

# Production of Carboxymethyl Starches from Oxidized Starches and Determination of Their Tanning Characteristics

by

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## Abstract

Hydrogen peroxide and sodium metaperiodate oxidation of starch and their possible utilization in tanning/retanning were examined in our previous studies. In the present part, accordingly with our previous findings, hydrogen peroxide and sodium metaperiodate oxidation products having appropriate molecular weight/size were selected and additionally carboxymethylated. The yields of the processes (carboxymethyl starches) were characterized comprehensively and the effect of carboxymethylation process on structures and tanning abilities were tried to be identified. The characterization results revealed that the carboxymethyl groups were successfully included into the structure and the water solubility of oxidized starches (especially periodate oxidized ones) increased by carboxymethylation process. From the evaluation of the tanning results and considering its properties i.e. gentle tanning effect with less astringency and correspondingly a relatively soft leather handle and smooth grain, it is concluded that dialdehyde carboxymethyl starch (CMS 1:0.7) can be utilized as yet another good alternative sustainable green tanning/retanning agent from starch.

## Introduction

The bio-based tanning/retanning agents which are able to replace mineral tanning agents have been the focus of interest in leather industry due to environmental regulations and coming into prominence of ecological chemical processes. In line with this purpose, leather chemists and manufacturers head towards production of bio-based tanning/retanning agents from inexpensive, ubiquitous, sustainable, biodegradable biopolymers. When viewed from this aspect, starch is an important raw material for producing sustainable green tanning/retanning agents. For this reason, we focused on different modification techniques of native corn starch for possible utilization in leather making as a tanning agent. In our previous studies,<sup>1,2</sup> native corn starch was oxidized by hydrogen peroxide ( $H_2O_2$ ) and sodium metaperiodate ( $NaIO_4$ ) oxidation methods in different molar ratios with the aim of reducing its molecular weight/size to penetrate between skin fiber matrix and introducing reactive groups to react and establish stable bonds with the active groups of collagen.

The obtained results encouraged us to investigate different modification methods and in this part of our study, we decided to focus on the carboxymethylation process. Carboxymethyl starch (CMS) has unique properties due to including a negatively charged functional group ( $CH_2COO^-$ ), this modification provides decreased gelatinization temperature, increased solubility and improved storage stability, in addition soluble starch in cold water can be produced depending on the degree of substitution (DS).<sup>3</sup> Besides, negatively charged  $CH_2COO^-$  groups can make additional bonds with the active groups of collagen. However, considering the promising results of our earlier studies and necessity of appropriate molecular weight/size, we have decided to apply carboxymethylation process on previously oxidized starch samples. For this purpose, oxidized starch samples, having appropriate molecular weight to penetrate within fiber structure of collagen were chosen (1:7, 1:9, 1:11 molar ratios from  $H_2O_2$  oxidation, 1:0.3, 1:0.5, 1:0.7 molar ratios from  $NaIO_4$  oxidation) to be used in carboxymethylation processes and the effect of carboxymethylation process on chemical structures, features and tanning abilities of oxidized starches were investigated.

## Materials

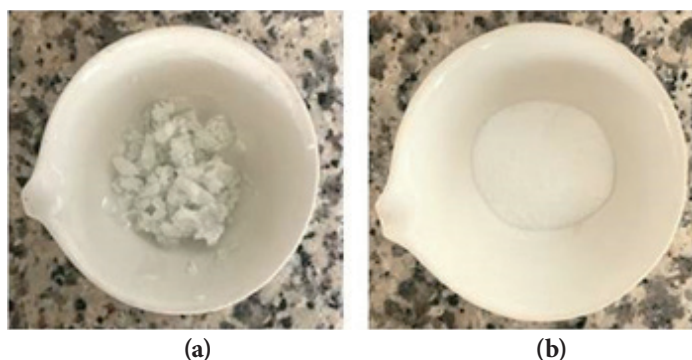
The picked  $H_2O_2$  and  $NaIO_4$  oxidized starch samples pursuant to our earlier studies<sup>1,2</sup> were used in carboxymethylation processes. Monochloroacetic acid ( $C_2H_3ClO_2$ , 99%), sodium hydroxide ( $NaOH$ , 98-100.5%) ethanol ( $C_2H_6O$ ,  $\geq 99.8\%$ ) were supplied from Sigma Aldrich and the remaining chemicals/solvents used in experiments were in analytical grade. In tanning experiments, pickled goat skins were used.

## Methods

**Carboxymethylation of  $H_2O_2$  and  $NaIO_4$  Oxidized Starch Samples:** In our former studies,<sup>1,2</sup> native corn starch was oxidized by  $H_2O_2$  and  $NaIO_4$  oxidation methods and the samples (1:7, 1:9, 1:11 molar ratios from  $H_2O_2$  oxidation, 1:0.3, 1:0.5, 1:0.7 molar ratios from  $NaIO_4$  oxidation) which were thought to be more favorable for tanning were picked and used in tanning trials. In present part of our study, these picked samples were synthesized pursuant to our earlier studies and subjected to a further modification by carboxymethylation process. Carboxymethylation was performed

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**Figure 1.** Carboxymethylated starches; (a) dried in an oven after carboxymethylation, (b) milled after drying.

in a similar way described by Hebeish et al.<sup>4</sup> with slight changes (molar ratios, reaction temperature, shaking and drying conditions). Firstly, 8.1 g oxidized starch sample, 9.45 g monochloroacetic acid, 10 mL of 5 N NaOH solution and 45 mL distilled water were added in a 100 mL flask (which corresponds to 1:2:1 molar ratios of Starch:Monochloroacetic acid:NaOH respectively). The mixture was continuously stirred to obtain a homogenous mixture. After that, the flask was transferred to a water bath at 50°C and the reaction was maintained for 1 h with continuous shaking at low constant speed. The products were precipitated in ethanol and washed for decontaminating from alkali then dried in a hot-air oven at 50°C for 48 h until constant weight (Figure 1). The product yields were determined by using the method described in our previous studies<sup>1,2</sup> and the yields were calculated according to the following formula 1. Finally, dried samples were milled to obtain the products in powder form.

