022.

water wash were repeated until no white depositions appeared. The resultant solution was centrifuged (10000 rpm, ~25 min), and the residue was lyophilized to obtain NBA particles.¹⁰

Characterization of the product NBA

Determination of Aldehyde Content

The amount of aldehyde present in the prepared NBA particles was estimated by the quantitative alkali consumption method.¹¹

Aldehyde content was calculated with the following formula,

$$\% \text{ of Aldehyde content} = \frac{(C_1 V_1 - 2C_2 V_2)}{(W/161 \times 1000)} \times 100$$

Where W is the mass of NBA in grams (g), and 161 is the average molecular weight of repeat unit in NBA.

- C_1 and C_2 are the concentrations of NaOH and H_2SO_4 respectively in mol/mL
- V_1 and V_2 is the volume of NaOH, and H_2SO_4 added respectively in (mL)

Fourier Transform Infrared (FTIR) Analysis

FTIR measurements of SS and NBA were measured by JASCO 4200 FTIR spectrometer. Entire spectrum was recorded by absorption mode at 4 cm^{-1} resolutions with a wavenumber range from $4000\text{-}400 \text{ cm}^{-1}$.¹²

Particle Size Analysis

Particle size was measured at 25°C using a dynamic light scattering (DLS) analyser (Malvern Nano-Zetasizer ZS, Malvern, UK). The SS and NBA samples were dispersed with distilled water to form a solution of 0.01% (w/v) concentration.¹³

Thermogravimetric Analysis (TGA)

TGA Q50 V200.5 Build 30 model Thermogravimetric analyser was used for thermal decomposition studies. Approximately 1.9 mg (dry basis) of samples were loaded into a platinum pan and heated under a steady flow of dry nitrogen maintained at a flow rate of 40 mL/min from 25° to 800°C at $10^\circ\text{C}/\text{min}$.¹⁴

Differential Scanning Calorimetric (DSC) Analysis

The DSC measurement was performed for SS and NBA to understand the thermal stability using Evo Robot gas option (DSC 2A - 00837) in N_2 atmosphere.¹⁵

Preparation of DAS and NBA tanned Leathers

Wet salted goat skins were processed through conventional method till pickling. Pickled pelt was divided into two halves, left side skin was used as control and the right side was processed for the experimental trials. pH of the pickled pelt was adjusted to the required pH by sodium formate and sodium bicarbonate and tanned with different concentrations of NBA viz., 1, 2, 3, 4, and 5% (based on the pickled pelt weight) for 4 h. The process and recipe formulation is given in Table I. The next day, post-tanning process (Table II) was carried out to evaluate the physico-chemical properties of the crust leathers.

Characterization of DAS and NBA Tanned Leathers

Hydrothermal stability measurement

Hydrothermal stability of DAS and NBA tanned leathers were measured. Hydrothermal stability of leather samples was measured using SATRA STD 114 Testing apparatus. Samples taken from official sampling positions.¹⁶

Mechanical strength

The tensile and tear strength were determined using the standard IULTCS methods.¹⁷⁻¹⁸ Mechanical properties of DAS and NBA

Table I
Experimental NBA tanning process

Process	Chemicals	%	Duration	Remarks
Tanning	Pickle liquor	50		pH 2.8
	NBA	*X	120 min	Check for penetration
	Water	50		
	Sodium formate	1	3×15 min	
	Sodium bicarbonate	1.5	3× 10 +60 min	pH Adjusted to 4.0; Drain
Washing	Water	100	15 min	Drain; aged for 24 h; sammed; shaved for thickness 1.0-1.1 mm

*X: 1%, 2%, 3%, 4% and 5% for tanning trial experiments. Piled overnight

Percentage (%) is based on the pickled pelt weight of the goat skins

Table II
Post tanning process

Process	Chemicals	%	Duration(min)	Remarks
Wetting	Water	200		
	Wetting agents	0.1	60	Drain
Neutralization	Water	150		
	Sodium bicarbonate	1	30	pH adjusted to 5
Washing	Water	150	15	Drain
Retanning	Water	100		
	Acrylic syntan	2		
	Phenolic syntan	2	30	
	Melamine syntan	8	45	
Dyeing and fatliquoring	Synthetic fatliquor	10	60	
	Acid dye brown	2.5	60	Penetration of dye checked
Fixing	Formic acid	1		
	Water	10	3×10+30	Drain
Washing	Water	100	10	Drain, leathers were piled O/N, set, dry, stake, trim and buff

tanned leather were determined using Instron series II Automated Materials Testing System.

