Alternative Tanning Agent for Leather Industry from a Sustainable Source: Dialdehyde Starch by Periodate Oxidation

by

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Abstract

Dialdehyde starches with different aldehyde content from native corn starch were prepared by sodium periodate oxidation to be used as a tanning agent in leather making. For this purpose, native corn starch was oxidized with sodium metaperiodate in different molar ratios. After oxidation processes, the yields, solubility in water and aldehyde contents of the obtained dialdehyde starches were determined as well as structure characterizations by Proton Nuclear Magnetic Resonance Spectroscopy, Fourier Transform Infrared Spectroscopy and Gel Permeation Chromatography. Evaluating the gel permeation chromatography data, the dialdehyde starch samples which were thought to be in appropriate molecular weight/size to penetrate into skin fibers were selected to be used in the tanning process. Their tanning abilities were evaluated by investigating hydrothermal stabilities, filling and fiber isolation characteristics and physical properties determined by mechanical tests and organoleptically. From the evaluation of the results, it was revealed that sodium metaperiodate oxidized starches which have appropriate molecular weight and adequate aldehyde content has a remarkable tanning effect and can be utilized as a tanning agent with the advantages of not necessitating pickling process which means saving time and simplifying the production but more importantly offering an important advantage from an environmental point of view.

Introduction

Starch is an important raw material for producing sustainable green chemicals due to its features that it is an abundant, biodegradable, naturally renewable and inexpensive natural biopolymer. Considering the potential properties of starch, we had started to study how to modify it in order to generate an alternative tanning agent having no or less risk on health & environment. However, native starch cannot be used directly in leather industry due to its drawbacks. It has high molecular weight which does not allow it to penetrate within fiber structure. It is insoluble in water (a tanning material must be soluble or well dispersible in water to be transferred into fiber structure via water) and has no reactive groups that can establish stable bonds with the functional groups of collagen in order to achieve collagen stabilization and tanning effect. For these reasons, native starch must be properly modified and gain the desired properties before use in leather processing as a tanning material.

Hence, in the light of the above concerns in first part of our study,[1] oxidation of starch with H_2O_2 was successfully performed and although the first aim was controlled (gradual) degradation, selected oxidized starches were used in tanning and up to 61°C shrinkage temperatures were obtained. In the second part of our study, we decided to focus on introduction of reactive groups that can give reaction with the active groups of collagen and constitute quite enough stable bonds. From the literature review, it was seen that it is possible to introduce aldehyde groups by periodate ($NaIO_4$) oxidation.[2-5] Periodate is highly selective oxidant to cleave the C-2 and C-3 linkage of anhydroglucose units of native starch and include dialdehyde groups to starch structure. Dialdehyde starches bearing reactive aldehyde groups are used as crosslinking agents in many industrial applications such as paper, textile, pharmaceutical, gelatin and leather.[2,6]

Within the scope of this study, firstly native corn starch was oxidized with periodate to introduce dialdehyde groups into its structure and to reduce its molecular weight. Then, the obtained products (dialdehyde starches (DAS)) were characterized in detail. Furthermore, the selected dialdehyde starch samples' tanning performances were examined. Even though there are several studies in literature regarding utilization of modified starch in leather making as a tanning agent,[7-13] recently published studies show that natural biopolymers have become popular again.[14-18] However, compared to the former studies in which native starch was directly oxidized with periodate and used as a tanning agent,[7,10,19] the present study was thought to make an important contribution to the literature in terms of both applied tanning process parameters and the subject being investigated in detail.

Materials and Methods

Corn starch was selected to be used as raw material and purchased from Hasal Starch Company Izmir/Turkey. Sodium metaperiodate ($NaIO_4$, extra pure (Merck)), the solvents and the chemicals (Sigma

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Aldrich) used in oxidation processes and analysis were analytical grade. For tanning trials, pickled goat skins (pelts) were selected to be used.

Sodium metaperiodate oxidation of native corn starch: Before oxidation processes, the native corn starches were kept in an oven at 50°C for 48 hours in order to remove its moisture content and prevent weighing mistakes. The periodate oxidation was performed as described by Zhang et al.[4] with this minor change, 20g native corn starch was suspended in 120 mL pure water (rather than 80 ml) to avoid paste formation in the following stages. Then, different amounts of $NaIO_4$ were added into the suspensions. The starch:periodate molar ratios 1:0.3, 1:0.5, 1:0.7, 1:0.9, 1:1.1, 1:1.3 and the amounts of starch to be used, were calculated taking in account the anhydroglucose units of starch molecule. The pH was adjusted to 3.0 with 2% HCl solution. Then, the mixture was effectively shaken in a water bath at 35°C for 4 h in dark ambient conditions. After oxidation processes, the reaction mixtures were filtered. The filtered samples were washed firstly 10 times with distilled water (10x100 mL), then once with 50 mL acetone. The obtained products (oxidized/dialdehyde starches) were transferred into glass dishes and taken into a hot-air oven to be dried at 50°C for 48 h and weighed. Then, the dried products were ground to obtain the products in powder form. For determination of the yields of oxidized starches, the method described by Kilicarislan Ozkan et al.[1] was used. The experiments were carried out in three repetitions and the yields were calculated according to the formula 1 given below.

$$\text{Yield \%} = \frac{\text{Obtained oxidized starch (g)}}{\text{Amount of native starch used (g)}} \times 100 \quad (1)$$

Determination of aldehyde group contents of oxidized starches**:** Rapid quantitative alkali consumption method described by Hofreiter et al.[20] and Zhang et al.[4] was used for determination of the aldehyde group contents of periodate oxidized starches. The experiments were done in three repetitions and the percentage of dialdehyde units (Da) was calculated by following formula 2:

$$\text{Da \%} = \frac{C_1.V_1 - 2.C_2.V_2}{\frac{W}{161} \times 1000} \times 100\% \quad (2)$$

C_1 and C_2: Normality (mol/L) of NaOH and H_2SO_4, respectively.