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

**Determination of degrees of substitutions:** The degree of substitutions (DS) of carboxymethylated starches (CMSs) were determined according to the titrimetric method which was described by Jiang et al.<sup>5</sup> The DS was determined by following formula 2.

$$\text{DS} = \frac{n_{\text{NaOH}} \times M_o}{m_c - n_{\text{NaOH}} \times M_R} \times 100\% \quad m_c = m_p - \left[ \frac{m_p \times F}{100} \right] \quad (2)$$

$M_o$  = the molar mass of anhydroglucose unit (162 g/mol)

$M_R$  = the molar mass of carboxymethyl residue (58 g/mol)

$n_{\text{NaOH}}$  = the quantity of sodium hydroxide used (mol)

$m_p$  = the weight of polymer taken (g)

$m_c$  = the corrected weight of polymer (g)

$F$  = the moisture (%)

**Determination of water solubility of CMSs:** The method given by Singh and Singh<sup>6</sup> was used to determine water solubility of carboxymethylated starches with minor modifications<sup>1,2</sup> and it was calculated by following formula 3.

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

**Structure characterizations:** The changes in the structures of native and carboxymethylated starches by modification were tried to be identified by FT-IR and <sup>1</sup>H-NMR analyses. The FT-IR spectra were recorded in the range of 4000-650 cm<sup>-1</sup> by Perkin Elmer Spectrum 100 FT-IR spectrometer. The <sup>1</sup>H-NMR spectra were gained on a MERCURYplus-AS 400 MHz spectrometer (Ege University, NMR Satellite Laboratory, Izmir/Turkey). DMSO-d<sub>6</sub> was used as solvent and the concentration was 20 mg/mL.

**Tanning trials:** Pelt pieces, 20x20 cm in size, from croupon areas of pickled goat skins were used in preliminary tanning trials. Since carboxymethylated derivatives of oxidized starch samples from NaIO<sub>4</sub> oxidation and H<sub>2</sub>O<sub>2</sub> oxidation bear different reactive groups (–COH & covalent bonds; –OH, –CO, and –COOH groups & hydrogen bonds and salt bridges) and therefore require different process parameters in order to achieve proper penetration and establish bonds with relevant functional groups of collagen, different tanning recipes were used for each product (Table I and Table II).

After assessment of the preliminary tanning trials' results; CMS sample having the best tanning effect was determined and a whole pelt was tanned with selected CMS according to similar recipe given in Table II with the changes: introduction of dialdehyde starch in 2 portions and running the drum for 120 min. 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%).

**Table I**  
**Tanning recipe for carboxymethylated H<sub>2</sub>O<sub>2</sub> oxidized starches**  
**(CMS 1:7, CMS 1:9, CMS 1:11)**

PROCESS	AMOUNT (%)	PRODUCT	TEMP. (°C)	TIME (min.)	pH
<b>Depickle</b>	150	Water 7 °Be NaCl	28-30	10	
	1	HCOONa		45	
	X	NaHCO <sub>3</sub>		120	5.0
Washing & Draining					
<b>Tanning</b>	100	Water 3 °Be	30	10	
	20	Starch sample		180 (left in bath overnight statically)	
	x	HCOOH		60	3.5
Washing & Draining					
<b>Neutralization</b>	100	Water	40		
	2	Neutralizing syntan		45	5.0-5.5
Fatliquoring	5	Natural+synthetic fatliquor combination	45	60	
	3	Sulfone synthetic fatliquor			
	2	Phosphoester based fatliquor			
<b>Fixation</b>	X	HCOOH		60	3.8-4.0
Washing					

**Table II**  
**Tanning recipe for carboxymethylated periodate oxidized starches (DCMSs)**  
**(CMS 1.0.3, CMS 1:0.5, CMS 1:0.7)**

PROCESS	AMOUNT (%)	PRODUCT	TEMP. (°C)	TIME (min.)	pH
<b>Depickle</b>	150	Water 7 °Be' NaCl	28-30	10	
	1	HCOONa		45	
	x	NaHCO <sub>3</sub>		120	5.5
Draining					
<b>Tanning</b>	100	Water	30		
	20	Starch sample		180	
	0.25	NaHCO <sub>3</sub>		30 (left in bath overnight statically)	
	0.25	NaHCO <sub>3</sub>		30	
	0.25	NaHCO <sub>3</sub>		30	
	x	NaHCO <sub>3</sub>		60	7.0-7.5
Washing & Draining					
<b>Fatliquoring</b>	100	Water	45		
	5	Natural+synthetic fatliquor		60	
	3	Sulfone synthetic fatliquor			
	2	Phosphoester based fatliquor			
<b>Fixation</b>	x	HCOOH		60	3.8-4.0
Washing					

**Determination of tanning effects:** The tanning abilities of carboxymethylated starch samples were evaluated by investigating hydrothermal stability,<sup>7</sup> filling<sup>1,2</sup> and fiber isolation characteristics (Hitachi TM-1000 table top scanning electron microscope (SEM) at 400 magnifications) of tanned leathers.

Physical characteristics of the leathers gained by carboxymethylated starch tanning were investigated by measuring the tensile strengths and percentages of elongation<sup>8</sup> and tear loads<sup>9</sup> of the samples. However, the whole leather which was tanned with selected CMS (having the best tanning effect) was additionally tested in terms of distension and strength of surface test.<sup>10</sup> Shimadzu AG-IS Tensile Tester and Trapezium-2 software program was used for all physical tests.

After performing the tests mentioned above, additionally leachability test was applied to the leather samples tanned with carboxymethylated derivatives of oxidized starches in preliminary tanning trials. Leather pieces, sized 2x5 cm, were placed in 250 mL flasks and agitated on a shaker for 24 hours at 120 rpm at room temperature with 100 mL of distilled water. Then, hydrothermal stability<sup>7</sup> tests are repeated in order to investigate irreversible binding abilities of the carboxymethylated derivatives of oxidized starches.

## Results and Discussion

### The yields of carboxymethylated starches (CMSs)

The yields of CMSs are shown in Figure 2. From the results, it was seen that the yields of carboxymethylated derivatives of oxidized starches reduced more or less with increasing amounts of oxidants previously used in reactions. Introduction of carboxymethyl groups into the oxidized starch structure and increasing water solubility came along with them was thought to be the reason for the decline in yields. Recalling that carboxyl and dialdehyde groups were introduced by peroxide and periodate oxidation reactions<sup>1,2</sup> respectively before carboxymethylation and considering the fact that while the carboxyl

groups redound to water solubility, dialdehyde groups do not have a significant contribution on it, the yields of carboxymethylated derivatives of oxidized starches with H<sub>2</sub>O<sub>2</sub> (CMS 1:7, CMS 1:9, CMS 1:11) were found to be lower than NaIO<sub>4</sub> oxidized ones (CMS 1:0.3, CMS 1:0.5, CMS 1:0.7) as expectedly.

