A Pragmatic Approach Towards the Manufacture of Wet-White Leathers Using a Bio-Polymeric Tanning System

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Abstract. Different tanning materials endow leather with varying colors observable in undyed leathers. Periodate-oxidized starch tanned leathers have a yellow tinge or light brown color and get darker with age. The color change in situ is ascribable to iodate ions that are products of the periodate oxidation reaction. Iodate ions undergo reduction to form iodine molecules that are yellow or brown in low or at higher concentrations. This study focuses on the removal of iodate ions from Dialdehyde Tapioca Starch (DTS) using a simple precipitation method. Preparation of DTS is by periodate oxidation and precipitation of iodate ions using an inorganic salt as a precipitant. The experiments for manufacturing wet-white leathers used delimed pelt and DTS (unmodified and modified) tanning agents at various percentages based on pelt weight. The percentage removal of iodate ions in modified DTS was 98%. Both unmodified and modified DTS had an aldehyde content of 70%. FT-IR analysis confirmed the aldehyde groups. Delimed pelt, DTS (Unmodified), and MDTS (modified) tanned leathers had shrinkage temperatures of 62, 80, and 82°C, respectively. The physico-mechanical properties of the leathers are comparable with the UNIDO specifications. The 'b' color value of DTS tanned leather was high at 36.6, confirming yellowing and subsequent browning of the leather. Wet-white leather tanned with MDTS had no discernible color change and affirms the effective removal of iodate ions. This study has overcome the drawback associated with periodate-oxidized starch tanning agents, viz. leather yellowing and darkening over time, considering the chemical and physico-mechanical properties of the resultant leathers.

1 Introduction

Animal skins/hides have been the predominant leather making material for centuries owing to leather's exceptional natural properties (Ockerman and Basu, 2004). Close to 90% of the 25-30% protein in the skin/hide is collagen (Kanagaraj et al., 2006). Collagen is the raw material for leather manufacture (Sizeland et al., 2015). It is thus necessary to preserve and protect the delicate protein matrix against microbial attack, chemical hydrolyzes, and thermo-mechanical stress (Krishnamoorthy et al., 2012). Plant polyphenols, metal ions, and aldehydes permanently preserve skins during tanning. Tanning is, therefore, the focal point and the basis of leather making (Kanth et al., 2009).

There is a wide range of tanning materials and techniques. Conventional chrome tanning accounts for 90% of the leather produced worldwide. Chrome tanned leather has by far the highest hydrothermal (shrinkage temperature = 110-115°C) and enzymatic stability (Covington, 2005; Liu et al., 2016). Pickled pelts use 60% of basic chromium(III) sulfate (BCS) during tanning. The remaining 40% BCS contributes to environmental pollution on release as part of the effluent (Sundar, Rao and Muralidharan, 2002; Liu et al., 2016). Chromium (whether Cr(+3) or Cr(+6)) has the distinct disadvantage of being environmentally persistent. The global leather industry discharges around 40,000 tons of BCS (Liu et al., 2016) and 548 billion liters of wastewater each year (Sathish *et al.,* 2015). Tannery wastewater treatment is complex, as it consists of various chemical substances used in leather processing.

Attention has, therefore, shifted to the possibility of finding an alternative tanning agent with properties that most closely match those of trivalent chromium (Musa *et al.,* 2009; Pati and

Chaudhary, 2014). Aldehyde tanning is a critical alternative that has gained prominence in the global leather industry over the years. Aldehydes, viz. aliphatic aldehydes, aldehydic agents, and dialdehydes starches are suitable for various practical applications of leather making, including tanning, retanning, and finishing. Aldehyde tanning produces high performance and thermally stable 'chrome-free' (wet white) leather with the thermal stability of around 85°C (Bowes, J. H. and Cater, 1965; Langmaier *et al.,* 2002; Sarkar, K.T. and Sorcar, 2005; Covington, 2009). Besides, aldehyde tanned leather possesses excellent properties - in particular, resistance to perspiration, a weak acid/ base, and moderate washing. White tanned leather becomes whiter under sunlight and is well-suited to produce pastel shade leather. Unlike chrome tanned leather, wet-white leather is incinerable without the hazard of chromium (+6) formation and, therefore, eco-friendly. Wet-white leathers find extensive use in a wide variety of applications - such as in the manufacture of automobile seats and interiors, furniture, apparel, footwear, bags, and accessories (Alderman, 1975; Sarkar, K.T. and Sorcar, 2005).

