

# Retanning Performance of Carboxymethyl Starch and Its Effects on Dyeing

by

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## Abstract

The tanning characteristics of starch samples modified by different methods were investigated in our previous studies. In this study, utilization of modified starch in leather making as a retanning agent and its effect on dyeing process have been investigated. For this purpose, the molecular size of native corn starch was reduced by H<sub>2</sub>O<sub>2</sub> oxidation and then carboxymethylated. A series of analyses (water solubility, degree of substitution, Fourier Transform Infrared Spectroscopy, Proton and Carbon Nuclear Magnetic Resonance Spectroscopy) were carried out for characterization. Then, carboxymethyl starches were used in retanning processes to be 3, 5 and 10% based on leather weight and the shrinkage temperatures and filling coefficients of the leathers were determined. Acid and metal complex dyestuffs were used in dyeing processes and the effect of carboxymethyl starch on dyeing was also investigated by examining dye consumption, dry and wet rubbing fastness and color of the leathers. From the results it was concluded that carboxymethyl starch showed a noticeable solo performance in terms of filling property and shrinking temperature without any considerable adverse effect on dyeing.

## Introduction

In recent years, the increasing awareness regarding the environment and human health, and the legal restrictions that have come into force in parallel, have significantly affected and put pressure on the leather industry as well as many other industries. This situation has made it necessary to replace existing production technologies and chemicals with more environmentally friendly technologies and chemicals. For this reason, many researchers have focused on the production of alternative chemicals from natural, renewable resources and the development of more environmentally friendly production methods. In fact, considering these consumer demands and trends for production, the sustainability of many products' production seems to depend on these studies. Because, whether the products are natural or not, their effects on the environment and human health are becoming more and more decisive in the purchasing behavior of consumers.

In line with these considerations, we focused on the usability of starch obtained from natural and renewable resources, which is

used as a raw material in many industries,<sup>1</sup> in the leather industry by changing its structure with different modification methods. In our previous studies,<sup>2-4</sup> we tried to determine the tanning properties by modifying starch with different methods. In this study, the performance of carboxymethyl starch in retanning, whose tanning efficiency was previously investigated, was examined. As it is known, almost any substance with tanning properties can be used in retanning process. However, the possible negative effects of these tanning agents, especially on dyeing and color, may limit their use in retanning in some cases. For this reason, this issue was especially taken into consideration within the scope of the research and the effects of carboxymethyl starch on dyestuff consumption, color and fastness properties were investigated as well as the retanning efficiency of it.

## Materials and Methods

### Materials

Native corn starch was used as raw material and purchased from Hasal Starch Company Izmir/Turkey. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 34.5-36.5%), copper (II) sulphate pentahydrate (CuSO<sub>4</sub>.5H<sub>2</sub>O, 99-100.5%), ethanol (C<sub>2</sub>H<sub>6</sub>O, 99.8%), hydrochloric acid (HCl, 37%), acetone (C<sub>3</sub>H<sub>6</sub>O, 99.5%), methanol (CH<sub>3</sub>OH, ≥99.7%), silver nitrate (AgNO<sub>3</sub>, 99.5%), sodium hydroxide (NaOH, 98-100.5%), hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl, ≥98%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95-97%) and monochloro acetic acid (C<sub>2</sub>H<sub>3</sub>ClO<sub>2</sub>, 99%) were used in starch modifications and analyzes. All chemicals were purchased from Sigma Aldrich. Wet-blue goat leathers were used in retanning experiments.

### Methods

#### Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) Oxidation of Native Corn Starch

Oxidation process of native corn starch was carried out as described by Zhang et al.<sup>5</sup> First of all, 10 grams of dehumidified starch was weighed and dispersed in 100 mL of distilled water. This mixture was stirred moderately with a magnetic stirrer at 80°C for 30 minutes. After that the temperature was reduced to 55°C and 0.1% CuSO<sub>4</sub>.5H<sub>2</sub>O (dissolved in enough water) was added to the mixture and stirred again for 30 minutes. Then H<sub>2</sub>O<sub>2</sub> was added and stirred another 30 minutes. In oxidation processes, the starch and H<sub>2</sub>O<sub>2</sub> molar ratio was taken to be 1:10 considering the data from our previous study<sup>2</sup> in which it was determined that oxidized starch

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Figure 1. Oxidized starch: after dry in oven (a) and after grind (b)

products with a molecular weight of 2737-2897 Da can be obtained by 1:10 molar ratio (starch:hydrogen peroxide) that can easily penetrate between leather fibers.  $\text{CuSO}_4$  and  $\text{H}_2\text{O}_2$  were calculated according to glucose units of starch molecules. After completion of the reaction, firstly the oxidized starch was precipitated in excess of ethanol and then centrifuged. The product was dried in an oven at  $50^\circ\text{C}$  for 48 hours. Finally, the dried product was ground.