V_1 and V_2: Total volume (mL) of NaOH and H_2SO_4, respectively.

W: Dry weight of DAS sample.

161: Average molecular weight of the repeat unit in DAS.

Determination of water solubility of dialdehyde starches: As described in our previous study,[1] in determination of water solubilities of native and dialdehyde starches the method given by Singh and Singh[21] was used with minor modifications. Native and dialdehyde starches' solubilities were calculated according to the formula 3 given below. The experiments were repeated three times and the results were given as mean values.

$$\text{Water solubility \%} = \frac{\text{Supernatant solid weight (g)} \times 2}{\text{Sample weight (g)}} \times 100 \quad (3)$$

Fourier transform infrared (FT-IR) spectroscopy: Perkin Elmer Spectrum 100 FT-IR spectrometer was used to record FT-IR spectra of native and dialdehyde starches in the range of 4000-650 cm^{-1}. The starch samples were kept in an oven at 50°C for 24 h to remove absorbed moisture before analysis.

Gel permeation chromatography (GPC): Native and dialdehyde starches' molecular weight distributions and polydispersity indexes were analyzed by using Malvern Viscotek GPCMax GPC device (Bozok University Science and Technology Application and Research Center, Yozgat/Turkey) according to the method used in our previous study.[1]

Nuclear magnetic resonance (NMR) spectroscopy: The structures of native corn starch and selected dialdehyde starches with molecular weights/sizes thought to be fit for penetrating into the skin fibers were also identified by ^{1}H-NMR spectroscopy. 10 mg of sample (native and dialdehyde starches) was accurately weighed with analytical balance and dissolved in 500 µL DMSO-d6 (Dimethyl sulfoxide). Then, the spectra of the samples were recorded on a liquid MERCURY plus-AS 400 NMR spectrometer at Ege University Science Technology Research and Application Center, Nuclear Magnetic Resonance Satellite Laboratory, İzmir/Turkey.

Tanning trials with dialdehyde starches: In order to obtain homogenous tanning material, the croupon areas of the pelts (pickled goat skins) were used in trials. After removing the bellies, flanks, head and butt edges of the pelts, the croupon areas were divided into 20x20 cm pieces and used in tanning processes. The selected dialdehyde starches were used in tanning of the pelts according to the recipe given in Table I as preliminary tanning trials. From the evaluation of the preliminary tanning trials' results the dialdehyde starch sample having the best tanning effect was used for tanning a whole pelt according to a similar recipe with the changes: introduction of dialdehyde starch in 2 portions and running the drum for 120 minutes after each introduction, raising the pH up to 7.5-7.8 at the end of tanning process, introduction of a replacement syntan (3%) and an amphoteric polymer (4%) before fatliquoring process and application of a fatliquoring process consisting of natural+synthetic fatliquor combination (4%), synthetic fatliquor (3%), sulfone synthetic fatliquor (2%), polymeric fatliquor (2%) and phosphoester based fatliquor (1%).

Determination of tanning effects of dialdehyde starches: The shrinkage temperatures,[22] filling coefficients[1] and the cross section images of fibril bundles of tanned leather (by using Hitachi

Table I

Tanning recipe for the pelt pieces

Process	Amount (%)	Product	Temperature (°C)	Time (min.)	pH
Depickle	150	Water 7 °Be' NaCl	28-30	10	
	1	HCOONa		45	
	x	$NaHCO_3$		120	5.5
Draining					
Tanning	100	Water	30		
	20	Dialdehyde starch		180	
	0.25	$NaHCO_3$		30 (left in bath overnight statically)	
	0.25	$NaHCO_3$		30	
	0.25	$NaHCO_3$		30	
	x	$NaHCO_3$		60	7.0-7.5
Washing & Draining					
Fatliquoring	100	Water	45		
	5	Natural+synthetic fatliquor combination		60	
	3	Sulfone synthetic fatliquor			
	2	Phosphoester based fatliquor			
Fixation	x	HCOOH		60	3.8-4.0
Washing					

TM-1000 table top scanning electron microscope (SEM) at 400 magnifications) were examined for evaluating the tanning effects of selected dialdehyde starches. On the other hand, the tensile strength and percentage of elongation at break[23] and tear load[24] of leathers were also analyzed so as to determine physical performance of the leathers tanned by dialdehyde starches. However, the distension and strength of surface test[25] was also performed for whole leather tanned with dialdehyde starch having the best tanning effect. Shimadzu AG-IS Tensile Tester and Trapezium-2 software was used for all physical tests. Three horizontal and three vertical samples were taken from each leather sample according to related standards. After testing all samples, the results were given as mean values. Before the tests, all leather samples were conditioned[26] at 23±2°C and 50±5% relative humidity for 48 hours. SATRA thickness gauge was used to measure the thickness[27] of the conditioned leathers.

Results and Discussion

The yields of periodate oxidized starches: From the evaluation of the data regarding the yields of $NaIO_4$ oxidized starches which are shown in Figure 1, it was seen that the yields of oxidation processes with different molar ratios were very close to each other (the difference between the lowest and the highest yields is 4.3%) which means intensity of oxidation process did not make a significant effect on product yields. Considering very high yields, it was concluded that including aldehyde groups did not increase the water solubility noticeably.