Dialdehyde starches (polysaccharides) are bio-polymeric tanning agents synthesized by periodate oxidation of carbohydrates (Alderman, 1975). Periodate-oxidized starch tanned leathers yellow and darken with time. The color change is attributable to iodate ions that are products of the periodate oxidation reaction between starch and sodium or potassium (meta)periodate. Iodate ions undergo reduction to form iodine molecules that are yellow or brown in low or at higher concentrations.

This study focuses on two primary objectives: one, the removal of iodate ions from Dialdehyde Tapioca Starch (DTS) using an inorganic salt as a precipitant; and secondly, the use of DTS as a tanning agent to make wet white leather.

2 Materials and methods

2.1 Preparation of dialdehyde tapioca starches

Preparation of DTS (unmodified) is by periodate oxidation of tapioca starch (TS) using 0.35M sodium (meta)periodate ($NaIO_4$), at pH 3.75, and 35°C for 48 h. Fourier-transform infrared (FT-IR) spectrophotometer (FT/IR-4700 type A) was used to confirm the presences of aldehyde groups on oxidation. The aldehyde group content was determined using the method of quantitative alkali consumption as previously reported by Wongsagon, Shobsngob and Varavinit (2005).

Iodate ions removal from the sample solution was by precipitation with a calculated amount of inorganic salt (precipitant). Iodate content of MDTS (modified) was determined by the redox titration method by first reacting the iodate with added iodide under acidic conditions to produce iodine, which was titrated with thiosulfate.

2.2 DTS Tanning

The experiments for manufacturing wet-white leathers used delimed goatskins (pH = 8.0) and DTS (unmodified and modified) as tanning agents at various percentages based on delimed pelt weight and a 48 h tannage time at pH 8.0. The ratio of liquor to delimed pelt was 5:1.

2.3 Analysis of Leather

2.3.1 Shrinkage temperature (Ts)

The Ts was determined using a Theis shrinkage tester and standard procedures. All tests were carried out in triplicate, and the results expressed as the means with standard deviations of ±1.

2.3.2 Color evaluation

Reflectance measurements were made on DTS and MDTS tanned leather samples using a Milton Roy Color mate HDS instrument. The L, a, b, and c values were calculated, and means reported.

2.3.3 Physical tests

The sampling of test samples was carried out in line with the International Union of Leather Technologists and Chemists Societies (IULTCS) - Standard Method (IUP/2 2000). The test samples were conditioned at 80±4°C and 65±4% R.H. for 48 h. Tensile strength, % elongation at break, tear strength, and grain crack strength were tested following the Society of Leather Technologist and Chemists (SLTC) standard methods; IUP/6 2000, IUP/6 2000, IUP/8 2000, and IUP/9 1996, respectively. Each value reported is an average of four (2 along the backbone, 2 across the backbone) measurements.

2.3.4 Softness

The softness of the leather samples was measured using ST 300D leather softness tester, in conformity with IUP/36/EN ISO 17235 method.

3 Results and discussion

Both unmodified and modified DTS had a percentage aldehyde group content of 70%. Fourier-transform infrared (FT-IR) spectra confirmed the formation of aldehyde groups (Fig. 1). Compared with the TS curve, peaks of 1764 and 1741 cm^{-1} appear in the curves of DTS and MDTS, respectively. The two peaks are attributed to characteristic absorption of carbonyl groups; C=O stretching vibrations in aldehyde groups.

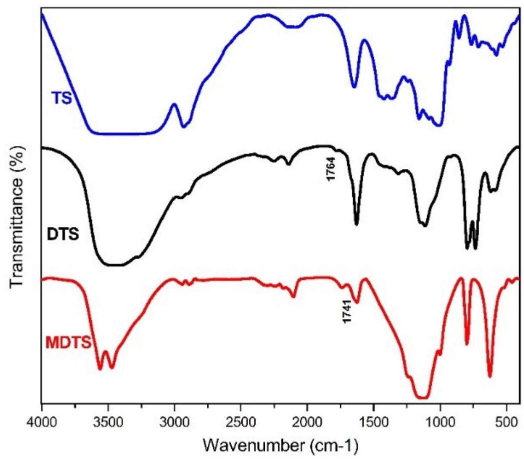

Fig. 1. FT-IR spectra of TS, DTS, and MDTS.