Then, the obtained powder oxidized starch samples were subjected to carboxymethylation. For this reason, oxidation and carboxymethylation processes were repeated a few times until adequate amount was achieved to be used in retanning processes.

#### Determination of Product Yields

The yield of  $\text{H}_2\text{O}_2$  oxidized starch was determined according to the method described by Kilicarislan Ozkan et al.<sup>2</sup> The experiments were performed in three repetitions and the yield of  $\text{H}_2\text{O}_2$  oxidation was calculated by Formula (1) given below.

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

#### Determination of carboxyl and carbonyl contents of $\text{H}_2\text{O}_2$ oxidized starch

The carboxyl and carbonyl contents of oxidized starch were determined according to the methods described by Chattopadhyay et al.<sup>6,7</sup> and Smith et al.<sup>7,8</sup> respectively. The experiments were performed with three replications and the results were given as mean data. Carboxyl and carbonyl contents were calculated according to Formula 2 and Formula 3, respectively.

$$\text{DO}_{\text{COOH}} = \frac{162C(V_1 - V_2)}{1000W - 36C(V_1 - V_0)} \quad (\text{Formula 2})$$

Where;  $C$ =NaOH solution concentration (mol/L),  $V_0$ =Volume of NaOH used for blank (mL),  $V_1$ =Volume of NaOH used for sample (mL),  $W$ =Dry weight of sample.

$$\text{DO}_{\text{CO}} = \frac{C(V_0 - V_1) \times (36\text{DO}_{\text{COOH}} + 162)}{1000W} \quad (\text{Formula 3})$$

Where;  $C$ =HCl solution concentration (mol/L),  $V_0$ =Volume of HCl used for blank (mL),  $V_1$ =Volume of HCl used for sample (mL),  $W$ =Dry weight of sample.

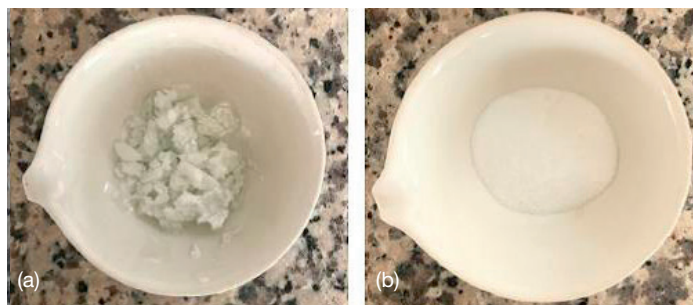


Figure 2. Carboxymethylated starch: after dry in oven (a) and after grind (b)

#### Carboxymethylation of $\text{H}_2\text{O}_2$ oxidized starch

Carboxymethylation process was also applied to the  $\text{H}_2\text{O}_2$  oxidized starch samples. Carboxymethylation was performed by the method described by Hebeish et al.<sup>9</sup> with slight modification.<sup>4</sup> First of all, 8.1 g oxidized starch, 9.45 g monochloroacetic acid, 10 mL of 5 N NaOH solution and 45 mL distilled water were added in a 100 mL flask. Oxidized starch:Monochloroacetic acid:NaOH molar ratios were taken to be 1:2:1. The mixture was stirred to obtain a homogenous mixture. Then, the flask was transferred into the water bath at  $50^\circ\text{C}$  and shaken for 1 hour. After that, the flask was removed from the water bath and the reaction products were precipitated with ethanol. Then it was washed with ethanol until the alkalis were removed. The obtained product was dried in an oven at  $50^\circ\text{C}$  for 48 hours and then ground to get powder form.

The yields were calculated according to the Formula 1, where *obtained carboxymethyl starch* value was used in numerator and *amount of oxidized starch* value was used in denominator.