Subjective evaluation of processed leathers

DAS and NBA tanned leathers were assessed for organoleptic properties. Functional properties of the leathers were rated on a scale of 0-10 points by three experts.

Morphological Evaluation

The morphological features of the prepared particles and tanned leathers were examined using scanning electron microscope (Tescan Clara, Newzeland).¹⁹

Results and Discussion

Starch is a biodegradable and biocompatible polysaccharide having varied applications in the field of translational research. As a cost-effective material, it has gained profound interest as an independent bi-functional material. Through micro-emulsion technique NBA is prepared by acid hydrolysis and periodate oxidation method.²⁰ Prepared NBA showed 85% of aldehyde content with 99% solubility at a minimal ratio (1:1.5) of periodate oxidation.

Structural alterations in NBA

Vibrational spectroscopy of SS and NBA are shown in Figure 1. From the spectrum it can be observed that the characteristic peak of O-H stretching and vibration is around 3481 cm^{-1} , C-H asymmetrical

stretching and vibration is exerted at 2932 cm^{-1} and O-H vibration of physically absorbed water is at 1651 cm^{-1} respectively, which correspond to starch. The absorbance peak around 1000-1200 cm^{-1} is attributed to C-O stretching in starch.²¹ However, when the stretching is compared with NBA; the characteristic peaks at 2897 cm^{-1} and 1735 cm^{-1} are attributed to the bonds of aldehyde carbonyl (C=O) and C-H stretching of aldehyde (-CHO). The FTIR spectrum confirms the presence of anhydride glucose units having -OH groups

