Dialdehyde Alginic Acid - A Novel Biopolymeric Tanning Agent

by

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Abstract

In the present investigation, a new class of tanning agent produced from a renewable biopolymer, alginic acid is reported. Dialdehyde alginic acid (DAA) of different oxidation levels was prepared from alginic acid. DAA at different degree of oxidation was found to be soluble in water. Solubility increased with increase in % oxidized DAA. Treatment of skins with DAA and the effect of the shrinkage temperature of leathers at different oxidation levels of alginic acid were studied. Leathers with 80ºC shrinkage temperature have been obtained by tanning at pH 8. The increase in shrinkage temperature was found to be dependent on the degree of oxidation of alginic acid. The scanning electron microscopy of the DAA tanned leathers had revealed coating of the fibre bundles. The fullness of the DAA tanned leathers was found to be relatively better than the chrome tanned leathers. The physical strength characteristics of the DAA tanned leathers are found to be comparable to that of conventional chrome tanned leathers.

Resumen

En la presente investigación, se informa sobre una nueva clase de agente curtiente producida a partir de un biopolímero renovable, el ácido algínico. El ácido dialdehido algínico (DAA) en diversos niveles de oxidación fue preparado a partir del ácido algínico. El DAA en diversos grados de oxidación es soluble en agua. La solubilidad aumentó con aumento en el % del DAA oxidado. El tratamiento de las pieles con DAA y el efecto de la temperatura de contracción de los cueros en diversos niveles de oxidación del ácido algínico fueron estudiados. Los cueros con temperatura de contracción de 80ºC han sido obtenidos curtiendo a pH 8. El aumento en la temperatura de contracción es dependiente del grado de oxidación del ácido algínico. La microscopia de barrido electrónico del cuero curtido con DAA ha relevado la capa de los paquetes de fibras. La plenitud de los cueros curtidos con DAA fue encontrada como relativamente mejor que los cueros curtidos al cromo. Las características de la fuerza física de los cueros curtidos con DAA son comparables a los cueros curtidos convencionalmente al cromo.

Introduction

Biopolymers and biodegradable polymers are important biomaterials, which are abundant in nature. Alginic acid is an important biopolymer, which is abundant in occurrence possessing a high degree of functionality. Alginic acid is one such material, which has already established its applications in food, pharmaceutical, and medical industries.[1] Molecular design of these materials play an important role in determining their suitability in such applications.[2] Alginic acid is a naturally occurring hydrophilic colloidal polysaccharide obtained from the various species of brown seaweed (*Phaeophyceae*) and is also present in some species of bacteria.[3,4] It is a linear copolymer consisting mainly residues of 1,4-linked α-L-guluronic acid and β-D-mannuronic acid.[5] These monomers are often arranged in homopolymeric blocks separated by regions of alternating sequence of the two 1,4-linked α-L-guluronic acid and β-D-mannuronic acid monomers.[6] Along the polymer chain the two residues are arranged in an irregular block-wise pattern.[7] There are three types of blocks: homopolymeric sequence of mannurronate (MM blocks) and guluronate residues (GG blocks) and a region where the two residues alternate (MG blocks).[8] The relative proportions of these block types are affected by several factors such as the botanical source, plant maturity, collection site and seasonal variations.[9,10] Alginic acid is the only polysaccharide, which naturally contains carboxyl groups in each constituent residue, and possesses various abilities for functional materials.[11] The formula weight of the each structural unit is 176.13 daltons. The molecular weight of the macromolecule varies between 10,000 - 600,000 Daltons (typical average).[12] Alginic acid occurs as white to yellowish brown filamentous, grainy, granular or powdered material insoluble in water and organic solvents. It dissolves slowly in solutions of sodium carbonate, sodium hydroxide and trisodium phosphate. In solution, alginates behave like flexible coils.[13] However on interaction with metal ions, they form ordered structure as evidenced by

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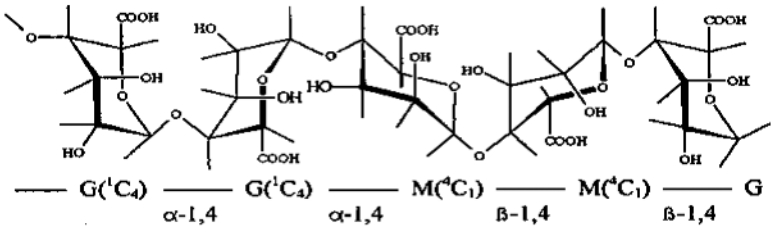


Scheme 1: Structure of alginic acid

their X-ray diffraction patterns.[14] Attempts have been made to covalently crosslink sodium alginate with gelatin and ethylene diamine using water-soluble carbodiimide.[15] To fulfill the demand for tailored end use applications the native biopolymers often need to be modified.