#### Determination of degree of substitutions

The degree of substitution (DS) of carboxymethylated starch (CMS) was determined according to the titrimetric method described by Jiang et al.<sup>10</sup> The DS was determined by using Formula 4 and Formula 5.

$$\text{DS} = \frac{n_{\text{NaOH}} \times M_o}{m_c - n_{\text{NaOH}} \times M_R} \quad (\text{Formula 4})$$

$$m_c = m_p - \left[ \frac{\text{mp} \times F}{100} \right] \quad (\text{Formula 5})$$

Where;  $M_o$ =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 Starches

The water solubility of native,  $\text{H}_2\text{O}_2$  oxidized and carboxymethylated starch samples were investigated to determine the extent of changes in water solubility with modifications. Water solubility was

determined according to the method described by Singh and Singh<sup>11</sup> with slight modification<sup>2-4</sup> and Formula 6 was used for calculation.

$$\text{Water solubility \%} = \frac{\text{Supernatant solid weight (g)} \times 2}{\text{Sample weight (g)}} \times 100 \quad (\text{Formula 6})$$

### Structure Characterizations

The changes in the structures of native, oxidized and carboxymethylated starches by modifications were identified by FT-IR, <sup>1</sup>H-NMR and <sup>13</sup>C-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 and <sup>13</sup>C-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.

### The Use of Carboxymethyl Starch in Retanning Process

In order to carry out the retanning trials with best possible homogenous materials; neck, flank and belly parts of the wet-blue goat leathers were removed and 30×30 cm size of pieces were cut from the remaining coupon part and used in retanning processes. The obtained carboxymethyl starches were used in retanning processes to be 3, 5 and 10% based on the chrome tanned leather weight. After retanning processes the leather samples were dyed with 3% of acid (Acid Blue 25) and metal complex (Acid Blue 360) dyestuffs, in order to investigate dyeing properties with alternative dyeing agents. The process recipe is given in Table I. Additionally, for each dyestuff, 2 samples were also processed according to the same recipe without carboxymethyl starch introduction to be used as blank samples.

**Table I**  
Retanning and dyeing recipe

PROCESS	AMOUNT (%)	PRODUCT	TEMP. (°C)	TIME (min.)	pH
Washing	200	Water	40		
	0,2	Cationic Wetting Agent		15	
Draining					
Washing	100	Water	25	5	
Draining					
Neutralization	200	Water	38		
	2	Neutralizing Syntan		10	
	0,25	NaHCO <sub>3</sub>		20	
Washing	100	Water	35	5	6.0
Draining					
Retanning	50	Water	37		
	x	CMS		45	
	3	Dyestuff		45	
	2	Phosphoester based fatliquor	50		
	5	Sulphite Natural+synthetic fatliquor combination			
	2	Synthetic fatliquor with high light fastness		45	
Fixing	0,8	HCOOH		20	
	0,7	HCOOH		30	3,5
Draining					
Washing	100	Water	25	10	
Draining					

### Post-Retanning Tests

- **Determination of filling coefficient**

The changes in leather thickness after retanning process were determined according to the TS EN ISO 2589<sup>12</sup> standard. Before retanning ( $T_1$ ) (after neutralization) and after retanning (after fixation) ( $T_2$ ) the thicknesses of the leathers were measured in wet form by using thickness gauge with 100 g pressure and the filling coefficients were calculated according to Formula 7.

$$\text{Filling coefficient (\%)} = \frac{T_2 - T_1}{T_1} \times 100 \quad (\text{Formula 7})$$

- **Determination of shrinkage temperature**

The shrinkage temperatures ( $T_s$ ) of the leather samples retanned with different ratios of carboxymethyl starches were measured according to ISO 3380<sup>13</sup>, in order to determine possible effect on hydrothermal stability of the leathers.

- **Dyestuff consumption**

Since retanning agents may alter the reactivity between leather and dyestuff, the amounts of dyestuffs remaining at the end of dyeing processes were measured by using Shimadzu UV-1601 spectrophotometer, so as to investigate probable favorable or unfavorable effect of carboxymethyl starch retanning on dye consumption.

- **Wet and dry rubbing fastnesses**

The wet and dry rubbing fastnesses of dyed leathers were determined according to TS EN ISO 11640<sup>14</sup> standard test method and the evaluation was done according to the Grey Scale Standard (ISO 105-A02<sup>15</sup> and ISO 105-A03<sup>16</sup>).

- **Determination of color changes**

Minolta CM-2600d spherical spectrophotometer with CIE 100 standard observer angle and CIE standard D65 daylight source was used to measure the colors and to evaluate the color differences of the leathers. The colors of all leather samples and differences compared with the control sample were evaluated according to the CIELAB color coordinate system.

### Results and Discussion

#### Moisture contents of starches

The moisture contents of native corn starch and oxidized starch were found to be 9.7% and 7.2%, respectively. Since the ratio of starch to reagents used in oxidation and carboxymethylation processes is an important parameter, the moisture contents of native and oxidized starches were taken into consideration and pre-dehumidified starches (in an oven at 50°C for 48 h) were used in modifications.

#### Product yields, DS and water solubilities of starches

The product yields, degree of substitutions and water solubilities of oxidized and carboxymethylated starches were comparatively given in Figure 3.