The percentage removal of iodate ions in MDTS was 98%. The effective removal of iodate ions guarantees that the ions are not present to undergo a reduction reaction subsequently generating iodine molecules that cause yellowing (at low concentration) and darkening (at high concentration) of materials over time.

Shrinkage temperature is a measure of the hydrothermal stability of leather and is characteristic of the effectiveness of a tannage (Ding, Taylor and Brown, 2008). The expected Ts of aldehyde-tanned leather is 70°C. The Ts of the delimed pelt, DTS and MDTS tanned leathers was 62, 80, and 82°C, respectively. Aldehydes combine with basic amino groups of skin/hide protein (collagen) and cross-react with adjacent basic groups in the collagen to form an interwoven matrix of intra- and intermolecular cross-links (Paul and Bailey, 2003; Covington, 2009). The formed covalent cross-links improve the hydrothermal stability of the protein and thus raise the Ts of DTS and MDTS tanned leathers.

The 'L' value for DTS tanned leather is 72.2 and 93.9 for MDTS tanned leather (Table. 1). Accordingly, MDTS tanned leather has a lighter shade. The 'a' values for both pieces of leather are greater than 0, indicating the presence of a red shade with DTS tanned leather having a higher value (9.0) than that of MDTS tanned leather (0.5). The 'b' values of DTS and MDTS tanned leathers are greater than 0, that is, 36.6 and 2.6, respectively, signifying the color has a yellow shade. The high 'b' value confirms the yellowing of DTS tanned leather caused by iodine molecules from the iodate ions reduction reaction. The low 'b' values of MDTS tanned leather corroborate the fact that there was effective iodate ion removal. The 'c' value of DTS tanned leather (37.6) was high compared to that of MDTS tanned leather (2.7) denoting high and low intensities of the respective colors (Fathima *et al.,* 2004).

The tensile strength, elongation at break, tear strength, and grain crack resistance (load and distension) values of both DTS and MDTS tanned leathers are comparable to United Nations Industrial Development Organization (UNIDO) specifications (Table.2.). Besides, the values are comparatively lower than those of chrome-tanned leather.

The respective softness values of DTS and MDTS tanned leathers are 7.0±1 and 6.5±1. Softness is a measure of the deformation response of a material to external forces and, thus, depicts the handle (feel) of the leather. On a scale of 0-10, the higher the softness value, the better the feel of leather. The leathers were relatively soft, indicating the fiber structures were not affected.

Table. 1. 'L', 'a', 'b' and 'c' values of DTS and MDTS tanned leathers.

Test sample	**L**	**a**	**b**	**c**
DTS tanned leather	72.2	9.0	36.6	37.6
MDTS tanned leather	93.9	0.5	2.6	2.7
*Values are mean ± standard deviations, n = 3				

Table. 2. Physical strength characteristics of DTS and MDTS tanned leathers.

Test sample	**Tensile Strength (N/mm2)**	**Elongation at break (%)**	**Tear Strength (N/mm)**	**Grain Crack Resistance**	
				Load (N)	**Distension (mm)**
DTS tanned leather	22.86±1	52±2	51.94±2	280.40±14	8.4±1
MDTS tanned leather	23.11±2	54±2	52.23±3	283.90±16	10.1±1
*Values are mean ± standard deviations, n = 4					

4 Conclusion

This study set out to remove iodate ions from Dialdehyde Tapioca Starch (DTS). The second object was to use DTS as a tanning agent to make wet white leather. A 98% iodate ions removal was achieved. The color values of MDTS tanned leather substantiate the effective removal of iodate ions. There is no observable yellowing or darkening of the leather. The shrinkage temperatures of the leathers tanned using DTS and MDTS are 80 and 82°C, respectively. The strength properties of the leathers are comparable to the UNIDO specifications. Taken together, these findings suggest that the novel iodate free MDTS can be scaled-up for commercial availability.

Acknowledgments

The authors acknowledge CSIR-Central Leather Research Institute (CLRI) for providing the equipment and the technical staff in carrying out this research work. Thank you for your incredible support.

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