### Degree of substitutions (DS)

Substitution degrees of CMSs are shown in Figure 3. From the results, it was seen that the number of carboxymethyl groups introduced into the structure of CMS 1:7, CMS 1:9 and CMS 1:11 samples were reduced in conjunction with increasing oxidation degree, contrary to dialdehyde carboxymethyl starches (DCMSs) (CMS 1:0.3, CMS 1:0.5, CMS 1:0.7). It is known that the hydroxyl groups in C-2 and C-3 of anhydrous glucose units are selectively oxidized to aldehyde groups in periodate oxidation while the hydroxyl groups in starch molecules are oxidized to carbonyl and carboxyl groups, primarily at C-2, C-3 and C-6 in peroxide oxidation. For this reason, there are more un-substituted groups in periodate oxidized starch samples. It was thought that the unsubstituted hydroxyl groups in C-6 of anhydrous glucose units in starch structure, which have the strongest reactivity, replaced with carboxymethyl groups by carboxymethylation process and resulted in higher substitution degrees. Accordingly, Hebeish et al.<sup>4</sup> remarked that the carbonyl and carboxyl groups included in starch molecule decrease the efficiency of carboxymethylation.

Although higher degrees of substitution were reported in literature, it was seen that in these studies isopropanol, methanol, ethanol or their mixture with a small amount of water was selected and used as solvent for carboxymethylation processes.<sup>11-15</sup> Pursuant to literature, in the present study these alcohols and their mixtures were tried to be used as solvent to carry out carboxymethylation process. But, oxidized starch samples became sticky immediately after mixing with them. Thus, water was decided to be used as solvent for reaction. As a matter of fact, there are a few studies in

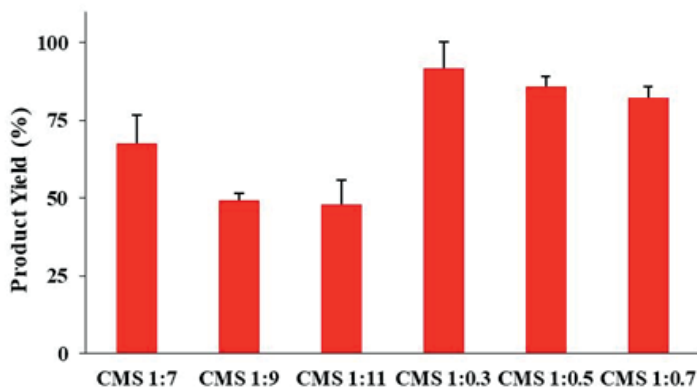


Figure 2. The yields of CMSs.

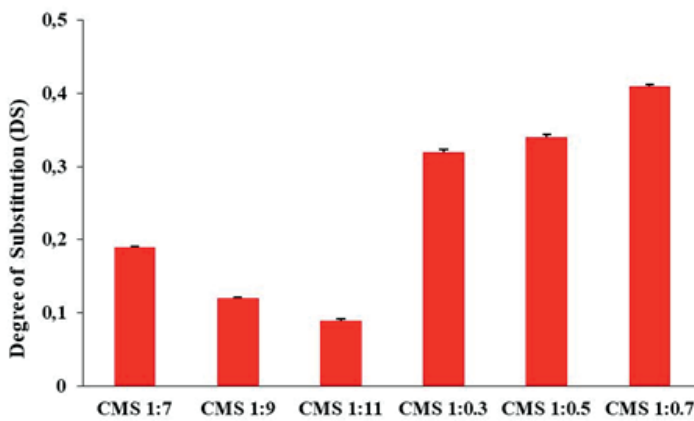


Figure 3. The degree of substitutions of CMSs.

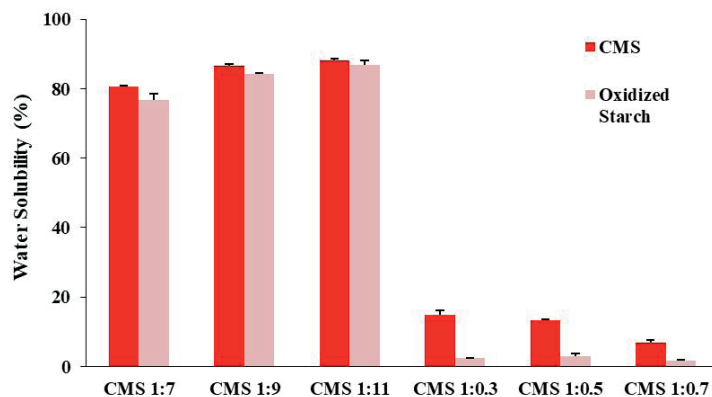


Figure 4. The water solubilities of CMSs.

literature on carboxymethylation of oxidized starches, and similar with our findings, lower degrees of substitution were obtained in carboxymethylation processes when the water was used as solvent.<sup>4,16</sup>

#### Water solubility of CMSs

The effect of carboxymethylation process on water solubility of oxidized starches is shown in Figure 4. From the evaluation of the data regarding the solubility of CMS 1:7, CMS 1:9, CMS 1:11 samples, it was noticed that the solubility of oxidized starches increased slightly by carboxymethylation process. In first place, the water solubility of H<sub>2</sub>O<sub>2</sub> oxidized starches<sup>1</sup> was found to be between 76.9 - 86.9%, 1.5-4.8% of additional increment arose from carboxymethylation process.

On the other hand, it was observed that the increase in water solubility of dialdehyde carboxymethyl starches (DCMSs) was more noticeable. The water solubility values of DCMSs were 3.8-6.2 times higher comparing with their oxidized forms<sup>2</sup> (between 1.8-2.9%). The increment in water solubility values of DCMSs was attributed to introduction of more CH<sub>2</sub>COO<sup>-</sup> groups into the structure. However, the water solubility of DCMSs decreased by increasing molar ratio of NaIO<sub>4</sub>, previously used for oxidation. The reason might be that higher degrees of oxidation with NaIO<sub>4</sub> resulted with introduction of higher number of aldehyde groups, correspondingly formation of more cross-links and finally at this stage resisted access of water molecules into the structure.