From the evaluation of the data regarding the yields of oxidized and carboxymethylated starches, it was observed that the yield of carboxymethyl starch is lower than oxidized starch. Correspondingly, it was concluded that the carboxymethyl groups included in the structure of oxidized starch by the carboxymethylation process increased the water solubility of oxidized starch and consequently the obtained yield value decreased. Indeed, the higher water solubility value of carboxymethylated starch compared to its oxidized form (Figure 3) supports this idea.

The intra-granular structure of starch becomes irregular by oxidative degradation and introducing carboxymethyl groups therefore the water can easily enter to amorphous regions along with disruption of intramolecular hydrogen bonds.<sup>17</sup> As a matter of fact, comparing with the water solubility of native starch (0.9%), it can be seen that the solubility of native starch increased significantly with oxidation. However, it was observed that the solubility of the oxidized starch, which has already good water solubility, increased a bit more by introducing carboxymethyl groups into the structure with carboxymethylation process. During hydrogen peroxide oxidation, hydroxyl groups in C-2, C-3 and C-6 of glucose units can be replaced by carbonyl and carboxyl groups. Although the primary group introducing into the starch structure by  $H_2O_2$  oxidation is carbonyl

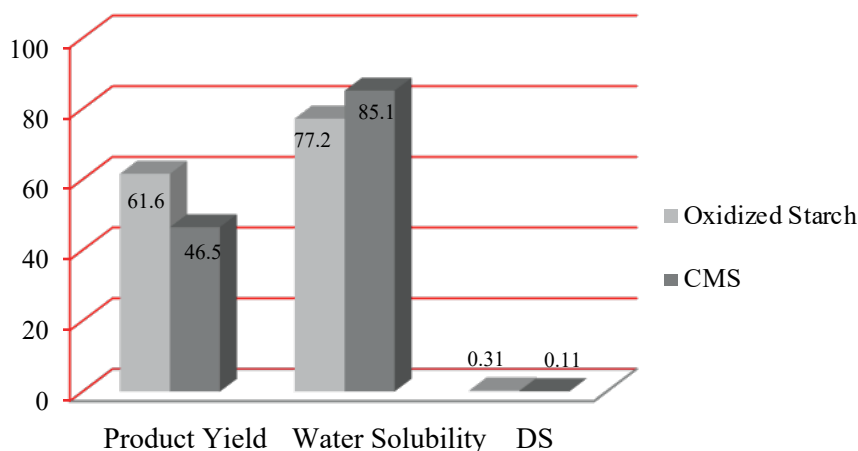


Figure 3. The product yields, degree of substitutions and water solubilities of oxidized and carboxymethyl starches



groups, a small amount of carboxyl groups are also included into the structure. The value 0.31 in Figure 3 shows the substituted carbonyl groups, however, the carboxyl groups included into the structure was determined to be 0.02. These results confirmed that carbonyl is the primary functional group produced in peroxide oxidized starches, although small amounts of carboxyl groups also formed. Throughout the first period of the reaction time in hydrogen peroxide oxidation, too much reagent is consumed for hydrogen removal during the formation of high amounts of carbonyl groups, less oxidant remains for the oxidation of carbonyl to carboxyl groups, for this reason the primary group formed by hydrogen peroxide oxidation is carbonyl group.<sup>18</sup>

Comparing degree of substitutions, it was determined that the degree of substitution from carboxymethylation is lower than oxidation. Which means the number of carboxymethyl groups introduced into the structure was determined to be less than the number of carbonyl groups. The underlying reason is that many of the hydroxyl groups having substitution ability in C-2, C-3 and C-6 in starch molecule have already been replaced mostly with carbonyl and smaller amounts of carboxyl groups by pre-applied oxidation process, therefore a few hydroxyl groups remained in oxidized starch molecule to substitute with carboxymethyl groups. Indeed, Hebeish et al.<sup>9</sup> similarly remarked that the carbonyl and carboxyl groups which included to structure by oxidation cause a decrease in carboxymethylation efficiency. Regarding the degree of substitution, it should be noted that starches with lower degree of substitution are obtained when water is used as the reaction medium in the carboxymethylation process. Spychaj et al.<sup>19</sup> also stated that when

the carboxymethylation of native starch is carried out by using water, the degree of substitution can be achieved up to 0.07.