As seen in Scheme 1,[12] there is a carboxyl group in C_6 position and two hydroxyls in C_2 and C_3. These two different reactive groups available in the alginic acid molecule react with different chemical reagents. Periodate oxidation specifically cleaves the vicinal glycols in polysaccharides to form their dialdehyde derivatives. This reaction is generally used for the elucidation of polysaccharide structure. Each α-glycol group consumes one molecule of periodate, and under given conditions, the rate of the reaction is dependent principally on the stereochemistry of α-glycol group. Usually, the reaction is carried out in aqueous medium. Recently it is reported that although higher molecular weight alginate is non-biodegradable, its dialdehyde derivative is biodegradable.[16]

The leather industry has implemented several pollution prevention techniques that improve efficacy and at the same time minimize environmental impacts. This has been possible through many ways like improvements in basic chromium sulfate for increased uptake and near zero waste concepts.[17] The most significant challenge for the leather industry arises from the need to dispose off chromium containing solid wastes as well as leather waste.[18] While technologies are available for the recovery of protein hydrolysates and chromium from shavings and buffing dusts as well as use of these wastes for the manufacture of basic chromium sulfate,[19] the need to dispose the sludge from effluent treatment plants and also finished leathers without the danger of conversion of Cr(III) to Cr(VI) is a matter of concern.[20] The possibility of land filling with chromium bearing sludge and finished leathers is restricted due to environmental legislation, apprehending the leachability of chromium. Chromium(III), which is believed to be safe, has recently been shown to bring about protein, DNA and even cell damage.[21,22] Hence to avoid Cr(III) in tanning a revisit of vegetable tanning has been appealing and it has been possible to render vegetable tanned leather soft. However, the land use pattern does not favor large-scale cultivation of vegetable tannins, unless biotechnology transforms forest management.[23] Organic tanning could at best occupy a 50% share in tanning of the future.[23] Aldehyde tanning and use of aldehydes like formaldehyde and glutaraldehyde has been in decline as they are established to be carcinogenic.[24,25] DAA has been proved to be biodegradable and toxologically acceptable natural chemical.[18] In the search of an effective organic tanning alternative from a sustainable resource, DAA, a

TABLE I
Tanning Process using DAA from Pickled Goat Skins

Process	Chemicals	%	Duration	Remarks
pH adjustment	Pickle liquor	50	3x15 min+	adjust to required pH
	Sodium bicarbonate (1:10 dilution with water)	1-3	30 min	
Tanning	Water	50	24[d] hrs.	Maintain required pH[c]
	DAAa	X[b]		Drain tan liquor
	Formic acid	1	3x10 min	pH adjusted to 4;
	Water	10	+30 min	Drain; aged for 24 hrs; sammed; shaved to thickness 1.0-1.1 mm

[a] - Tanning with DAA at different oxidized levels viz., 33, 66 and 99%
[b] - Tanning carried out at varied DAA (@varying oxidation levels) amounts viz., 5, 10, 15 and 20% at constant pH 8 for 24 hrs
[c] - Tanning carried out at different pH viz., 6, 7, 8, 9 and 10 at 10% DAA offer (@varying oxidation levels) for 24 hrs
[d] - Tanning trials at varying time intervals viz., 4, 8, 16, 24, 48 and 72 hrs, at 10% DAA (@varying oxidation levels) and pH 8