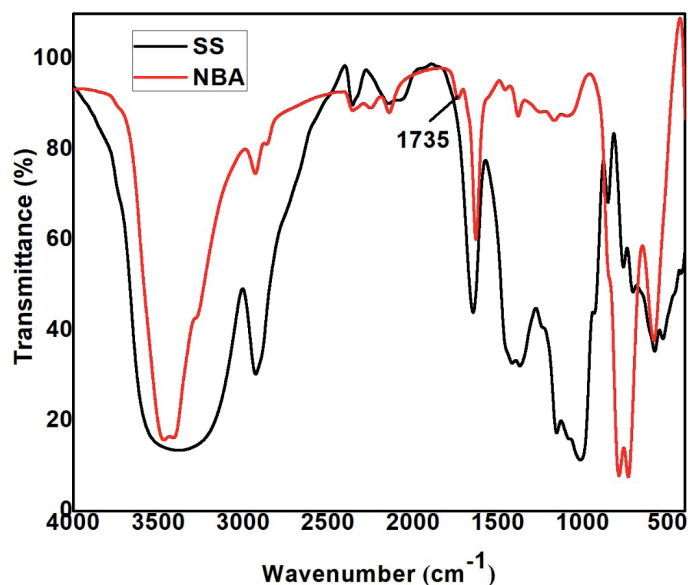


Figure 1. FTIR spectra of SS and NBA

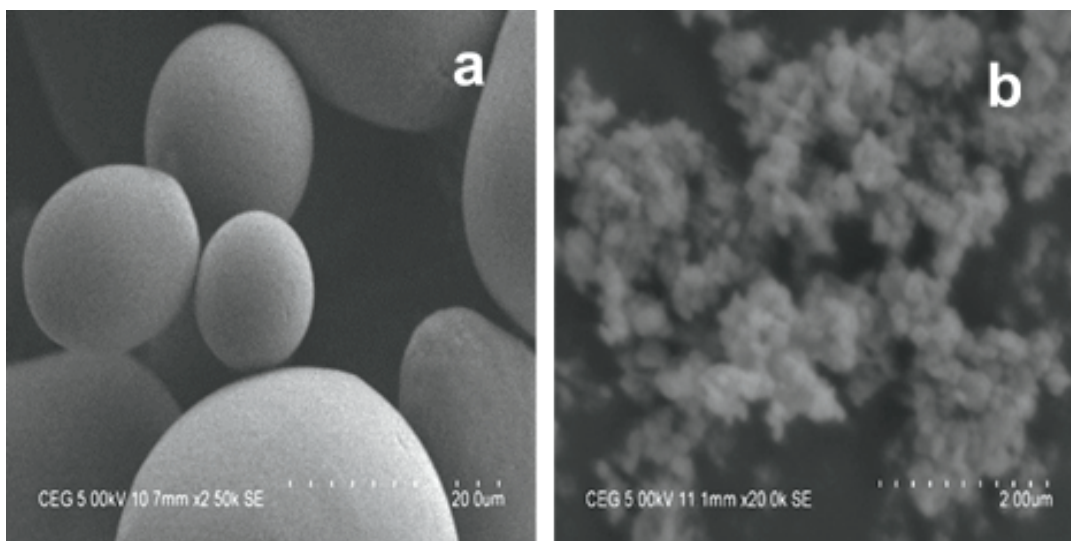


Figure 2. Scanning electron microscopy images of (a) SS scale bar-20µm and (b) NBA scale bar-2µm.

at 2,3 carbon positions, and the oxidation mainly replaces the 2,3 positions (OH) with the aldehyde group.²² Moreover, the vibrational spectroscopic studies confirm the presence of dialdehydes which is a pre-requisite for an effective aldehyde tanning system.

The morphological structure of SS and NBA

The morphological variation of SS and NBA samples are shown in Figure 2. In Figure 2(a), SS appears spherical with loosely bound grains. Figure 2(b) shows the nano system of SS into NBA, which shows molecular size ~86 nm. SEM images depict the phase transition of the SS to NBA correlated to the size reduction (micron to nano).

Characteristics of the prepared particles

The particle size distribution of the prepared particles is shown in Figure 3. The native SS has particle size of ~5.4 µm, and that of NBA is 41 nm, showing significant reduction in size due to hydrolysis of SS prior to oxidation. The prepared NBA resulted in a diameter of 41 nm and a polydispersity index value of 0.997. The PDI value shows that the particle size of NBA has narrow size distribution.

Thermal properties of SS and NBA

The thermal degradation of SS and NBA were studied through TGA (Figure 4). Figure 4 indicates thermal degradation of SS and NBA. The results obtained from TGA indicate NBA has enhanced thermal resistance than SS.²³

The DSC thermogram of SS and NBA is shown in Figure 5. SS resulted in T_o and T_p values between 86°C and 189°C, whereas NBA resulted in one sharp peak value at 134°C. NBA showed increase in gelatinization peak temperature compared to SS, which is due to the decreased crystallinity. In the process of acid hydrolysis and oxidation treatment, the amorphous region of starch has been

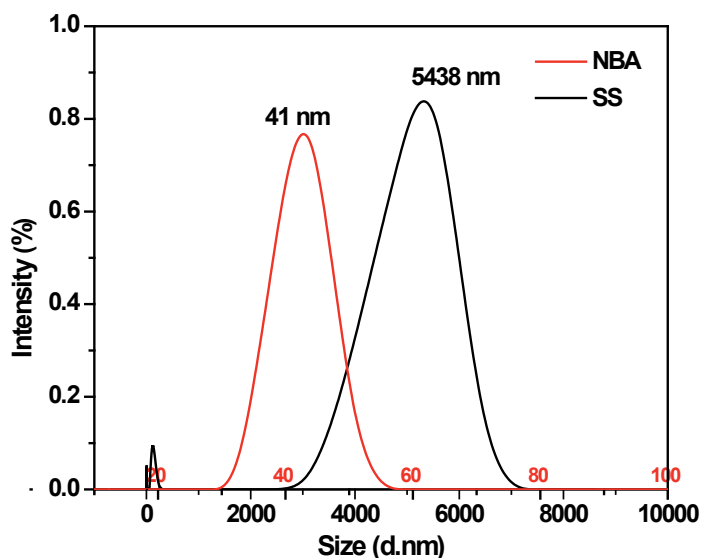


Figure 3. Dynamic light scattering measurements of SS (black line) and NBA (red line).