### Structure Characterizations

The FT-IR spectra of native, oxidized and carboxymethyl starches were shown in Figure 4. As it is seen, although all starch samples have a very similar structure, some minor changes in the spectra of modified starches show that modification processes (oxidation and carboxymethylation) were carried out effectively. Comparing with the spectrum of native corn starch, a new absorption band at 1733.02  $\text{cm}^{-1}$  was seen in spectrum of oxidized starches and it is assigned to C=O stretching vibration.<sup>5,20-22</sup> This peak indicates the addition of carbonyl and/or carboxyl groups to the native starch structure.

From examining the CMS spectrum, the new peak occurred at 1731.57  $\text{cm}^{-1}$ , distinct from native starch, belongs to C=O stretching vibrations. Although this peak was also previously seen in the FT-IR spectra of oxidized starches with  $\text{H}_2\text{O}_2$  at 1733.02  $\text{cm}^{-1}$ , 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 1733.02  $\text{cm}^{-1}$ .<sup>23,24</sup> In addition, the peaks at 1603.18 and 1234.34  $\text{cm}^{-1}$  which are attributed to characteristic carboxylate (-COO-) absorption peaks of carboxymethyl starch<sup>10,24</sup> became more prominent and OH absorption peak of native starch at 1358.21  $\text{cm}^{-1}$  decreased with carboxymethylation.<sup>25</sup> The obtained FT-IR spectra proved that the carboxymethylation process applied to hydrogen peroxide oxidized starches was successfully carried out.