#### Characterizations of CMSs

Structures of carboxymethylated derivatives of H<sub>2</sub>O<sub>2</sub> and NaIO<sub>4</sub> oxidized starches were confirmed by FT-IR as shown in Figure 5 and Figure 6. The comparative study between the FT-IR spectra of native starch and CMSs shown the new peaks occurred by carboxymethylation process. Comparing with the native starch (Figure 5), the new peak at 1730.79 cm<sup>-1</sup> which expands gradually according to the degree of oxidation belongs to C=O stretching vibrations. Although this peak was also previously seen in the FT-IR spectra of oxidized starches with H<sub>2</sub>O<sub>2</sub>,<sup>1</sup> it was noticed that it was more pronounced in carboxymethylated derivatives. This is an evidence for including additional carboxyl groups into the structure because the protonated carboxylic groups (-COOH) similarly give the C=O band at 1730.79 cm<sup>-1</sup>.<sup>17,18</sup>

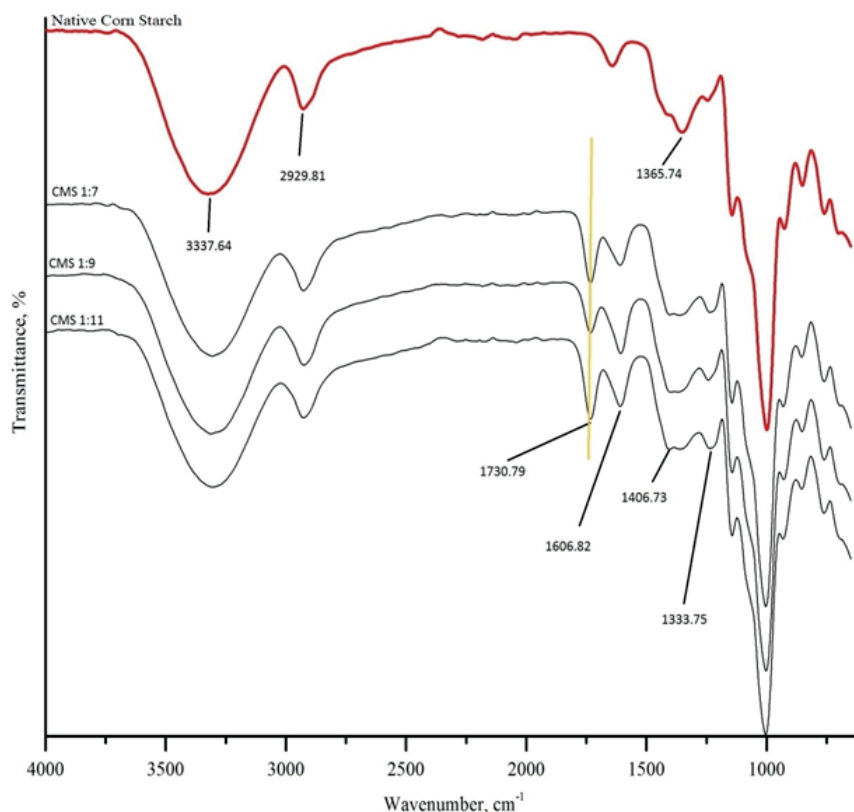
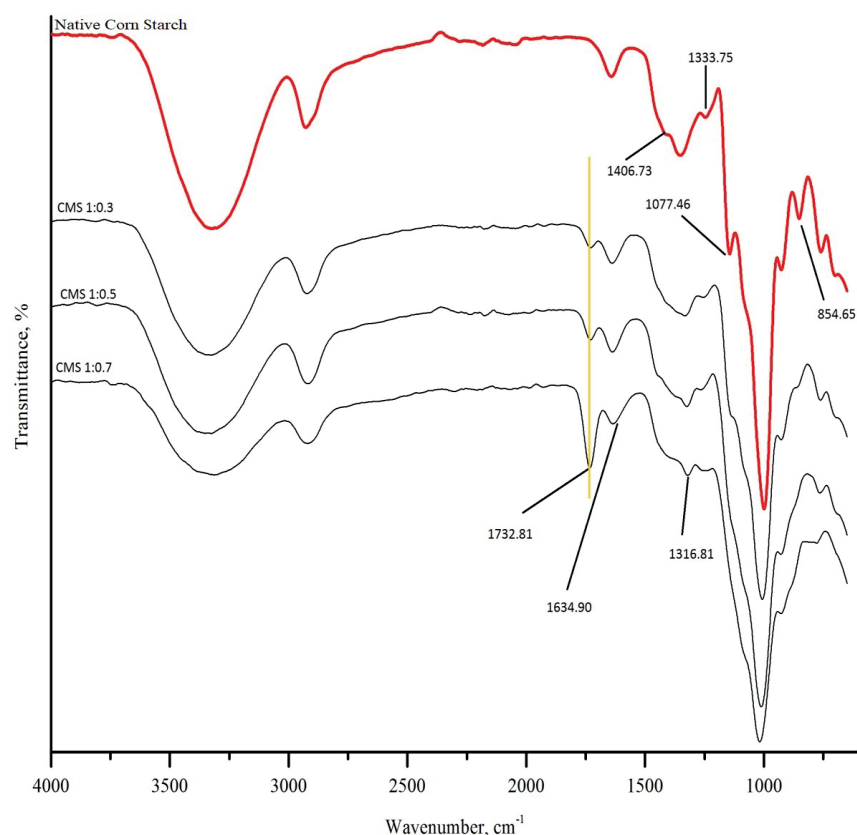


Figure 5. The FTIR spectra of native and carboxymethylated derivatives of H<sub>2</sub>O<sub>2</sub> oxidized starches.