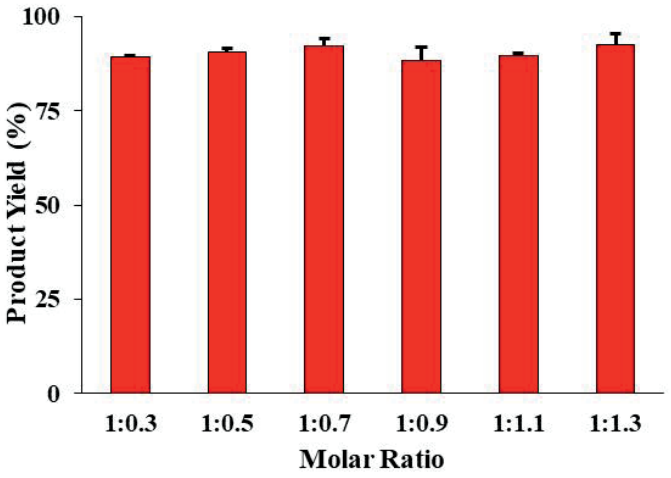

Figure 1. Yields of $NaIO_4$ oxidized starches

However, Zhang et al.[4] reported that the yields decreased in conjunction with increasing molar ratios (from 94.12% to 75.4%) by periodate oxidation of yam starch. The authors remarked that excessive amounts of periodate used in oxidation process may cause further degradation and thus increase starch molecule's solubility in water which results in a diminished yield of dialdehyde starch. However, it was noticed that there is no data on water solubility of obtained dialdehyde starches in mentioned study. On the other hand, it has been reported in many studies that the water solubility of dialdehyde starches obtained by periodate oxidation is low.[2,28-30]

Aldehyde group contents of starch samples oxidized by periodate: Dialdehyde starches (DAS) were obtained from periodate oxidation of native corn starch. Considering the results, it was clear that increasing the starch:periodate molar ratio provoked a significant increment in included aldehyde groups on starch molecule. Thus, it was confirmed that periodate is a selective oxidant and it can open C-2, C-3 bonds of anhydrous glucose units by formation of dialdehyde groups.

As can be clearly seen in Figure 2, the increase in aldehyde content was particularly pronounced from 1:0.3 to 1:0.9 molar ratios, and aldehyde content reached to 93.8% at 1:0.9 molar ratio. On the other hand, the increase in aldehyde content was only 5.3% between 1:0.9 and 1:1.3 molar ratios, while aldehyde content reached to 98.8% at 1:1.3 molar ratio. The similar results were also reported by Yu et al.[31] and Zhang et al..[32]

Water solubility of dialdehyde starches: Figure 3 shows the water solubility values of starches oxidized by periodate. From the obtained results, it was observed that the water solubilities of dialdehyde starches were very low, as expected. Comparing with the water solubility of native corn starch (0.9%), it was determined that water solubility did not increase noticeably by periodate oxidation, contrary to peroxide oxidation (51.7% to 86.9%).[1] The water solubilities of dialdehyde starches were found to be between 1.4% and 2.9%.

From the evaluation of solubility results shown in Figure 3, it was noticed that solubility in water decreased slightly by increasing molar ratio. At this juncture, water solubility may be decreased due to the difficulty of entering water into the molecule depending on the number of aldehyde groups included to structure of native starch by increasing amount of periodate, on account of possible crosslinking between aldehyde groups. A similar approach was expressed by Veelaert et al..[28] The authors remarked that aldehyde groups in C-2 and C-3 tend to form inter- and intra-molecular hemiacetal and acetal cross-links, and the low solubility of dialdehyde starch in water may be due to these bonds. Similarly, Yi et al.[30] reported that native starch and dialdehyde starch do not dissolve in cold water due to their crystal structure and acetal groups, respectively.

Wongsagon et al.[2] examined the water solubility at 60°-90°C of dialdehyde starches obtained by periodate oxidation from tapioca starch. They reported that the highest solubility values (between 30-48%) were achieved at 90°C and the solubility at 60°C were between 1-4%. In another study, Para[29] remarked that the water solubility at 25°C of dialdehyde starch obtained from potato starch by periodate oxidation was 1.8%.

Characterizations

The FT-IR spectra of native starch and dialdehyde starches are shown in Figure 4. As previously mentioned, OH groups in C-2, C-3 of anhydrous glucose units replaces with the aldehyde group by periodate oxidation. From the spectra, it was seen that the most characteristic absorption peak of C=O vibrations of aldehyde groups occurred at 1726.94 cm^{-1}, distinct from native starch spectrum. The intensity of this peak is very weak due to the hemiacetal bonds that occur between oxidized and non-oxidized starch residues during preparation.[33] However, the intensity of this peak has become more

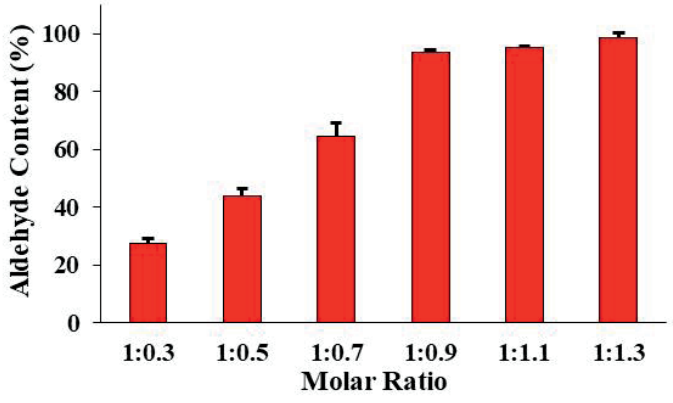

Figure 2. Aldehyde contents of oxidized starches prepared at different molar ratios by $NaIO_4$ oxidation