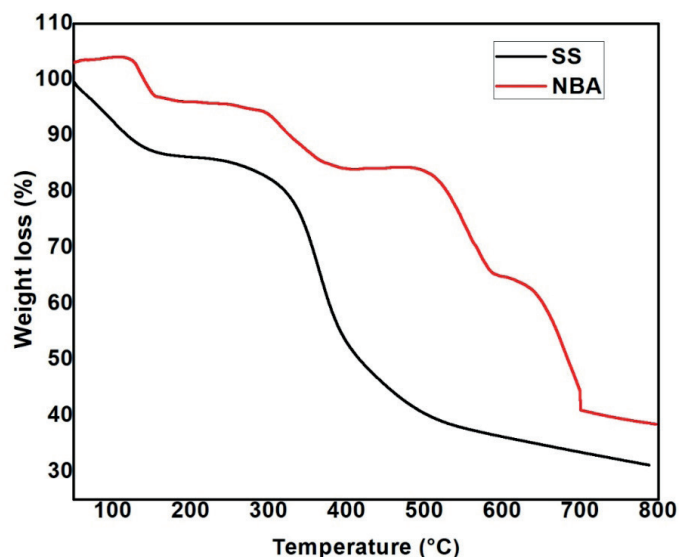


Figure 4. TGA analysis of SS and NBA

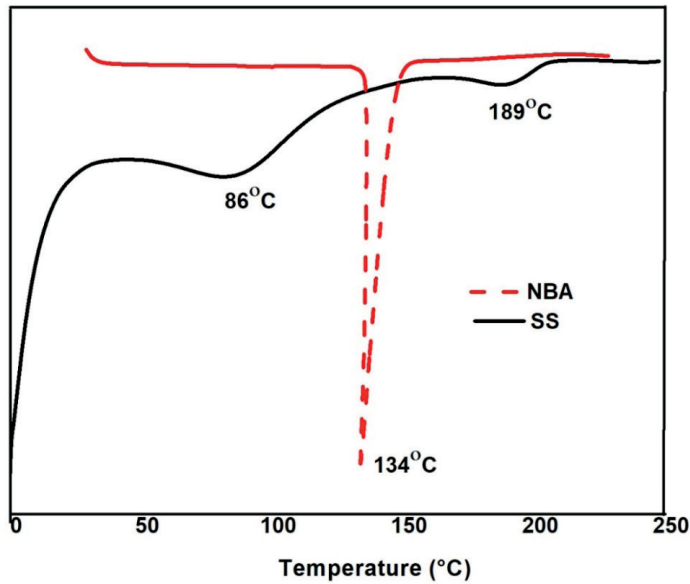


Figure 5. Differential scanning calorimeter analysis of SS and NBA

destroyed leading to instability in the crystalline and amorphous regions.²⁴⁻²⁵

Hydrothermal resistance of tanned leathers

The hydrothermal resistance of experimental NBA tanned leather was compared with DAS tanned leather. The modified skin upon tanning with NBA increased the degree of crosslinking, which eventually led to an increase in shrinkage temperature. The higher shrinkage temperature of the leather indicates better thermal stability, which could possibly be due to a high degree of crosslinking between the tanning agent and the collagen matrix. The hydrothermal stability measurements of native collagen (raw hide) show shrinkage temperature of about $60^{\circ}\pm 0.26^{\circ}\text{C}$. As a function of concentration, the shrinkage temperature of collagen exhibited $65^{\circ}\pm 0.16^{\circ}\text{C}$ (@1% NBA), $75^{\circ}\pm 0.32^{\circ}\text{C}$ (@2% NBA), $87^{\circ}\pm 0.25^{\circ}\text{C}$ (@3% NBA), $90^{\circ}\pm 0.35^{\circ}\text{C}$ (@4% NBA) and $90^{\circ}\pm 0.55^{\circ}\text{C}$ (@5% NBA) respectively. Experimental NBA tanned leather (5%) showed that the thermal stability of leather measured about $90^{\circ}\pm 0.55^{\circ}\text{C}$ when compared with control DAS tanned leather ($85^{\circ}\pm 1.00^{\circ}\text{C}$). There is no significant increase in the shrinkage temperature of leather above 4% offer of NBA, and hence the same has been considered to be the optimum offer for tanning.