**Figure 6.** The FT-IR spectra of native and carboxymethylated derivatives of  $\text{NaIO}_4$  oxidized starches.

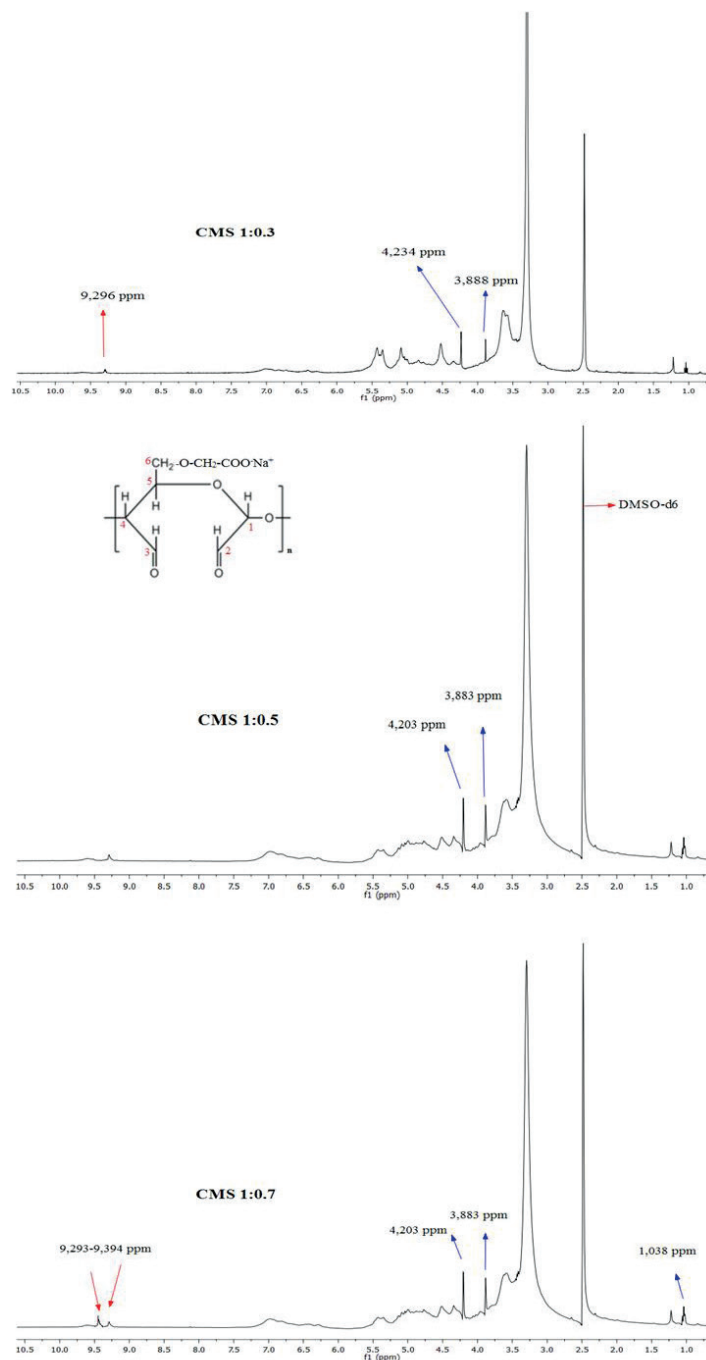
In addition, it was observed that the peaks at 1606.82, 1406.73 and  $1333.75\text{ cm}^{-1}$  which are attributed to characteristic carboxylate ( $-\text{COO}-$ ) absorption peaks of carboxymethyl starch<sup>5,18</sup> became more prominent and OH absorption peak of native starch at  $1365.74\text{ cm}^{-1}$  gradually decreased with carboxymethylation.<sup>19</sup> The obtained FT-IR spectra proved that the carboxymethylation process applied to hydrogen peroxide oxidized starches was successfully carried out.

Figure 6 shows the FT-IR spectra of native starch and DCMSs. It was noticed that DCMS samples had a new peak at  $1732.81\text{ cm}^{-1}$  and this peak gradually increased with increasing oxidation degree. In the FT-IR spectra of periodate oxidized starches,<sup>2</sup> this peak occurred with a lower intensity at  $1726.94\text{ cm}^{-1}$ , but the increasing intensity of this peak after carboxymethylation shows that additional carboxyl groups were included into the structure of periodate oxidized starches. As a matter of fact, protonated carboxylic groups ( $-\text{COOH}$ ) also give a  $\text{C}=\text{O}$  band in this area, as mentioned before. In addition, it was observed that the peaks at  $1077.46\text{ cm}^{-1}$  and  $854.65\text{ cm}^{-1}$ , which show the C-O bond stretching of the C-OH group in the glucose chain of native starch and the skeletal stretching vibration of the starch respectively, disappeared with carboxymethylation.

The structural changes in chemical structure of oxidized starches by carboxymethylation were also verified by  $^1\text{H-NMR}$  (Figure 7 and 8). The  $^1\text{H-NMR}$  spectrum of 1:9  $\text{H}_2\text{O}_2$  oxidized starch<sup>1</sup> was also presented as a reference in order to clearly discern the changes in the

structure of oxidized starches by carboxymethylation. Comparing with the spectra of oxidized form (Figure 7), it was seen that the new signals between 3.8–4.5 ppm occurred in  $^1\text{H-NMR}$  spectra of carboxymethylated derivatives of  $\text{H}_2\text{O}_2$  oxidized starches and it was revealed that carboxymethylation process was effective on oxidized starches. It was noticed that the OH-6 proton signal in the spectrum of oxidized starch gradually disappeared by increasing oxidation degree in the spectra of carboxymethylated derivatives, which shows that carboxymethylation preferentially occurs on C-6. Cízová et al.<sup>20</sup> remarked that the peak at 4.3 ppm attributed to the protons of the substituted carboxymethyl. However, the signal at 1.8 ppm which is attributed to the protons of the  $\text{CH}_2$  group next to the carbonyl or carboxyl group in oxidized starches disappeared by carboxymethylation, it also confirms that the carboxymethyl groups are mostly substituted with the group in C-6. On the other hand, the occurring alterations in OH-2 and OH-3 signals in the spectrum of oxidized starch after carboxymethylation revealed that substitution actualize also in these groups.