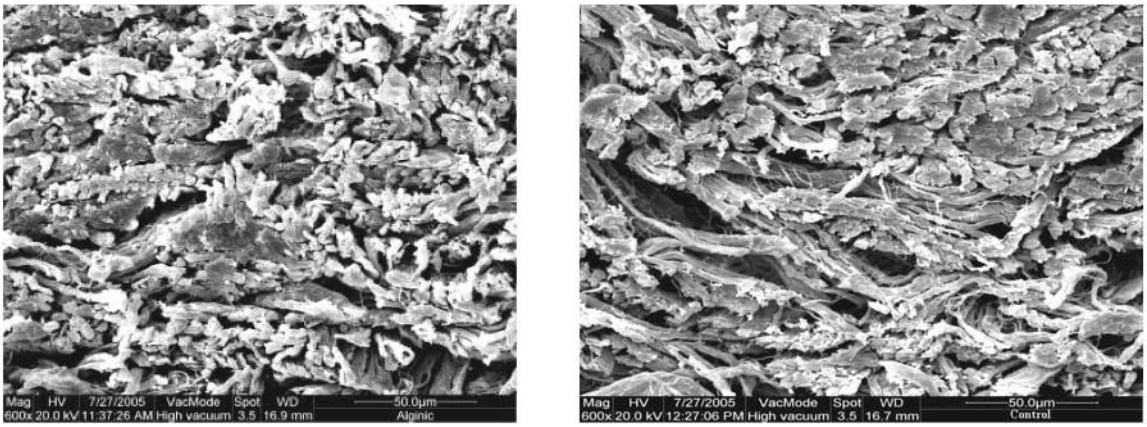


Figure 1: Scanning electron micrograph of cross-section(X 600) of a) DAA tanned leather and b) chorme tanned control

modified biopolymer of alginic acid appears to be an attractive option for tanning.

Leather research, in the recent times is being focused in the development of leathers that are eco-acceptable. DAA is a modified natural tannin and eco-acceptable. Hence DAA has the dual advantage of being a biodegradable tanning material that brings about stabilization or tanning of another biodegradable biopolymer, collagen. The leathers after tanning will result in conversion of biodegradable collagen into leathers that resist biodegradation after tanning, post tanning and finishing by this biodegradable tanning agent. These products after usage will not have disposal problems that can be biodegradable under certain environmental conditions.[26] A natural tanning agent/system that can result in good hydrothermal stability, strength characteristics, organoleptic properties is the current challenge and future trend of the leather tanning industry. In the present work, alginic acid has been oxidized to DAA using sodium periodate and the effect of DAA as a tanning agent has been explored.

EXPERIMENTAL

Reagents and Chemicals

Alginic acid and other chemicals purchased from S.D fine chemicals, India were used. Basic chromium sulfate (BCS) and other auxiliaries used for post tanning are of commercial grade. The raw material used for all trials were pickled goatskins (@ pH 2.5 - 2.8) processed from wet salted goatskins selected in the weight range of 1kg per skin.

Periodate Oxidation of Alginic Acid

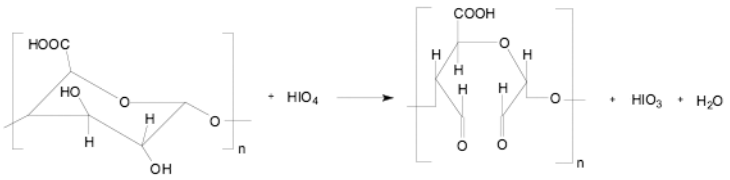
DAA was prepared using a modified oxidation process using different amount of sodium metaperiodate to obtain different degrees of oxidation.[27,28] Oxidized alginic acid at 33, 66 and 99% were prepared. The degree of oxidation was followed by determining the concentration of periodate left unconsumed by iodometry after 24 hrs. The reaction mixture was neutralized with sodium bicarbonate solution and the liberated Iodine (after the addition of KI solution and leaving it in dark) was titrated with standardized sodium thiosulphate solution using starch as an indicator. Oxidized alginic acid was precipitated by centrifugation. The product was then dried at ~60°C.

Solubility of DAA

Solubility of DAA at different oxidation levels was determined by gently dissolving DAA in 100 ml of demineralized water at 25°C by stirring continuously for one hour. The % solubility was determined based on the mass of DAA left undissolved.