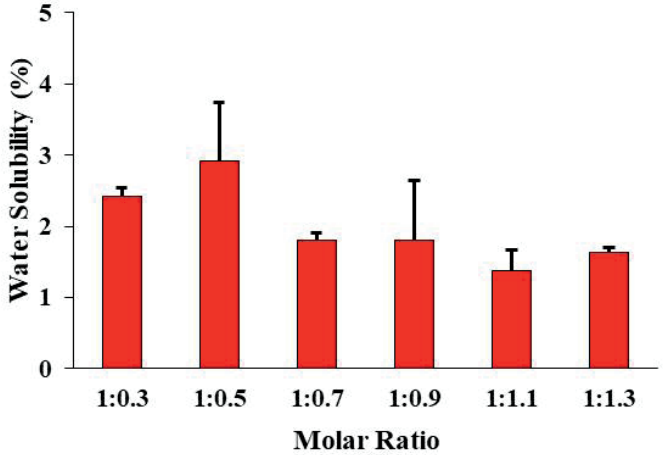

Figure 3. Water solubilities (%) of oxidized starches at room temperature

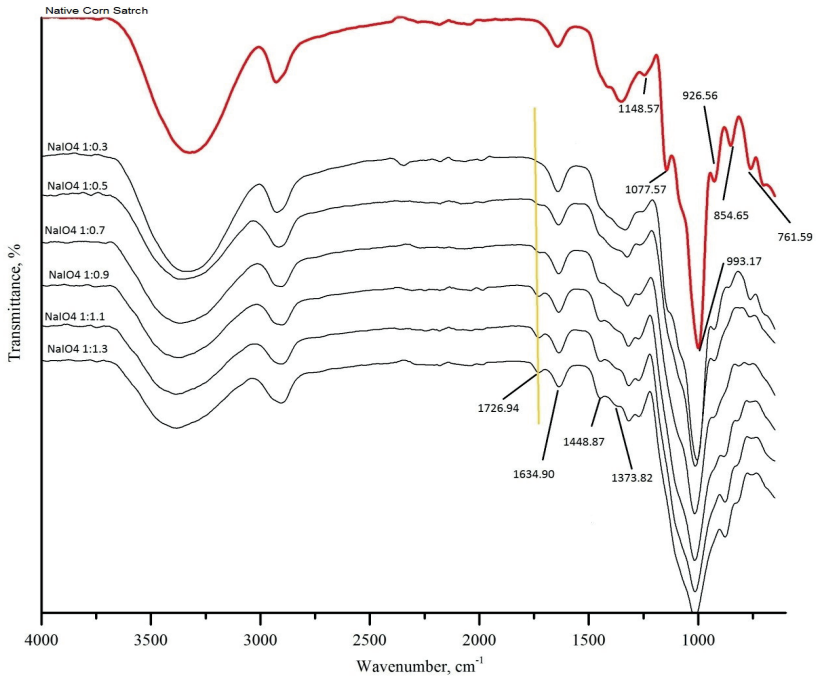

Figure 4. FT-IR spectra of native and dialdehyde starches

apparent by increasing amount of periodate used in oxidation. Because, by increasing intensity of oxidation the amount of non-oxidized starch residues remain less with higher aldehyde content. The peaks at 1148.57, 1077.57, 993.17 and 926.56 cm^{-1} are attributed to C-O bond stretching. The peaks at 1634.90 and 1448.87cm^{-1} are attributed to scissoring vibrations of two O–H bonds of water and CH_2, respectively. The bands at 854.65 and 761.59 cm^{-1} are due to skeletal stretching vibrations of starch. It was observed that the intensity of these peaks decreased in conjunction with increasing oxidation degree. While the characteristic peak for C=O groups (C-C in C-CHO) at 1373.82 cm^{-1} increased with increasing aldehyde group content, the peaks at 1148.57 and 1077,57 cm^{-1} which are attributed to C-O bond stretching of C-OH group weakened in spectra of oxidized samples. Zhang et al.[4] reported that the reason might be that the periodate oxidation mainly results in a cleavage at C-2 and C-3 bonds of anhydroglucose units of starch molecule and occurred aldehyde groups replace with the C–OH groups at C-2 and C-3.

Native corn starch and dialdehyde starches were also characterized by gel permeation chromatography (GPC) and the results were given in Table II. From the measurements, it was observed that Mw, Mn and Mw/Mn values decreased for all starch samples oxidized with periodate compared to native corn starch. This is attributed to cleavage of C-2 and C-3 bonds in glucose units of native starch.