The  $^1\text{H-NMR}$  spectra of DCMSs are shown in Figure 8. The new signals, distinctively from their oxidized forms,<sup>2</sup> are indicated by the blue arrow in the  $^1\text{H-NMR}$  spectra of the carboxymethylated derivatives. The signals at 3.8 and 4.2 ppm were attributed to methylene protons in  $\text{C-CH}_2\text{-O-R}$  ( $\text{R:CH}_2\text{COONa}$ ) group and carboxymethyl protons in O-6, respectively. However, it was seen that the signals of the aldehyde groups included in starch structure

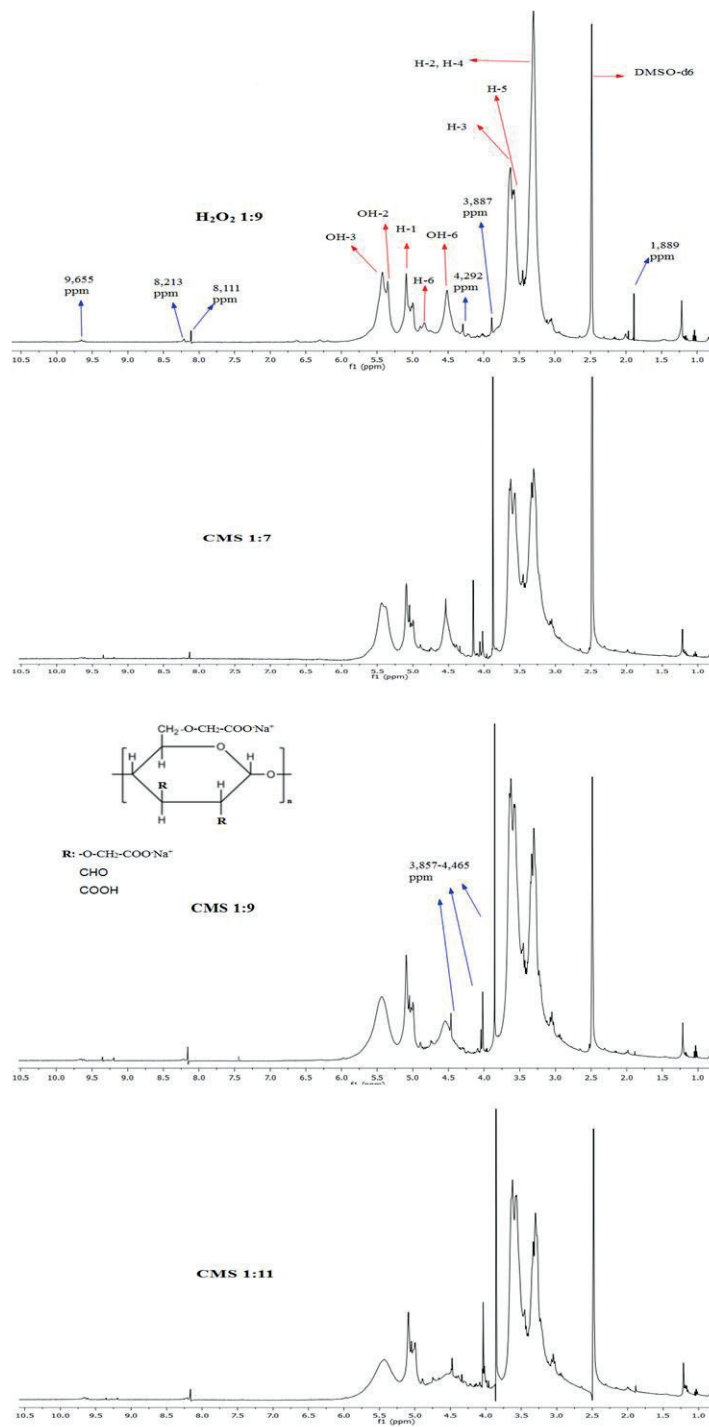


**Figure 7.** NMR spectra of carboxymethylated derivatives of  $\text{H}_2\text{O}_2$  oxidized starches.

after  $\text{NaIO}_4$  oxidation did not change markedly. Thus, it was thought that the carboxymethyl group included in the structure by carboxymethylation mostly replaced with the hydroxyl group in C-6 and it was confirmed with the signal seen at 4.2 ppm.

#### Tanning effects of CMSs

The data related to tanning abilities of carboxymethylated derivatives of oxidized starches were given in Table III. Considering



**Figure 8.** NMR spectra of carboxymethylated derivatives of  $\text{NaIO}_4$  oxidized starches.

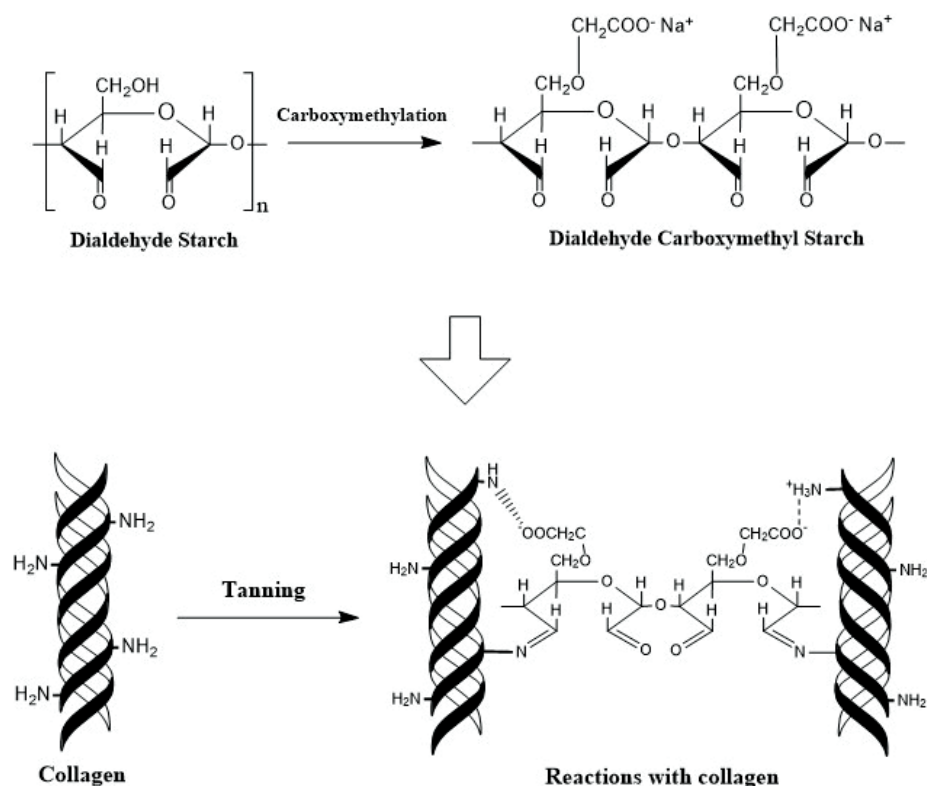
the filling properties of CMSs, it was determined that the filling coefficients of DCMSs were slightly better than carboxymethylated derivatives of peroxide oxidized starches and the highest filling effect was obtained with CMS 1:0.7 among all samples. However, it was noticed that the filling coefficient values significantly regressed by carboxymethylation especially in  $\text{NaIO}_4$  oxidized starch samples comparing with our previous study.<sup>2</sup>