TABLE II
Tanning Process for Control Leathers

Process	Chemicals	%	Duration (min.)	Remarks
Tanning	Pickle Liquor	50		(% chemical addition is based on pelt weight)
	BCS	8	120	
	Water	100		
	Sodium formate	1	30	
	Sodium bicarbonate (1:10 dilution with water)	1.25	3x15 + 60	pH increased to 4.0; Drain
Washing	Water	100	10	Drain, Piled and aged for 2days; sammed, shaved to thickness 1.0-1.1 mm



Scheme 2: Oxidation of alginic acid to dialdehyde Alginic acid

TABLE III
Tanning Process for Control Leathers

Process	Chemicals	%	Duration (min.)	Remarks
Wetting	Water	150	60	(% chemical addition for
	Wetting Agent	0.1		subsequent operation is
				based on shaved weight)
Neutralisation	Water	150		
	Sodium bicarbonate	0.5%	30	pH adjusted to 5
	Basyntan P	1%	30	Drain
Washing	Water	200	15	Drain
Retanning, dyeing	Water	150		
and fatliquoring	Relugan RE	2	30	
	Basyntan DI	4		
	Basyntan FB6	4	30	
	Relugan S	4	30	
	Lipoderm Liquor SO (Cationic fatliquor)	4	60	
	Acid dye	2	30	Check penetration
	Lipoderm Liquor SLW (synthetic fatliquor)	6	60	
	Basic dye	1	45	Check exhaustion
	Lipoderm Liquor SO (Cationic Fatliquor)	2		
	Basyntan FB6	2	60	Check exhaustion
Fixing	Formic acid	1		
	Water	10	3x10+30	Drain
Washing	Water	100	10	Drain, piled O/N, set, dry, stake, trim & buff

Experimental Tanning Trials using DAA - Effect of Various Conditions for Tanning

The experimental trials were carried out using pickled goat skins at varying tanning conditions. Three pieces of size 15X15 cm^2 of pickled goat skins (butt region) were taken for each experimental trial.

Effect of pH, Concentration and Time at varied oxidation levels of DAA:

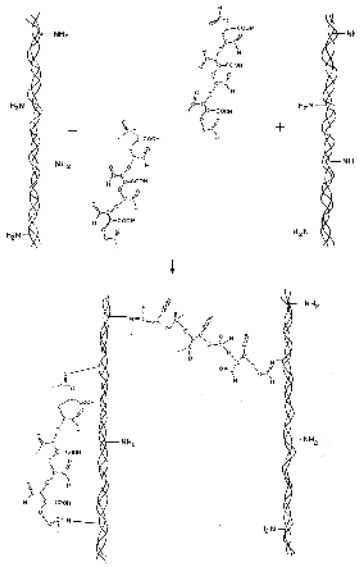
Tanning trials at different pH, amount of DAA and time were carried out at different oxidation level of DAA viz., 33, 66 and 99% and the process details are given Table I.

Effect of fatliquor in tanning:

Tanning trial as mentioned in Table I with 10% offer of DAA (@ different oxidation levels) at pH 8 for 24 hrs has been carried out with 4% offer of neat's-foot oil based fatliquor, after tanning, in a fresh float using 100% water. The fatliquoring treatment was carried out for 1 hr and the fatliquor was fixed using 1% formic acid (1:10 diluted with water) given in 3 feeds at 10 minutes interval.

Comparison of DAA Tanned Leathers with Control Leathers

Matched pair comparison of experimental and control processing were carried out using four pickled goat skins. Right halves of four



Scheme 3: Cross-linking of collagen with dialdehyde alginic acid

pickled goat skins were used for experimental process. The experimental process was carried out adjusting the pickled goat skins to pH 8 and tanned using 99% oxidized DAA at 10% offer for 24 hrs following the process mentioned in Table I. Subsequent to the tanning, fatliquoring treatment using 4% neat's-foot oil based fatliquor was carried out as mentioned in the previous section. Left halves of the four pickled goat skins were taken for control chrome tanning process as mentioned in Table II. All the experimental and control tanned leathers were post tanned using the process mentioned in Table III.