From examining the data, it was noticed that the molecular weight of dialdehyde starches decreased gradually up to 1:0.7 molar ratio, however the molecular weight of dialdehyde starches increased with increasing molar ratios. At this point increasing aldehyde groups in starch molecule are led to formation of intermolecular cross-links, thereby causing an increase in molecular weight of

Table II

Molecular weight distribution of native and oxidized starches

Sample	Oxidation Method/ Molar Ratio	M_w(Da)	M_n(Da)	M_w/M_n
Native corn starch	—	2.23Kx10^3	271K	8.22
Oxidized Starch	$NaIO_4$ Oxidation/1:0.3	6.16K	2.76K	2.23
Oxidized Starch	$NaIO_4$ Oxidation/1:0.5	3.68K	1.92K	1.92
Oxidized Starch	$NaIO_4$ Oxidation/1:0.7	2.35K	1.70K	1.38
Oxidized Starch	$NaIO_4$ Oxidation/1:0.9	18.86K	5.33K	3.55
Oxidized Starch	$NaIO_4$ Oxidation/1:1.1	11.03K	4.20K	2.63
Oxidized Starch	$NaIO_4$ Oxidation/1:1.3	13.09K	6.28K	2.08

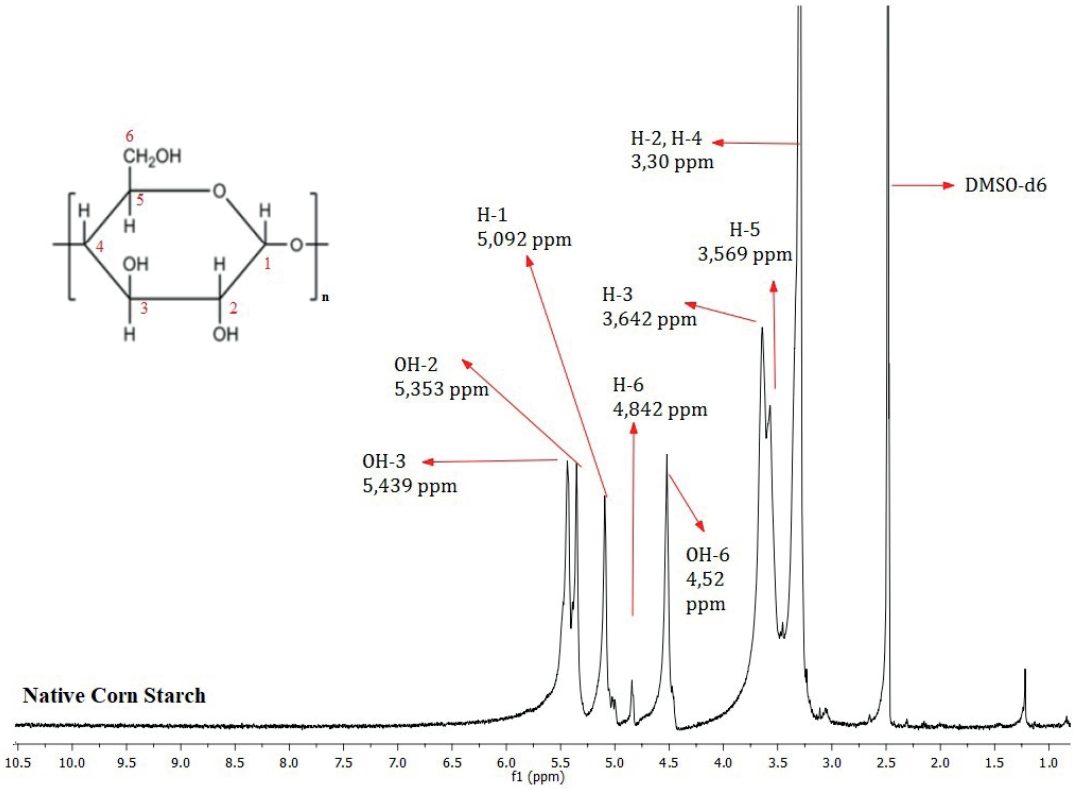

Figure 5. NMR spectrum of native corn starch

dialdehyde starches. Comparing with native and dialdehyde starches regarding polydispersity index (Mw/Mn), it was determined that polydispersity indexes of oxidized starches significantly decreased. Especially, the polydispersity index was quite low at 1:0.7 molar ratio (Mw/Mn=1.38) which means that the oxidized starch has a high homogeneity. Considering the necessity of a tanning material's molecular size should allow it to penetrate into the collagen fiber structure; it was decided that the molecular weights/sizes of dialdehyde starch samples obtained by 1:0.3, 1:0.5 and 1:0.7 molar ratios of $NaIO_4$ oxidation are more appropriate for penetrating into the collagen fiber structure and picked to be used in tanning trials.

The ^{1}H-NMR spectrum of native corn starch was shown in Figure 5. Some characteristic peaks at 4.520-5.439 ppm are attributed to proton signals of hydroxyl groups at C-2, C-3 and C-6. The signal at 5.092 ppm and the small peak at 4.842 ppm are attributed to anomeric H-1 proton at α-1,4 linkage and protons at α-1,6 branching point, respectively. The proton signals of CH and CH_2 groups of starch unit were determined between 3.30 and 3.642 ppm. On the other hand, the signal of H-3, overlapping signal of H-3 and H-5, combined signal of H-2 and H-4 were observed at 3.642, 3.569, 3.30 ppm, respectively.[34,35]

The ^{1}H-NMR spectra of dialdehyde starches (1:0.3, 1:0.5 and 1:0.7) which were selected to be used in tanning trials are shown in Figure 6. Comparing with the spectra of native corn starch, the small peaks occurred between 9.095-9.585 ppm (aldehydic proton) in ^{1}H-NMR spectrum of dialdehyde starches confirmed that periodate oxidation performed successfully. However, since the aldehyde groups are in balance with the hemiacetal formations, the intensity of signals in this range is very weak. Also, additional peaks in dialdehyde starches are attributed to the protons of –OH and –CH groups in hemiacetal structures.[36,37] Furthermore, while the peak related to aldehyde protons was seen at 9.292 ppm in 1:0.3 molar ratio oxidized starch sample, as well as this peak, new peaks were occurred at 9.095 and 9.585 ppm in 1:0.5 and 1:0.7 molar ratio oxidized starches respectively which proves that more aldehyde groups were introduced into the structure by increasing oxidation degrees.