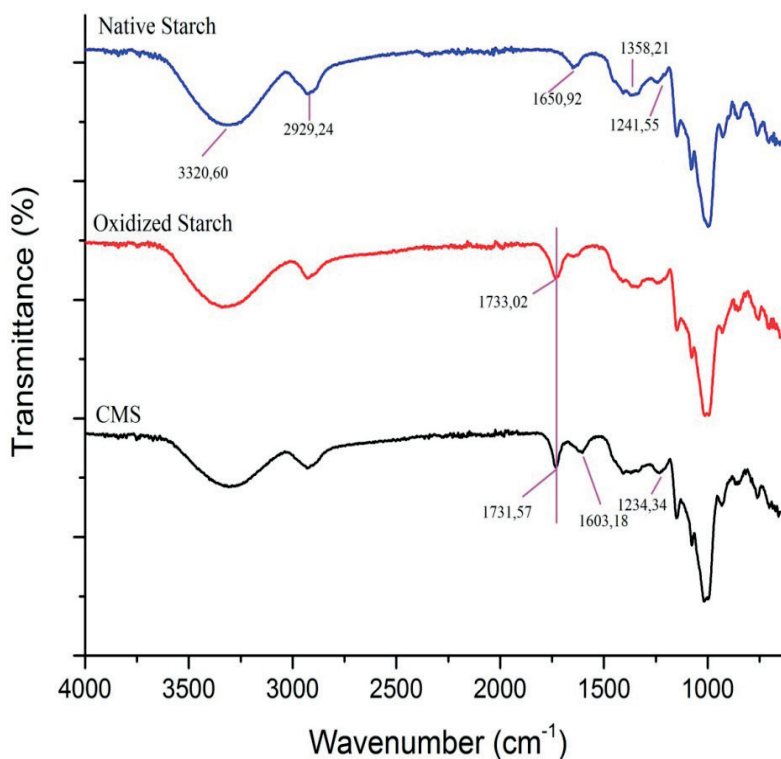


Figure 4. FT-IR spectra of native, oxidized and carboxymethylated starches

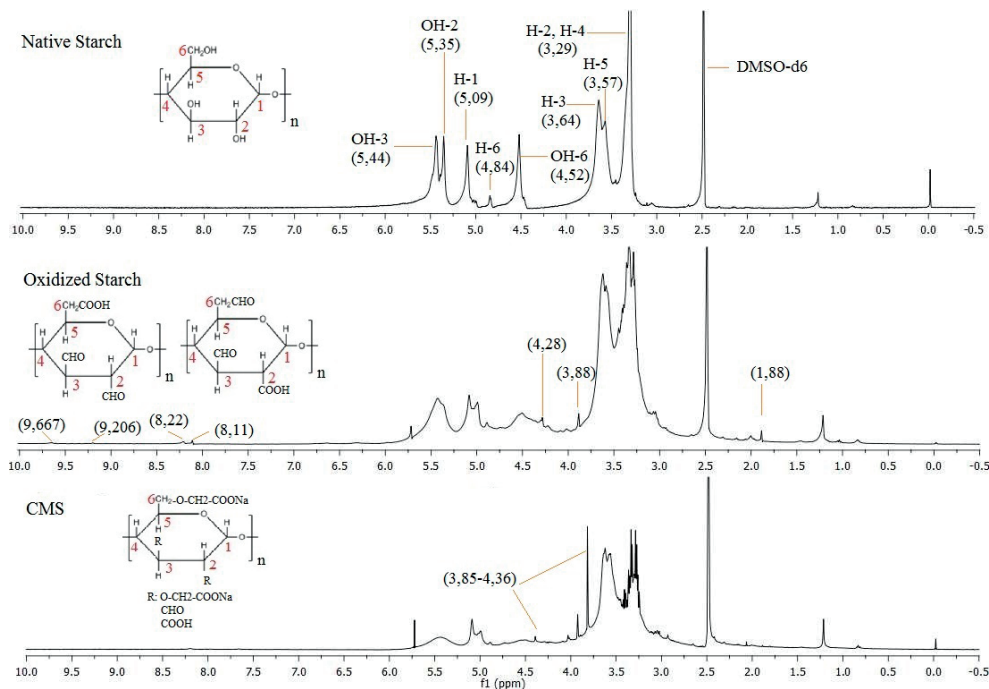


Figure 5.  $^1\text{H}$ -NMR spectra of native, oxidized and carboxymethylated starches

Native starch, oxidized starch and CMS were also analyzed by NMR in order to see more clearly the changes occurred in chemical structure by oxidation and carboxymethylation processes. The  $^1\text{H}$ -NMR spectra of starches were shown in Figure 5. Firstly,  $^1\text{H}$ -NMR spectrum of native corn starch was inspected in order to identify the changes occurred in structure by modifications and some characteristic peaks were indicated in the native starch spectrum.

Comparing the  $^1\text{H}$ -NMR spectra of native and oxidized starches, it was observed that the intensity of peaks, which indicate the proton signals of OH groups in C-2, C-3 and C-6 of native corn starch, decreased significantly with oxidation which indicates that the hydroxyl groups at C-2, C-3 and C-6 of glucose units substituted to some extent. On the other hand, the observed changes in the spectrum of native corn starch in H-1 (5.09 ppm) and H-6 (4.84 ppm) proton signals at the  $\alpha\rightarrow 1.4$  and  $\alpha\rightarrow 1.6$  junctions confirmed that these bonds were broken down during oxidation. Unlike native starch, the small signals seen around 9.21-9.67 ppm in the spectrum of oxidized starch are ascribed to protons of carbonyl groups (aldehydic group),<sup>26,27</sup> the new signals at 8.11-8.22 ppm and 3.88-4.28 ppm are attributed to the protons of -OH and -CH groups of hemiacetal structures.<sup>27</sup>

From the  $^1\text{H}$ -NMR spectrum of CMS (Figure 5), the new signals occurred between 3.85-4.36 ppm, differently from oxidized starch, showed that carboxymethylation process is effective on oxidized starches. However, OH-6 proton signal (4.52 ppm) which was seen in the spectrum of oxidized starch disappeared in the carboxymethylated starch that indicates that the carboxymethylation preferably takes place on C-6. On the other hand, comparing with the spectra of oxidized starch, the loss of the signal at 1.88 ppm which is attributed to the protons of the  $\text{CH}_2$  group next to the carbonyl or carboxyl group in oxidized starch also confirmed that

the carboxymethyl groups mostly replaced with the group in C-6. In addition, the changes seen in the OH-2 and OH-3 signals in the spectrum of oxidized starches after carboxymethylation showed that the substitution also actualized in these groups.

$^{13}\text{C}$ -NMR spectra of native, oxidized and carboxymethyl (CMS) starches were shown in Figure 6. The signals seen at 60.87, 71.99-73.63, 79.15 and 100.47 ppm in  $^{13}\text{C}$ -NMR spectrum of native starch are attributed to the C-6, C-2, C-3, C-5, C-4 and C-1 carbons, respectively.<sup>28</sup> Comparing with the  $^{13}\text{C}$ -NMR spectrum of native starch, the intensity of C-1 peak decreased and two peaks (102.51 and 99.14 ppm) appeared here because of the carboxymethylation status of C-2. In this respect, two different situations could occur for C-1, depending on if there is carboxymethyl substitution of C-2 or not. These peaks suggested that the carboxymethyl substitution at C-2 causes a shift  $\sim 1$  ppm on C-1.<sup>29</sup> Differently from native starch; the signals seen at 163.48 and 174.84 ppm in the spectrum of oxidized starch are attributed to carbonic and carboxylic carbons, respectively.<sup>28</sup> As seen in the spectra of oxidized starch, the peak of CHO group is slightly clear than the peak of COOH group it confirms that the primary group introducing into the structure in peroxide oxidation is carbonyl group. In addition, the intensity of C-2 and C-4 signals significantly decreased in comparison to the native starch spectrum. This decline in signal levels may arise from starch depolymerization mainly in  $\alpha$ -(1 $\rightarrow$ 4)-glucosidic linkages.<sup>30</sup>