Physical strength characteristics of the crust leathers

The physical strength of DAS and NBA tanned leather is given in Table III. From the results it can be observed that the physical

Table III

Physical strength properties of control and experimental NBA tanned leather

Sample Tanning	Tensile Strength (N/mm ²)	Tear Strength (N)
DAS tanned	19.42±1.3	51.11±5
NBA tanned	24.90±1.6	90.83±2

Table IV

Organoleptic properties of NBA tanned leather

Parameters	Control DAS	Experimental NBA
Grain smoothness	8.5	8.7
Grain softness	8.1	8.2
Fullness	8.0	8.3
General appearances	8.5	8.5

strength viz., tensile strength, and tear strength of the experimental NBA tanned leathers are found to be better when compared to the minimum requisite values.

Subjective evaluation of the tanned crust leathers

The results of the organoleptic assessment of the crust leather are given in Table IV. From the results, it can be ascertained that the fullness characteristics of NBA tanned leathers are slightly better than DAS tanned leathers. NBA crust leathers were observed to have reasonably good strength and organoleptic characteristics than DAS. The overall appearances of the NBA crust leathers are comparable to that of the conventionally processed crust leather samples from DAS tanning system. Hence, NBA as a tanning system may suit the requirement for processing wide range of leathers.

Morphological structures of control and experimental tanned leathers

Surface morphology of NBA and DAS tanned leathers are shown in Figure 6. Figure 6A shows the SEM images of the control leathers (DAS tanned leather) and Figure 6B shows the experimental leathers (4% NBA tanned leathers). DAS tanned leather at 800x shows some physical deposition in the surface (Figure 6A (a)) and cross-sections (Figure 6A (b)). Whereas in experimental NBA tanned leather, there is no physical deposition and observed compact grain and cross-sections (Figure 6 B (c, d)).