Tanning properties of dialdehyde starch samples

The results of hydrothermal stability and filling coefficient of pelt pieces tanned with dialdehyde starches were given in Table III. Comparing with intact pelt, it was determined that tanning with dialdehyde starches resulted a remarkable increase in shrinkage temperature (25.5° - 29.5°C) as well as filling coefficient (25.7-34.6 %). From the evaluation of filling effect gained to the pelts, it was determined that the thickness of leathers increased in conjunction

Table III

Tanning properties of oxidized starches

Sample	Filling coefficient (%)	Shrinkage temperature (°C)
Intact Pelt	—	43.5(±0.9)
$NaIO_4$ 1:0.3	25.7(±0.3)	69.0(±0.6)
$NaIO_4$ 1:0.5	30.6(±0.5)	70.0(±0.3)
$NaIO_4$ 1:0.7	34.6(±0.6)	73.0(±0.5)
Tanned Whole Pelt	—	74.5(±0.4)

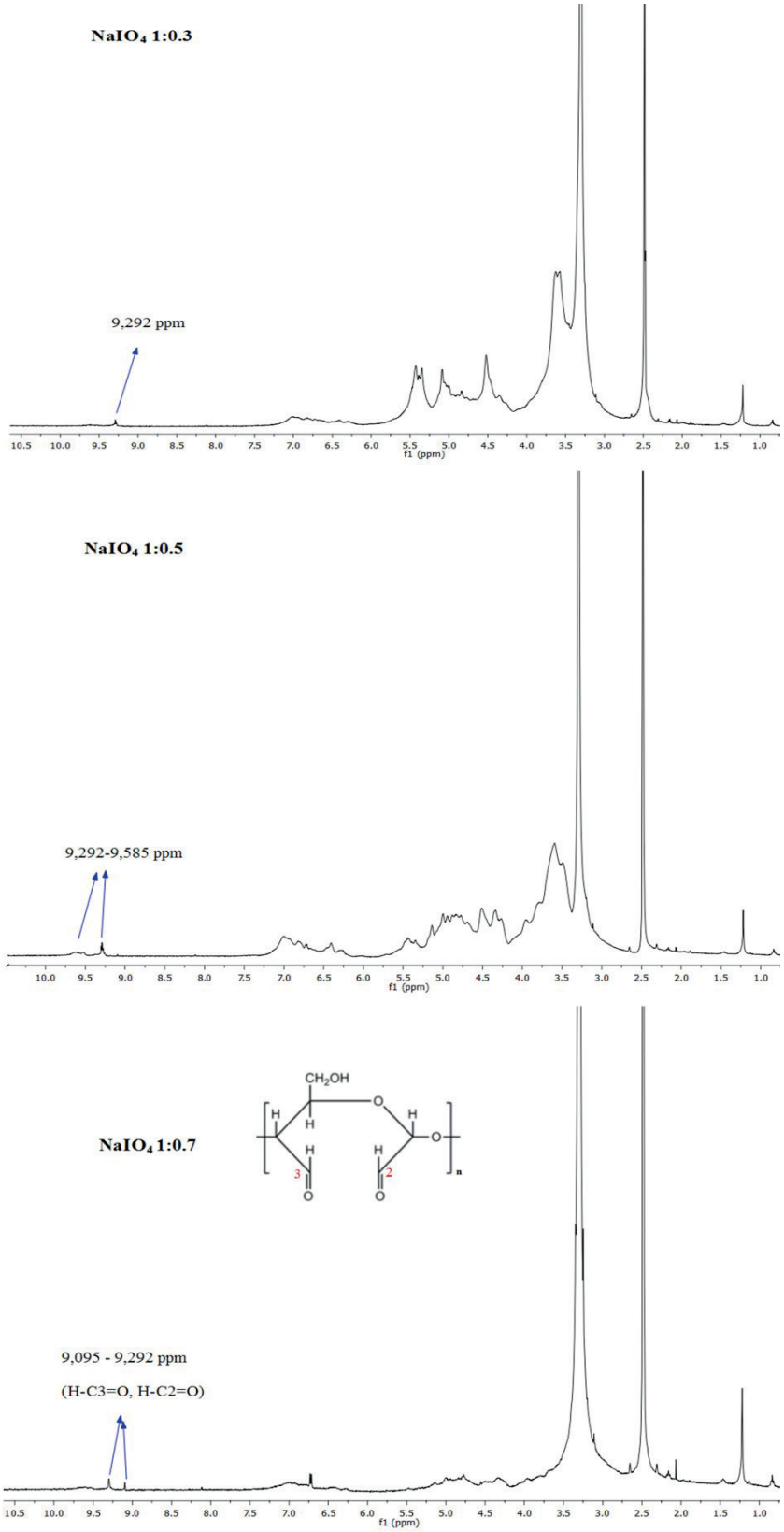

Figure 6. NMR spectrums of dialdehyde starches

with increasing molar ratio. As mentioned earlier, the molecular weight distributions decreased with increasing oxidation degree. So, it is commented that oxidized starches having smaller molecular weight could penetrate into the fiber structure of the pelts quite easily and result in a higher filling effect.