However, the intensity of C-2, C-3 and C-6 signals in native starch spectrum significantly decreased by oxidation, it is shown that OH groups at C-2, C-3 and C-6 of glucose units replaced with CHO and COOH groups.<sup>28</sup> Differently from  $^{13}\text{C}$ -NMR spectra of native and oxidized starches, the peak clearly seen at 180.42 ppm is attributed to the -CO carbon of carboxymethyl group and proves

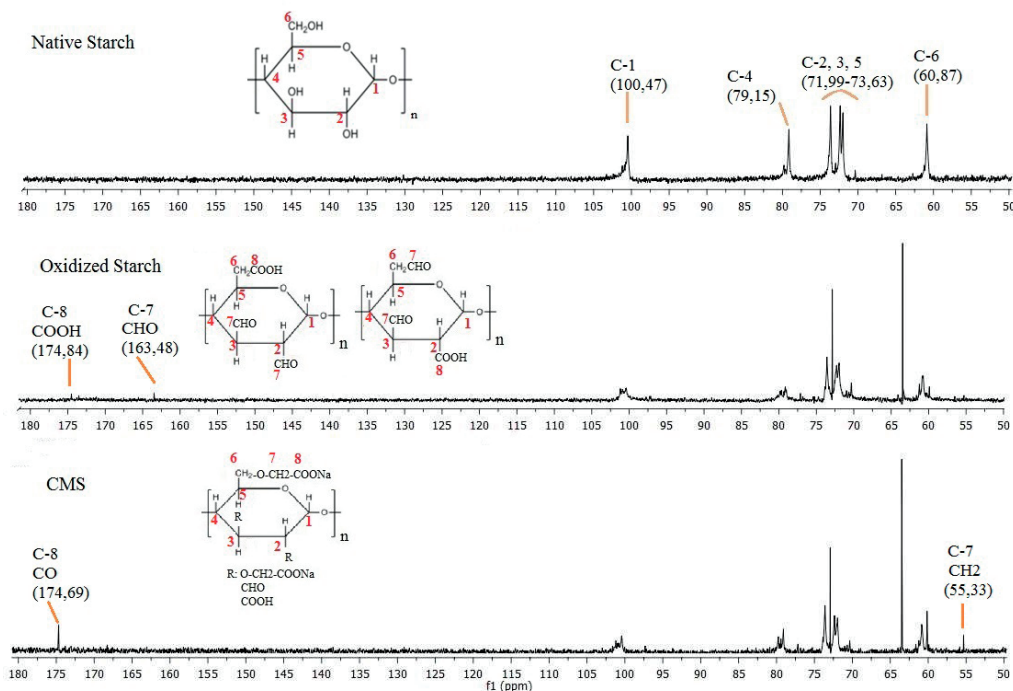


Figure 6.  $^{13}\text{C}$ -NMR spectra of native, oxidized and carboxymethylated starches

that the carboxymethylation process is carried out effectively. In addition, it is seen that the signal of C-1 in oxidized starch spectrum does not change remarkable in CMS spectrum. It confirms that carboxymethylation mostly takes place in the C-6 position.<sup>29</sup>

### Retanning and dyeing experiments

Hydrothermal stability and filling coefficient test results of the leathers retanned with 3, 5 and 10% of CMS were given in Table II. From the evaluation of the results, it was seen that the thicknesses and shrinkage temperatures of the leathers increased for all CMS treated samples in conjunction with increasing amount used in retanning. However, the maximum increments in shrinkage

temperature and filling coefficient were determined to be 5-6 °C and 6.3-7.1%, respectively with 10% CMS ratio which can be regarded as a noticeable solo performance for retanning.

### Consumption of Dyestuff

The amounts of dyestuffs remaining in the bath at the end of the dyeing processes are given in Table III. From the evaluation of the results, although a noticeable increase (amount of dyestuff remaining in the bath) was detected especially for the 10% of CMS retanned sample comparing with blank sample, in general considering the amounts of dyestuffs remaining in the baths (especially 3 and 5% of CMS introductions) it is possible to say that dye consumption values after CMS retannage are in acceptable limits and does not have drastic negative effect on it.

### Wet and dry rubbing fastness of dyed leather samples

Dry and wet rubbing fastness tests were applied to the CMS retanned and dyed leather samples in order to investigate possible effect of CMS retannage on dyed crust leathers' fastness properties.