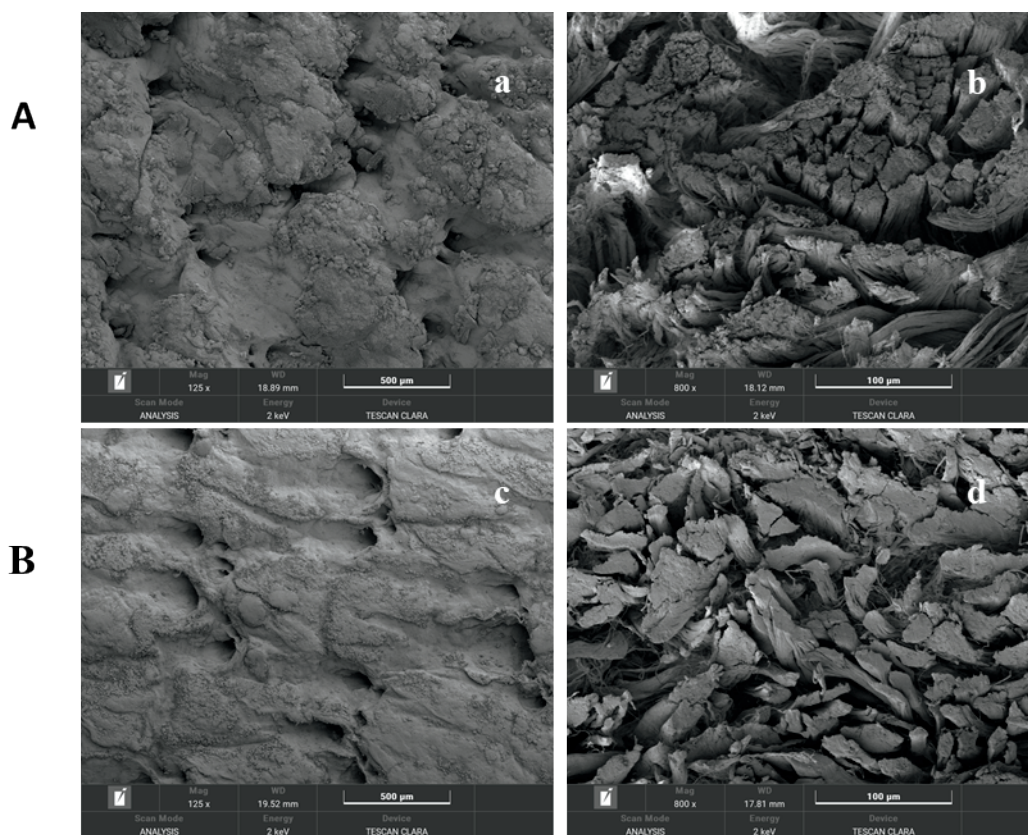


Figure 6. SEM images of DAS tanned leather surface and cross-section A (a, b) and NBA tanned leather surface and cross section B (c, d)

Conclusion

The present work aimed to develop a biologically eco-benign tanning system using NBA. The current study looked upon using nano tanning system using dialdehyde starch. The NBA as a tanning agent was prepared using water in oil emulsion technique. NBA has proved to be a potential eco-friendly tanning material for leather tanning process. NBA was synthesized from soluble starch. NBA can be a novel aldehyde tanning agent in leather making. A maximum shrinkage temperature of about $90^{\circ}\pm 0.35^{\circ}\text{C}$ was achieved with 4% NBA. The tanned leather met the standards norms of physical characteristics of upper leather. The present study resulted in a sustainable solution for metal free tanned leathers using nano-tanning system.

Acknowledgements

A. Yasothai gratefully acknowledges the technical support from the Department of Chemistry and Department of Leather Technology (Housed at CSIR-Central Leather Research Institute (CLRI)), Alagappa College of Technology, Anna University (Chennai, India). Authors thank CATERS, CSIR-CLRI (Chennai, India) for their

support in testing and characterization techniques and Department of Mechanical engineering, Anna University for SEM analysis and acknowledge CSIR-Integrated Skill Initiative Program NWP-0100 for their funding support. CSIR CLRI communication number is 1689.

References

1. Bienkiewicz, K.; *Physical chemistry of leather making*; Robert. E. Krieger Publishing Co. Malabar, FL, **33**, 1983.
2. Covington, A.D.; Modern tanning chemistry. *Chem. Soc. Rev* **26(2)**, 111-126, 1997.
3. Fathima, N.N., Madhan, B., Rao, J.R., Nair, B.U., Ramasamy, T.; Interaction of aldehydes with collagen: effect of thermal and enzymatic and conformation stability. *Int. J. Biol. Macromo* **34(4)**, 241-247, 2004.
4. Bowes, J. H., Cater, C.W.; The interaction of aldehydes with collagen. *Biochim. Biophys. Acta, Protein Struct* **168(2)**, 341-352, 1968.
5. Kanth, S.V., Nirenjana, N., Archana, T.N., Madhan, B., Rao, J.R., Nair, B. U.; Dialdehyde alginic acid - A novel biopolymeric tanning agent. *JALCA* **102(11)**, 353-361, 2007.