Considering the shrinkage temperatures, it was seen that a significant increase occurred in shrinkage temperature, expectedly due to the introduction of increasing number of aldehyde groups which can bond with reactive sites of collagen (-NH_2), with increasing oxidation degrees (Figure 7). From the tanning trials with pieces of pelts, the

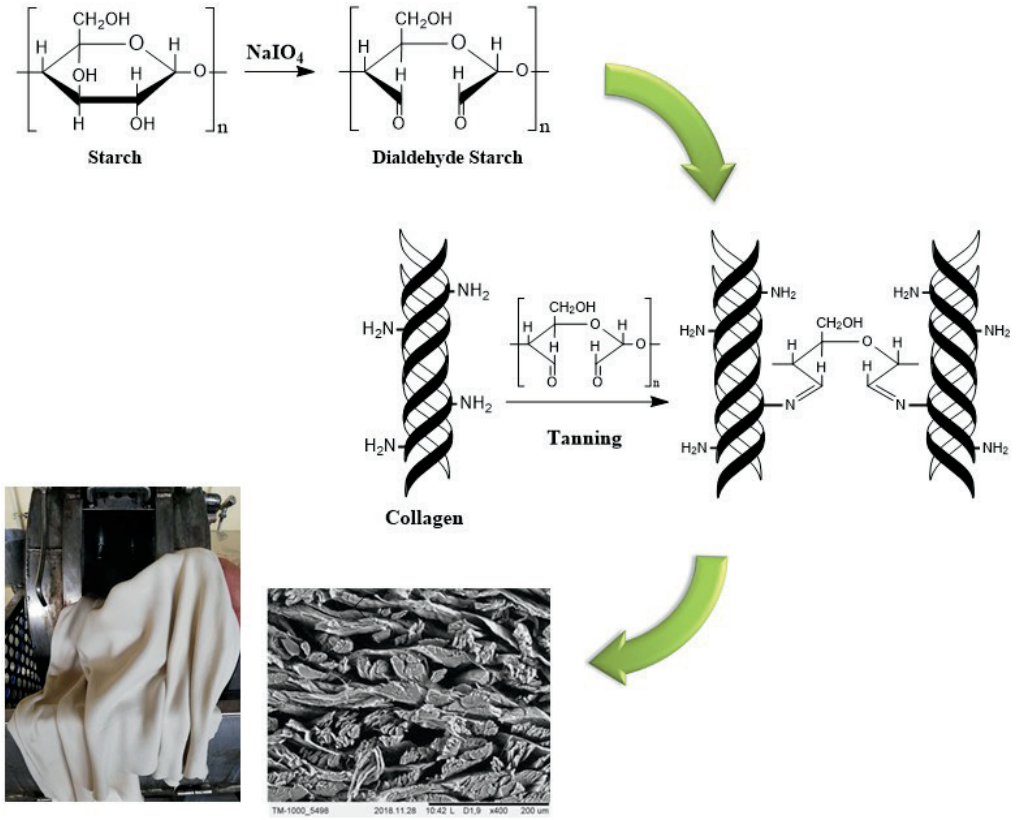

Figure 7. Dialdehyde starch production from native corn starch by $NaIO_4$ oxidation and dialdehyde & collagen reaction mechanism in tanning

highest shrinkage temperature (73°C) and filling coefficient (34.6%) were obtained with 1:0.7 molar ratio oxidized starch sample. However, since it had a quite high astringency and resulted rough handle and loss of area, 1:0.5 molar ratio oxidized starch sample, having more gentle tanning effect, was chosen among dialdehyde starches as having the best tanning effect and decided to be used in tanning of a whole pelt.

From the tanning of the whole pelt with 1:0.5 molar ratio oxidized starch sample, 74.5°C of shrinkage temperature was obtained which means 31°C of increase was achieved comparing with shrinkage temperature of intact pelt. From the comparison of the shrinkage temperature increases with limited studies in literature,[7,10,19] it was seen that they were also achieved approximately same ranges of increases (26°-32°C) in shrinkage temperatures.

At this point another issue which is needed to be discussed in detail is that from the literature review of many research studies[7,10,19] the introduction pH to the tanning process was rather high (pH:10). In spite of expecting a very rapid reaction considering reaction parameters and behavior of aldehyde groups at this pH, accordingly with previous studies in our preliminary tanning trials we also used pH:10 for introduction to tanning process. However, suddenly swelling and correspondingly loss of area occurred over pH:8 as foreseen. For this reason, lower introduction pH (pH:5.5) was decided to be tried. However, at pH:5.5 the oxidized starch samples showed poor solubility which was not surprising recalling their solubility results. So, after starting the tanning process, the pH was decided to be increased. After the first partial additions of alkali, it was observed that the solubility of the dialdehyde starches in tanning bath increased along with increasing pH and thus their penetration into the pelts was also started to increase. The final pH was raised up to 7.0-7.5 (just below the swelling pH of collagen, taking in account of a possible swelling) by gradual addition of alkali and frequently checking. Thus, a safer and complete tanning was achieved without any drawback such as swelling, excessive astringency, coarse or pebbled grain or loss of area etc.

The scanning electron micrographs (SEM) of intact pelt and the leathers tanned with dialdehyde starch samples are shown in Figure 8. From the comparison of the cross-section images of pickled goat skin with tanned leathers it was clear that the fibril bundles of the tanned leathers were isolated indicating that dialdehyde starch samples performed a tanning effect. However, it was also clear that isolation of fibril bundles was increased especially in leathers tanned with higher degree oxidized starch samples (1:0.5, 1:0.7).