Table II

The results of hydrothermal stability and filling coefficient gained to the wet-blue goat leathers

The Group Dyed with Acid Dyestuff		
CMS amount used in retanning	Filling coefficient (%)	Shrinkage temperature (°C)
(Control Sample)	0.7	109
3%	3.5	112
5%	4.4	113
10%	6.3	115
The Group Dyed with Metal-Complex Dyestuff		
CMS amount used in retanning	Filling coefficient (%)	Shrinkage temperature (°C)
(Control Sample)	0.9	109
3%	4.6	111
5%	6.4	112
10%	7.1	114

Table III

The amounts of dyestuffs remaining in dyeing baths (g/L)

CMS amount used in retanning	Acid Blue 25 (Acid Dyestuff)	Acid Blue 360 (Metal-Complex Dyestuff)
	Start conc. 60	Start conc. 60
Control sample	0.009	0.010
3%	0.022	0.019
5%	0.025	0.024
10%	0.036	0.071

**Table IV**  
Wet and dry rubbing fastness results of dyed leather samples

		Dry Rubbing		Wet Rubbing	
		Acid Dyestuff	Metal-Complex Dyestuff	Acid Dyestuff	Metal-Complex Dyestuff
Control	Leather	4/5	4/5	3/4	3/4
	Felt	4	4	2	4
3% CMS	Leather	3/4	4/5	4	3/4
	Felt	4	4	2/3	4
5% CMS	Leather	4	4/5	4	4
	Felt	4/5	4	2/3	4/5
10% CMS	Leather	4	4/5	4/5	4/5
	Felt	4/5	4	2	4/5

The test results were given in Table IV. From the evaluation of the results it was seen that use of CMS as retanning agent did not result in a remarkable effect on leathers' crust fastness properties. This also means that CMS retannage did not cause accumulation of dye on leather surface. However, predictably dying with metal-complex dyestuff resulted in better fastness properties comparing to dying with acid dyestuff especially for wet-rubbing tests.

#### Color Differences

Another important issue on retannage and dying is retanning agents' possible effect on color and shade depending on their structure and color. So as to determine any effect on color/shade, the colors of the CMS retanned leathers were measured and also compared with the control sample. The color measurements and comparisons with control sample data were given in Table V.

From the examination of the data (Table V), it was determined that the color slightly shifted towards green compared to the control sample in conjunction with increasing amount of CMS in leathers dyed with acid dyestuff which cannot be perceived with naked eye. However, in metal-complex dyed leathers, although any alteration

in shade was not detected, a significant alteration was detected in L value which means the color intensity of leathers increased by CMS introduction in retannage.

#### Conclusion

The molecular size of native corn starch ( $2.227 \times 10^6$  Da) which is too large to penetrate between leather fibers was reduced by  $H_2O_2$  oxidation (between 2737-2897 Da) then oxidized starch was also carboxymethylated. A series of analysis (water solubility, degree of substitution, FT-IR,  $^1H$ -NMR,  $^{13}C$ -NMR) were carried out for characterization and to investigate the structural changes by modifications. The results obtained from analysis confirmed that the modifications were successfully carried out. Considering the test and analysis results of the retanning performance of carboxymethyl starch, it was concluded that it showed a remarkable retanning effect in terms of filling property and shrinking temperature increment without any considerable adverse effect on dyestuff consumption, color fastness and color properties, which are also should be taken in account in performance evaluation of a retanning agent.

**Table V**  
Color measurement values of leathers retanned with CMS at different ratios and dyed afterwards

<i>The Group Dyed with Acid Dyestuff</i>							
Sample	L	a	b	dL	Da	db	dE
Control	33.71	0.49	-35.62				
3% CMS	34.39	-0.50	-34.08	0.68	0.99	1.54	1.95
5% CMS	35.38	-0.86	-37.01	1.67	1.35	1.39	2.56
10% CMS	34.23	-1.19	-35.51	0.52	1.68	0.11	1.76
<i>The Group Dyed with Metal-Complex Dyestuff</i>							
Sample	L	A	b	dL	Da	db	dE
Control	36.14	-1.24	-17.73				
3% CMS	33.09	-1.11	-17.36	3.05	0.13	0.37	3.08
5% CMS	34.53	-1.06	-17.18	1.61	0.18	0.55	1.71
10% CMS	32.25	-0.72	-16.63	3.89	0.52	1.10	4.08

Where: L: lightness / brightness (L=0 black, L=100 white), a: red/green color (+a red, -a green), b: yellow/blue color (+b yellow, -b blue) and dL, da, db and dE the changes in color compared to the control sample.



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