**Table III**  
Tanning properties of CMSs

	Modification Methods	Sample Name	Filling coefficient (%)	Shrinkage temp. Ts (°C)	Ts (°C) after leaching
Tanning with pelt pieces	H <sub>2</sub> O <sub>2</sub> Oxidation (1:7 molar ratio) + Carboxymethylation	CMS 1:7	4.2(±0.4)	52.5(±0.7)	53.0
	H <sub>2</sub> O <sub>2</sub> Oxidation (1:9 molar ratio) + Carboxymethylation	CMS 1:9	4.9(±0.3)	54.0(±0.5)	54.5
	H <sub>2</sub> O <sub>2</sub> Oxidation (1:11 molar ratio) + Carboxymethylation	CMS 1:11	10.5(±0.6)	54.5(±0.6)	55.0
	NaIO <sub>4</sub> Oxidation (1:0.3 molar ratio) + Carboxymethylation	CMS 1:0.3	4.7(±0.5)	65.5(±0.8)	62.5
	NaIO <sub>4</sub> Oxidation (1:0.5 molar ratio) + Carboxymethylation	CMS 1:0.5	5.5(±0.6)	66.0(±0.8)	63.5
	NaIO <sub>4</sub> Oxidation (1:0.7 molar ratio) + Carboxymethylation	CMS 1:0.7	14.0(±0.3)	67.0(±0.5)	64.5
Tanned whole pelt	NaIO <sub>4</sub> Oxidation (1:0.7 molar ratio) + Carboxymethylation	CMS 1:0.7	-	71.0(±0.4)	-

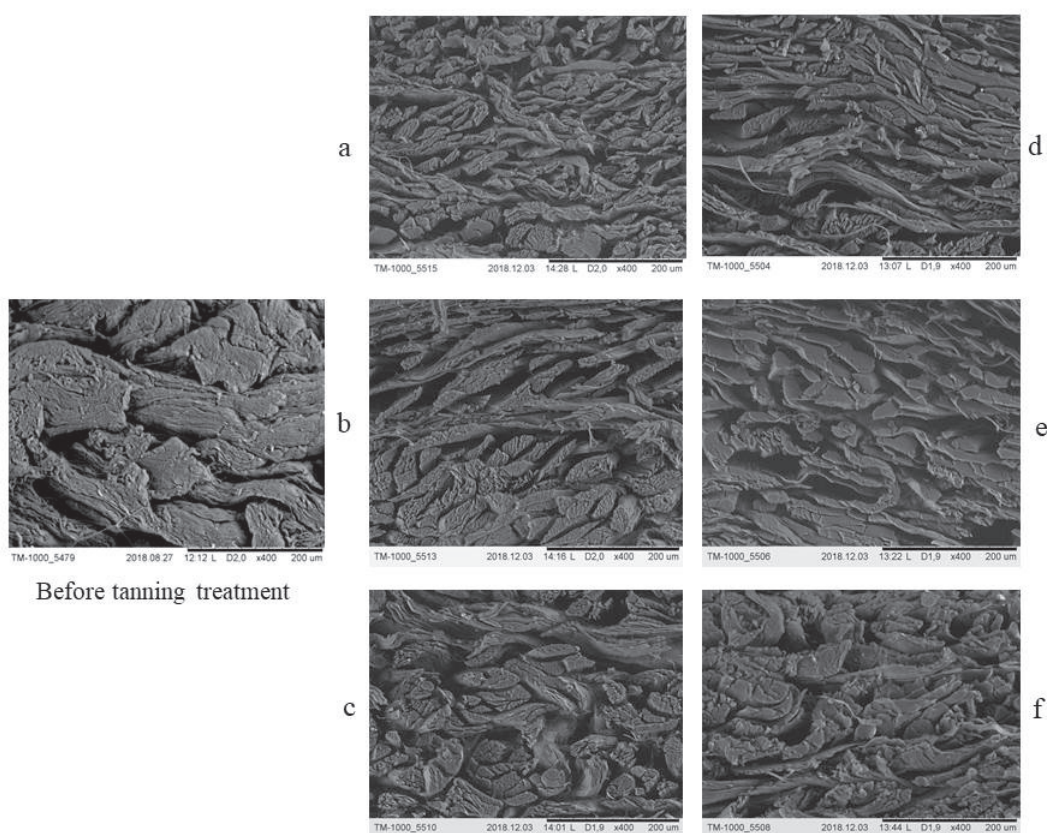
From the evaluation of hydrothermal stabilities gained to the leathers, it was noticed that the shrinkage temperatures of leathers increased little by little in conjunction with increasing previously applied oxidation molar ratio. However, it is clearly seen that the shrinkage temperatures of leathers tanned with DCMS samples are higher than carboxymethylated derivatives of peroxide oxidized starches, as expected. The underlying reason is that the incorporated aldehyde groups into the structure of DCMSs by NaIO<sub>4</sub> oxidation are linked to collagen by more robust covalent bonds, while the carbonyl/carboxyl groups and carboxymethyl groups, which are incorporated into the starch structure by peroxide oxidation and

carboxymethylation processes respectively, are essentially linked to collagen by feeble ionic and/or hydrogen bonds (Figure 9). Although the highest shrinkage temperature was obtained by CMS 1:0.7, between 9 and 23.5°C increase was achieved in tanned samples comparing with the intact pelt's hydrothermal stability (43.5°C). The preliminary tanning trials' results showed that CMS 1:0.7 sample has the best tanning effect thus a whole pelt was also tanned with this CMS sample. From the tanning of the whole pelt with CMS 1:0.7 sample, the shrinkage temperature of the leather was found to be 71°C, which means that 27.5°C of increase at shrinkage temperature was achieved comparing with the intact pelt.