As already mentioned, preliminary tanning trials were carried out with pieces. Then, a whole pickled goat skin was tanned with selected modified starch (1:0.5 molar ratio) having the best tanning effect. For this reason, physical test results for both pieces and whole

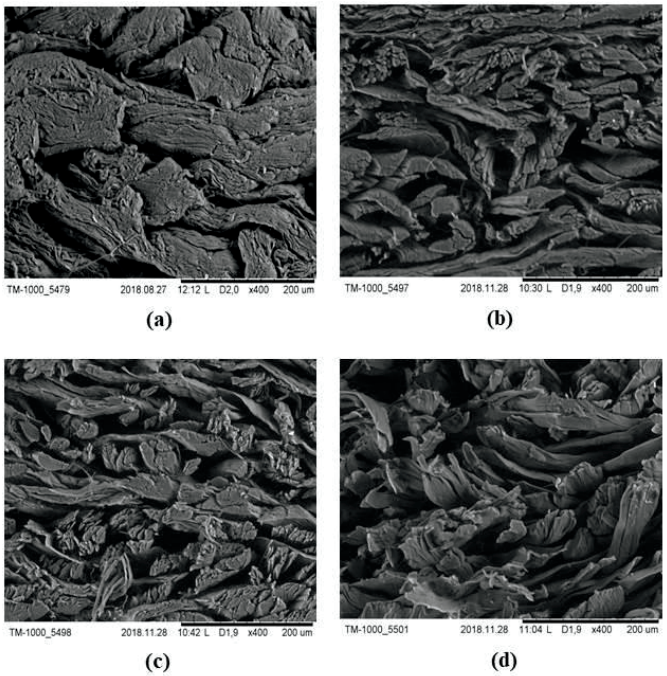

Figure 8. SEM images of **a)** pickled goat skin, **b)** 1:0.3, **c)** 1:0.5, **d)** 1:0.7 oxidized starch tanned leathers

leathers were given in Table IV. Comparing with the tensile strength and tear strength results of the leathers tanned with dialdehyde starch samples with recommended value for goat leathers (20 N/mm^2 for tensile strength and 40 N/mm for tear strength) by UNIDO,[38] excluding the tensile strength value (17.4 N/mm^2) of the leather which was tanned with 1:0.7 periodate oxidized starch, all leather samples meet the recommended values.

Additionally, the whole leather which was tanned with 1:0.5 molar ratio oxidized starch was also tested in terms of distension and strength of surface and the cracking and bursting values were found to be 32±1.2 kgf, 41±1.4 kgf and 16.2±1.6 mm respectively which meets the recommended value (min. 7mm) for shoe upper leathers by UNIDO[38].

On the other hand, after drying, the leather samples were mechanically softened and evaluated organoleptically (Table V) and from the evaluation, it was seen that the dialdehyde starch tanned leathers were bone colored, firm and had a compact structure similar with vegetable tanned leathers.

Conclusion

Native corn starch was oxidized with different molar ratios of $NaIO_4$ to obtain dialdehyde starches bearing different amounts of aldehyde groups to be used as a tanning agent in leather making. Modified starch samples were characterized by FT-IR, NMR, GPC and aldehyde contents revealed that periodate oxidation of native corn starch was carried out successfully. Afterwards, the selected modified starch samples were used in tanning and tanning abilities of oxidized starches were evaluated in terms of shrinkage temperature, filling coefficient, isolation of fibril bundles. Also, physical performances of the leathers tanned by modified starch samples were determined and the leathers were evaluated organoleptically. From the evaluation of all results, it was concluded that $NaIO_4$ oxidation product of corn starch (dialdehyde starch) has a remarkable tanning effect and can be utilized as a tanning agent in leather making. Thus, besides

Table IV

Physical properties of tanned leathers with oxidized starches.

				Tear Strength	
	Oxidized Starch	**Tensile Strength (N/mm^2)**	**Elongation (%)**	**Max. Force (N)**	**Thickness (mm)**
Tanning with pelt pieces	1:0.3	35.9(±6.6)	55.6(±4.5)	106.0(±10.5)	0.6(±0.03)
	1:0.5	26.8(±5.0)	57.6(±8.1)	103.3(±2.8)	0.8(±0.02)
	1:0.7	17.4(±5.2)	55.2(±11.8)	86.0(±12.1)	1.1(±0.10)
Tanning with whole pelt	1:0.5	28.2(±2.9)	72.9(±10.1)	97.4(±1.2)	0.84(±0.02)

Table V

Organoleptical properties of tanned leathers with oxidized starches.

	Oxidized Starch	**Color**	**Handle**	**Grain smoothness**
Tanning with pelt pieces	1:0.3	Bone c.	Firm	Slightly rough
	1:0.5	Bone c.	Firm	Slightly rough
	1:0.7	Bone c.	Very firm	Rough
Tanning with whole pelt	1:0.5	Bone c.	Firm	Slightly rough

detailed investigation and characterization of dialdehyde starch, a safer way of tanning without any drawback such as swelling, excessive astringency, coarse or pebbled grain or loss of area etc., was developed by optimizing tanning process conditions different from the existing studies in literature. Since the new tanning process does not necessitate a pickling process, it brings the advantages of saving time and simplifying the production but more importantly by avoiding use of acids and salts it offers an important advantage from an environmental point of view.

The results obtained from our first and the present studies strongly encourage us regarding utilization of starch as a source for a natural based tanning agent and we think that further studies should be carried on alternative modifications within this scope considering its advantages of being generated from renewable natural sources with biodegradable property which has big importance in terms of sustainability, human & environmental health.

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