Estimation of DAA Fixed to Collagen

The solution after tanning with DAA from matched pair experimental processing was collected and the uptake of DAA was determined using the method described by Wise and Mehltretter.[29] The amount of aldehyde fixed to collagen after tanning, calculated on protein weight was determined.[30] The leathers after ageing for 24 hours were taken for the determination of moisture and ash.[31] The total nitrogen content was measured by semi micro method.[32]

Shrinkage Temperature Measurements

The shrinkage temperature of tanned leathers, which is a measure of hydrothermal stability of leather, was measured and determined using a Theis shrinkage meter.[33] The values reported are average of three measurements for each experiment.

Physical Testing Analysis

The leather samples made from matched pair control and experimental processes were taken for physical testing measurements and the samples were cut from the official sampling position (IUP 2[34] method). The leather samples were conditioned at 80±4ºC and 65±4% R.H. for 48 hours. The tensile strength, elongation at break, tear strength and grain crack strength were measured as per IUP 6,[35] IUP 8,[36] and IUP 9[37] methods. Four samples have been used for each measurement.

Measurement of Softness

The leathers made from matched pair control and experimental processes were taken for softness measurements and the samples (three) were cut from the official sampling position (IUP 2[34]). The leather samples were conditioned at 20±2ºC and 65±4% R.H. for 48 hours. The softness of the leathers was measured using ST 300D leather softness tester as per IUP 36[38] method. The softness tester measures the deflection of leather by a fixed diameter plunger (20 mm) when a force (500 g) is applied to it.

Scanning Electron Microscopic (SEM) Measurements

Samples from 99% oxidized DAA tanned experimental crust leathers were cut into specimens from official sampling position.[32] A Quanta 200 series scanning electron microscope was used for the analysis. The micrographs for the cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 20 KV.

Organoleptic Properties of Tanned Leathers

The post tanned crust leathers of matched pair control and DAA tanned leathers were assessed for fullness, grain smoothness, softness and general appearance by standard tactile evaluation technique. The functional properties of the leathers in a scale of 0 -10 points was rated by four experienced tanners and the averaged values were reported. Higher values indicate better property.

Results and Discussion

Preparation of DAA - A Novel Tanning Agent

There are two hydroxyl groups attached to carbons at 2,3 position and one carboxyl in 6 position in each dehydrated glucosidal unit in alginic acid. Periodate oxidation specifically cleaves the vicinal glycols i.e. C_2-C_3 bond between the two adjacent hydroxyl groups and the 1,2--diol group in polysaccharides to form their dialdehyde derivatives. Each α-glycol group consumes one molecule of periodate, and under

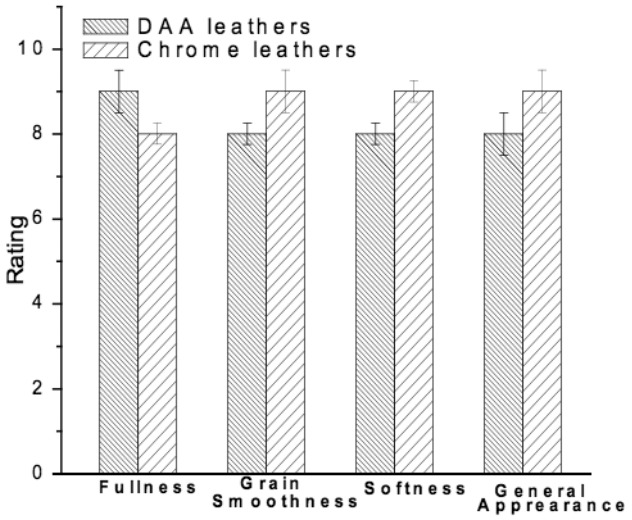


Figure 2: Graphical representation of organoleptic properties of control (chrome) and DAA tanned leathers

TABLE IV
Periodate Oxidation of Alginic Acid and its Solubility Properties

Periodate equivalent (%)	Degree of oxidation (%)	Solubility (%)
40	32±0.4	10±0.18
70	65±0.4	18±0.15
100	99±0.2	26±0.12

Note - Values reported are mean ± standard deviation

given conditions, the rate of the reaction is dependent principally on the stereochemistry of the α-glycol group. (Scheme 2) Usually, the reaction is carried out in aqueous medium. Alginic acid form highly viscous solutions even at low concentrations and are difficult to handle. Therefore, the reaction was carried out in heterogeneous medium (0.5:1.0, ethanol: water) as a dispersion. By doing the reaction in this medium, solvent quantity needed was small even for preparing large quantity of the oxidized product. The oxidation proceeded smoothly giving rise to DAA of different degrees of oxidation depending on the quantity of periodate employed (Table IV).