**Figure 9.** Schematic illustration for the reaction of collagen with DCMS.





**Figure 10.** SEM images of pickled goat skin, carboxymethylated derivatives of  $\text{H}_2\text{O}_2$  oxidized starches (a, b, c) and carboxymethylated derivatives of  $\text{NaIO}_4$  oxidized starches (d, e, f).

Additionally leachability test was applied to the leather samples obtained from preliminary tanning trials. From the comparison of the shrinkage temperature ( $T_s$ ) values of the leathers before and after leaching, it was determined that while there was no considerable change in the shrinkage temperatures of the leathers tanned with the  $\text{H}_2\text{O}_2$  oxidized and carboxymethylated samples, 2-3°C of decreases were detected in shrinkage temperatures of the leathers tanned with  $\text{NaIO}_4$  oxidized and carboxymethylated samples (Table III). Considering the shrinkage temperature changes occurred after leaching, it was concluded that modified starch samples established stable bonds with the functional groups of collagen to a certain extent.

However, comparing the tanning characteristics of 1:0.7 periodate oxidized starch<sup>2</sup> (dialdehyde starch) with CMS 1:0.7 it was observed that the astringency of dialdehyde starch reduced and it gained gentler tanning effect by carboxymethylation. For this reason, although slightly lower shrinkage temperature (71°C) was obtained with carboxymethylated derivatives of periodate oxidized starch

compared to its oxidized form (73°C) it is concluded that DCMS is more favorable to be used as a tanning agent in leather production considering its properties i.e gentle tanning effect with less astringency and as a result of this a leather relatively soft handle and smooth grain.

The SEM graphics of pickled goat skin and CMS tanned leathers at a magnification of 400× are shown in Figure 10. The SEM investigations showed that isolation of fibril bundles was performed for all CMS tanned leather samples which indicate the tanning effect.

The physical test results of pieces tanned with CMSs and the whole leather tanned with CMS 1:0.7 were given in Table IV. Comparing with the recommended values for goat leathers (20 N/mm<sup>2</sup> for tensile strength, 40 N/mm for tear strength) by UNIDO,<sup>21</sup> excluding the tensile strength values of the leathers which were tanned with CMS 1:0.3 and CMS 1:0.5 samples, all leather samples meet the recommended values.

**Table IV**  
Physical properties of tanned pelt pieces and whole leather

	Sample	Tensile Strength (N/mm <sup>2</sup> )	Elongation (%)	Tear Strength	
				Max. Force (N)	Thickness (mm)
Tanned pelt pieces	CMS 1:7	23.1(±1.3)	37.2(±1.7)	105.5(±6.3)	0.8(±0.05)
	CMS 1:9	29.9(±1.6)	42.0(±3.5)	138.2(±7.4)	0.9(±0.01)
	CMS 1:11	25.8(±2.6)	49.9(±1.0)	124.3(±7.3)	0.9(±0.07)
	CMS 1:0.3	9.9(±1.1)	18.2(±2.9)	116.8(±3.6)	1.0(±0.2)
	CMS 1:0.5	10.8(±0.2)	22.0(±1.0)	126.8(±5.49)	0.8(±0.01)
	CMS 1:0.7	20.7(±3.1)	59.6(±1.8)	94.4(±5.1)	1.0(±0.05)
Tanned whole pelt	CMS 1:0.7	20.88(±3.5)	81.48(±6.2)	69(±1.7)	0.75(±0.02)

**Table V**  
Cracking and bursting values of tanned whole leather with CMS 1:0.7

Cracking		Bursting	
Cracking load (Kgf)	Distension at crack (mm)	Bursting load (Kgf)	Distension at burst (mm)
30(±1.3)	15.61(±1.1)	35.3(±2.2)	16.89(±1.8)

**Table VI**  
Organoleptical properties of tanned leathers with CMSs

	CMS Sample	Color	Handle	Grain smoothness
Tanning with pelt pieces	CMS 1:7	Beige light c.	Slightly Firm	Slightly rough
	CMS 1:9	Beige light c.	Slightly Firm	Slightly rough
	CMS 1:11	Beige light c.	Slightly Firm	Slightly rough
	CMS 1:0.3	Beige c.	Very Firm	Rough
	CMS 1:0.5	Beige c.	Firm	Slightly Rough
	CMS 1:0.7	Beige c.	Firm	Smooth
Tanning with whole pelt	CMS 1:0.7	Beige c.	Firm	Very Smooth

Additionally, the whole leather which was tanned with CMS 1:0.7 was also tested in terms of distension and strength of surface. The cracking and bursting values (Table V) meets the recommended value (min. 7mm) for shoe upper leathers by UNIDO.<sup>21</sup>

From the evaluation of the tanned leather by organoleptically (Table VI), it was observed that the leathers tanned with CMSs were beige colored and has firm and compact structure similar with synthetic/vegetable tanned leather.

## Conclusion

In our earlier studies<sup>1,2</sup> it was revealed that native corn starch can be oxidized by H<sub>2</sub>O<sub>2</sub> and NaIO<sub>4</sub> and oxidation products having appropriate molecular weight/size and bearing functional groups that can establish stable bonds could be utilized as tanning and/or retanning agent in leather processing. In the present part, H<sub>2</sub>O<sub>2</sub> and NaIO<sub>4</sub> oxidation products of starch were additionally carboxymethylated. Besides comprehensive characterization of

the CMSs, the effect of carboxymethylation process on structure and tanning ability tried to be identified. From the preliminary tanning trials with pieces of pelts, CMS 1:0.7 was chosen as the sample having the best tanning ability and a whole pelt was also tanned with it. Then, the tanned whole leather was evaluated physically and organoleptically. The characterization results demonstrated successful preparation of CMSs from oxidized starches by  $\text{H}_2\text{O}_2$  and  $\text{NaIO}_4$  oxidation methods. Compared with oxidized forms, it was determined that the carboxymethyl groups were successfully included into the structure and the water solubility of oxidized starches (especially  $\text{NaIO}_4$  oxidized ones) increased by carboxymethylation process. From the evaluation of the tanning results and considering its properties i.e. gentle tanning effect with less astringency and correspondingly a relatively soft leather handle and smooth grain, it is concluded that 1:0.7 DCMS can be utilized as yet another good alternative sustainable green tanning/retanning agent from starch.

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