6. Zhang, S. D., Zhang, Y. R., Zhu, J., Wang, X. L., Yang, K. K., Wang, Y. Z.; Modified corn starches with improved comprehensive properties for preparing thermoplastics. *Starch-Stärke* **59(6)**, 258-268, 2007
7. Kanth, S.V., Madhan, B., Rao, J.R., Nair, B.N., Ramasami.T.; Studies on the stabilization of collagen using dialdehyde starch: Part I. Effect of autoclaving on dialdehyde starch. *JALCA* **101(12)**, 444-453, 2006.
8. Chen, Y., Hao, Y., Ting, K., Li, Q., Gao, Q.; Preparation and emulsification properties of dialdehyde starch nanoparticles. *Food Chem* **286**, 467-474, 2019.
9. Lu, W., Shen, Y., Xie, A., Zhang, W.; Preparation and protein immobilization of magnetic dialdehyde starch nanoparticles. *J. Phys. Chem B* **117(14)**, 3720-3725, 2013.
10. Yu, D., Xiao, S., Tong, C., Chen, L., Liu, X.; Dialdehyde starch nanoparticles: Preparation and application in drug carrier. *Chin. Sci. Bull* **52(21)**, 2913-2918, 2007.
11. Hofreiter, B.T., Alexander, B.H., Wolff, I. A.; Rapid Estimation of Dialdehyde Content of Periodate Oxystarch through Quantitative Alkali Consumption. *Anal. Chem* **27**, 1930-1931, 1955.
12. Chen, C., Sun, W., Yao, W., Wang, Y., Ying, H., Wang, P.; Functional polymeric dialdehyde dextrin network capped mesoporous silica nanoparticles for pH/GSH dual-controlled drug release, *RSC Adv* **8(37)**, 20862-20871, 2018.
13. Haaj, S. B., Thielemans, W., Magnin, A., Boufi., S.; Starch nanocrystals and starch nanoparticles from waxy maize as nano reinforcement: A comparative study. *Carbohydr. Polym* **143**, 310-317, 2016.
14. Zuo, Y., Liu, W., Xiao, J., Zhao, X., Zhu, Y., Wu, Y.; Preparation and characterization of dialdehyde starch by one-step acid hydrolysis and oxidation. *Int. J. Biol. Macromol* **103**, 1257-1264, 2017.
15. Zhou, L., He, X., Ji, N., Dai, L., Li, Y., Yang, J., Sun, Q.; Preparation and characterization of waxy maize starch nanoparticles via hydrochloric acid vapor hydrolysis combined with ultrasonication treatment. *Ultrason Sonochem* **80**, 105-836, 2021.
16. IUP 2: Sampling. *JSLTC* **84**, 303-308, 2000.
17. IUP 6: Measurement of tensile strength and percentage elongation. *JSLTC* **84**, 317-318, 2000.
18. IUP 8: Measurement of tear load. *JSLTC* **84**, 27-29, 2000.
19. Gonçalves, P. M., Noreña, C.P.Z., da Silveira, N.P., Brandelli. A.; Characterization of starch nanoparticles obtained from *Araucaria angustifolia* seeds by acid hydrolysis and ultrasound. *LWT - Food Sci. Technol* **58(1)**, 21-27, 2014.
20. Fiedorowicz, M., Para, A.; Structural and molecular properties of dialdehyde starch. *Carbohydr. Polym* **63(3)**, 360-366, 2006.
21. Francl, J., Kingery, W.D.; Thermal conductivity: IX, Experimental investigation of effect of porosity on thermal conductivity. *J. Am. Ceram. Soc* **37(2)**, 99-107, 2015.
22. Yu, J., Chang, P.R., Ma, X.; The preparation and properties of dialdehyde starch thermoplastic dialdehyde starch. *Carbohydr. Polym* **79(2)**, 29-30, 2010.
23. Minakawa, A.F.K., Faria-Tischer, P.C.S., Mali, S.; Simple ultrasound method to obtain starch micro- and nanoparticles from cassava, corn and yam starches. *Food Chem* **283**, 11-18, 2019.
24. Jenkins, P. J., Donald, A. M.; The effect of acid hydrolysis on native starch granule structure. *Starch-Stärke* **49(7-8)**, 262-267, 1997.
25. John, J. K., Raja, K. C. M., Rani, S., Moorthy, S. N., Eliasson, A.; Properties of arrowroot starch treated with aqueous HCl at ambient temperature. *J. Food Sci* **67(1)**, 10-14, 2002.