DAA at different levels of oxidation were found to be soluble in water. The solubility of DAA was found to increase with increase in degree of oxidation. The DAA, having a degree of oxidation of 66%, showed only 18% solubility. The highest solubility of 25% was obtained with 99% oxidized DAA. Solubility was limited to 10% for DAA having a degree of oxidation of 33%. The greatest advantage of using DAA for tanning is its solubility characteristics due to the presence of carboxyl groups and aldehyde functionality that brings about stabilization of collagen. Solubility results from de-polymerization of the alginic acid during oxidation. De-polymerization of alginates is a free radical mediated reaction during oxidation due to the presence of alcohols, which is used as a co-solvent for the periodate oxidation.[27] Degradation or de-polymerization of DAA could be due to the generation of reactive 1-hydroxyethyl radicals during oxidation (as opposed to the more stable and less reactive 2- hydroxypropyl radicals) along with hydroxyl radicals cleaving the glycosidic bonds. This may be due to the presence of excess alcohol in the reaction medium predominantly influencing the de-polymerization of the alginate. At very high periodate equivalent, the effect is believed to be synergic, both alcohol and the periodate influencing the cleavage of the glycosidic bonds in alginic acid chains.

Tanning trials with DAA

Shrinkage temperature at varying tanning conditions

The shrinkage temperatures measured for the DAA tanned leathers at different oxidation levels and tanning conditions are given in Table V. The results obtained with respect to the effect of pH on the shrinkage temperature indicate shrinkage temperature increases with increase in pH. It is also seen that shrinkage temperature of DAA tanned leathers increases with increase in degree of oxidation. Maximum shrinkage temperature of 82°C is observed at pH 10 at DAA oxidation of level of 99%. There is an increase in uncharged amino groups (NH_2) of the side chain functional groups of amino acids like lysine and arginine with increased pH, which favors improved fixation, as the aldehydic groups can covalently crosslink with amino functional groups of the protein.

The shrinkage temperature at different concentrations of DAA treatment is given in Table V. As seen from Table V, the shrinkage temperature does not vary substantially after an offer of 10% DAA. Above 10% offer of DAA at pH 8, there is no significant increase in the shrinkage temperature of the tanned leathers. Hence, 10% offer appears to be sufficient for the stabilization of collagen matrix. From the table it is seen that the shrinkage temperature of leathers increases gradually with the duration of DAA treatment. It requires minimum of 8 hours to bring about significant stabilization of collagen matrix resulting in shrinkage temperature of 74°C. At 24 hours of treatment time, the shrinkage temperature is around 80°C and on further increase in time duration; the shrinkage temperature of DAA tanned leathers did not increase much. Increase in time to 48 and 72 hours resulted in shrinkage temperature of 82°C. Tanning trials at higher temperatures were attempted; however there were no major changes in shrinkage temperature and leather properties observed. The energy requirement for a long tanning period at higher temperatures is high and hence tanning at room temperature (~30°C) was considered to be optimum.

Characteristics of DAA Tanned Leathers

Solubility of the chemicals is essential for transporting the chemicals i.e. the tanning agent into the skin matrix. The results obtained with respect to the effect of 99% oxidized DAA on the shrinkage temperature and also fixation of DAA to the collagen matrix is shown in Table VI. Maximum DAA fixation of 7.12% and shrinkage temperature of 80°C has been observed at a pH of 8 for 99% oxidized DAA tanned leathers. The amount of DAA fixed to the collagen matrix is measured

TABLE V
Shrinkage Temperature of Leathers at Different Oxidation Levels of DAA, pH, Concentration and Time

Process	Parameters	Shrinkage Temperature (°C) 33%	66%	99%
Tanning at varying	6	62±0.5	62±0.5	72±0.5
pH conditions @ 10%	7	66±1	68±1	76±1
DAA for 24 hrs	8	68±1	71±1	80±1
	9	69±1	72±1	81±1
	10	69±1	72±1	82±1
Tanning at	5	62±1	66±1	70±1
varying concentration	10	68±1	71±1	80±1
@ pH 8 for 24 hrs	15	69±1	72±1	81±1
	20	69.5±1.5	73±1.5	82.5±1.5
Tanning at	4	60±1	66±1	69±1
varying time	8	60±1	69±1	74±1
@ 10% DAA, pH 8	16	61.5±0.5	70±0.5	79.5±0.5
	24	62±1	71±1	80±1
	48	63±1	72±1	81±1
	72	63±1	73±1	82±1

Shrinkage temperature reported are mean of three samples ± standard deviation

TABLE VI
Shrinkage Temperature and % Aldehyde Fixed of Matched Pair DAA Tanned Leathers

Type of leather	Degree of oxidation (%)	Shrinkage temperature (°C)	% DAA (aldehyde) fixed	% Uptake of DAA* in process liquor
Chrome tanned leather	-	122±1	-	-
DAA tanned leathers (99% oxidized)	99	80±1	7.12±0.43	94.3±0.41

Values reported are mean ± standard deviation

through the amount of DAA left in the process solution, which is given in Table VI. From the table it is seen that 94.3% of DAA (99% oxidized) is taken up by the collagen matrix of the skin. Based on the dry weight of protein, it is estimated that around 7.12% of DAA is fixed to collagen matrix. The slight difference in the uptake of DAA and the amount fixed to collagen could be due to the differences in some of the loosely bound dialdehyde, which could have been removed by washing after treatment with DAA.

It is essential to study the characteristics of leathers tanned with DAA at different oxidation levels to optimize the tanning conditions. In each experiment, effect of four variables such as degree of oxidation, pH of tanning, concentration and time of tanning and fatliquoring of tanned leathers have been studied. At 33% oxidation levels, the quality of DAA tanned leathers were graded as untanned. The leather on drying was hard and stiff. It almost looked like parchment leather on drying. The same was also observed for 66% oxidation levels. The leathers were thin and flat and were of poor quality. At 99% oxidation level, the leathers were fairly tanned (at pH 8, 9 and 10) and looked off white in color. The leather like drying of these leathers (tanned at pH 8, 9 and 10, 99% oxidized) was however not as expected. The leathers dried out little harder, but better than 33% and 66% oxidized DAA tanned leathers. Hence, one set of all the experimental leathers (33, 66 and 99% oxidized DAA @ pH 8) were fatliquored with 4% neat's-foot oil based fatliquor in the drum for 1 hour after tanning. The leather like properties using 33% and 66% oxidized DAA after fatliquoring were improved compared to unfatliquored leathers, but were far below than the properties of 99% oxidized DAA tanned and fatliquored leathers. The fatliquored DAA tanned leathers (at pH 8, 99% oxidized, 10% offer for 24 hours) exhibited better leather like characteristics and on drying resembled slightly light brown color. Also these leathers resulted in better organoleptic properties compared to other oxidized DAA tanned leathers. Hence the leathers tanned using these conditions (at pH 8, 99% oxidized, 10% offer for 24

TABLE VII
Strength Properties of Control and Matched Pair DAA Tanned Leathers

Sample	Tensile Strength (Kg/cm²)	Extension at break %	Tear Strength (Kg/cm)	Grain Crack Resistance	
				Load (Kg)	Distension (mm)
Chrome tanned leather	258±12	65±3	41±4	33±2	12.6±0.4
DAA tanned leathers (99% oxidized)	265±13	66±5	39±3	34±3	13.2±0.5

Values reported are mean ± standard deviation

hours, fatliquored) have been considered for processing matched pair comparison with control chrome tanned leathers.

Evaluation of Strength Characteristics

It is essential to study the influence of the tanning system on the strength properties of leathers. Tensile, tear and grain crack tests were carried out for the control and matched pair DAA tanned crust leathers and the data are given in Table VII. It is observed that the tensile strength characteristics of DAA tanned crust leathers is found to be marginally higher comparable to that of the control leathers, whereas the tear strength and grain crack resistance of both control and experimental leathers are found to be comparable.

Evaluation of Softness of DAA Tanned Leathers

It is important to evaluate the extent of softness on the final leathers. Objective assessment of softness for both chrome tanned and DAA tanned crust leathers has been measured. The softness of the crust leathers measured in 20 mm diameter ring is 5.9±0.2 mm and 5.3±0.1 mm for chrome tanned and DAA tanned crust leathers respectively. Higher values signify more softness of the leather. It is evident that the DAA tanned crust leathers exhibit comparable softness with that of chrome tanned crust leathers.

Plausible Mechanism for Crosslinking of Collagen with DAA

Bowes and Cater[39] have shown that the amino groups present in the collagen are involved in the crosslinks with formaldehyde and other dialdehydes. The most probable reaction of unifunctional aldehydes is the formation of Schiff's base type compounds with the amino functional groups in the collagen and they may not be able to form a crosslink with the amino functional group in the neighboring polypeptide chain of the collagen. For effective crosslink formation, the molecule used for cross-linking should posses difunctionality to exhibit reactivity between two polypeptide chains. Hence, dialdehydes can act as good crosslinking agents for collagen. An earlier study on the treatment of collagen with glyoxal had resulted in a decrease in lysine and hydroxylysine recoverable on hydrolysis, suggesting that the bond formed is relatively stable.[40] Cross-linking in DAA is predominantly due to Schiff's base formation between the ε-amino groups of lysine or hydroxylysine side groups of collagen and the available aldehyde. The amino groups are generally protonated at lower pH and hence aldehyde interaction with proteins is preferable at pH above iso electric point (IEP) of the protein. The IEP of acid pretreated (alkali followed by acid) collagen is 4.7 and above this pH, collagen will remain negatively charged and amino sites are available for the interaction of aldehydes. Earlier studies indicate pH 8 is conducive for the interaction of aldehydes with collagen.[41] The high fixation of DAA (94.3%) with collagen, as observed from Table VI can be attributed to strong binding between the two, as DAA can have both covalent and non-covalent interaction with collagen. The aldehydic functionality in the DAA can covalently bind with amino groups of the collagen and the carboxyl groups of the DAA can also involve in electrostatic interaction with side chain functional groups available in collagen matrix. Crosslinking is predominantly due to the Schiff's base formation between the ε-amino group of lysine and hydroxylysine side chain groups of collagen and the aldehyde functional groups of DAA. The possibility of inter and intra chain crosslinking between collagen and DAA transpire within the collagen matrix as shown in Scheme 3.

Scanning Electron Microscopic (SEM) Analysis of DAA Tanned Leathers

The Scanning electron micrographs of the cross section of matched pair experimental and control crust leathers are shown in Figures 1a and b. It is essential to study the fibre structure orientation of the leathers tanned with DAA. The cross sectional view of the DAA tanned leather at a magnification of 600X appears to be coated. The coating around the fibres could be due to the presence of DAA. The cross section of both control and experimental appears to be comparable.

Organoleptic Properties of Crust Leathers from DAA Tanned Leathers

The crust leathers made in this study were assessed for organoleptic properties. Experimental (tanning with 10% DAA at 99% oxidation levels, pH 8, 24 hours, followed by fatliquoring) and control (chrome tanning) leathers have been processed using matched pair skins and the leathers were subsequently post tanned using the process given in Table III. The organoleptic properties of experimental and control leathers are shown in Figure 2. The softness and the grain smoothness of DAA tanned crust leathers appear to be in comparison with chrome tanned crust leathers. The experimental leathers showed firm grain with fullness compared to chrome tanned control leathers. The color of the DAA tanned leather is light brown.

CONCLUSIONS

The present study explores the possibility of making leathers using a novel modified product obtained from a natural renewable source, alginic acid. The work clearly indicates that the biopolymer alginic acid in oxidized form as DAA can be used in tanning for the stabilization of collagen matrix. Approaches have been made to identify suitable processing conditions for tanning in order to provide stability to the collagen matrix. Tanning of skins with DAA has resulted in leathers with shrinkage temperature around 80°C. The increase in thermal stability is found to be dependent on the degree of oxidation of alginic acid. The formation of the crosslinked network between DAA and collagen renders the collagenous matrix, thermally stable up to 82°C. Hence, DAA can be used as an effective tanning agent.

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