STRUCTURE AND TANNING PROPERTIES OF DIALDEHYDE CARBOXYMETHYL CELLULOSE: EFFECT OF DEGREE OF SUBSTITUTION

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Abstract. Developing novel tanning agents from renewable biomass is regarded as an effective strategy for sustainable leather industry. In this study, a series of dialdehyde carboxymethyl cellulose (DCMC) were prepared by periodate oxidation of carboxymethyl cellulose (CMC) with varying degree of substitution (DS: 0.7, 0.9 and 1.2). The structural properties of DCMC were characterized. Size Exclusive Chromatography measurements showed that CMC underwent severe degradation during periodate oxidation, resulting in the decline of weight-average molecular weight from 250,000 g/mol to around 13,000 g/mol. ^{1}H NMR and FT-IR analysis illustrated that aldehyde group was successfully introduced into DCMC. The aldehyde group content of DCMC decreased from 8.38 mmol/g to 2.95 mmol/g as the DS rose from 0.7 to 1.2. Interestingly, formaldehyde was found to be produced in DCMC, and its content was 3.45, 2.99 and 2.18mg/g, respectively when the DS of CMC was 0.7, 0.9 and 1.2, respectively. Further analysis by HPLC confirmed that glucose and fructose were formed during oxidative degradation, and were subsequently oxidized to generate formaldehyde. Higher DS resulted in lower formaldehyde content in DCMC. Tanning trials showed that the shrinkage temperature and thickening rate of DCMC tanned leather decreased as the DS increased. This should be due to the difference in aldehyde content of DCMC. Leather tanned by DCMC-0.7 (DS of CMC was 0.7) had the highest shrinkage temperature of 81°C and thickening rate of 76%. In general, we hope the work on dialdehyde tanning agent derived from CMC could provide some essential data for the development of sustainable tanning material and process.

1 Introduction

Carboxymethyl cellulose (CMC), an anionic linear polymer derived from cellulose, poses advantages of renewability, nontoxicity, excellent biocompatibility and biodegradability [1]. CMC is widely used in various fields including paper, textile, food, pharmaceutical industries and mineral processing[2]. It can be converted to its dialdehyde derivatives (DCMC) by periodate oxidization since sodium periodate can specifically oxidize the adjacent hydroxyl groups on C2 and C3 of the anhydroglucose unit (AGU) to form two aldehyde groups[3]. DCMC has been proved to be an ideal crosslinking agent for preparation of gelatin films and collagen cryogels since the Schiff's base is formed between aldehyde groups of DCMC and amino groups of gelatin or collagen[4,5]. Hence, DCMC is supposed to be used as tanning agent since leather is actually a collagen fiber matrix. It is known that the use of existing aldehyde tanning agents would introduce free formaldehyde into leather, leading to potential risk to human health. We hope the use of DCMC whose aldehyde groups are located on the polysaccharide chains could solve this problem.

With respect to the degree of substitution (DS) of CMC, three hydroxyl groups at the 2, 3, and 6 positions in AGU of cellulose can be substituted by carboxymethyl group. Thus, the average number of substituted hydroxyl groups per AGU, viz. DS, ranges from 0 to 3 theoretically[6]. The substitution reactivities of hydroxyl groups on C2 and C6 were equal and significantly higher than that on C3 when CMC was prepared by traditional slurry process[7,8]. Substitution on C2 may hinder the periodate oxidation of CMC and the formation of aldehyde group. This means that DS of CMC would probably affect the tanning performance of DCMC. Therefore, the aim of this study was to explore the effect of DS on the structure and tanning properties.

In the present work, CMC with DS of 0.7, 0.9 and 1.2 were oxidized to DCMC. The structural parameters of CMC and DCMC were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. Moreover, the aldehyde group content and formaldehyde content of DCMC were also determined. Then the tanning performance using DCMC with different DS was evaluated.

2 Materials and Methods

2.1 Materials

Sodium carboxymethyl cellulose (CMC) with DS of 0.7, 0.9 and 1.2 were of analytical grade and purchased from Sigma-Aldrich Co. LLC. (St. Louis, USA). Sodium periodate and hydroxylamine hydrochloride were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). Pickled cattle pelt was supplied by a local tannery. The other chemicals used in tanning were of commercial grade.

2.2 Preparation of DCMC and H-DCMC

Sodium periodate was solubilized in 500 mL distilled water away from light, then 25.0 g CMC (DS: 0.7, 0.9 and 1.2) was added into the sodium periodate solution under stirring at 25°C. The mol ratio of sodium periodate to monomeric unit of CMC was 1:1. After the mixture was stirred in the dark for 24 h, the oxidized product, referred to DCMC (Figure 1) was obtained.

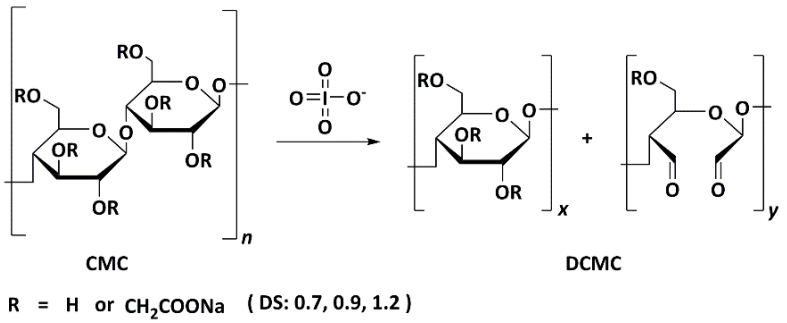

Figure 1. The illustration of periodate oxidization of CMC to DCMC.

25.0 g CMC (DS=0.7) was uniformly dispersed in 500 mL distilled water at 90°C. Then 5 mL concentrated hydrochloric acid was added into the blend under stirring with 1 h interval (totally 25mL). After hydrolysis for 6 h, the solution was cooled to room temperature and its pH was adjusted to 5.0 by the addition of a 50% (w/w) NaOH solution. This acid hydrolyzed CMC solution was labeled as H-CMC. Subsequently, sodium periodate with a mole ratio of 1:1 was added into H-CMC and stirred in the dark at 25°C for 24 h, then the oxidative product, labeled as H-DCMC, was acquired.

2.3 Determination of molecular weight

Weight-average molecular weight (Mw), number-average molecular weight (Mn) and polydispersity (Mw/Mn) of CMC and DCMC were determined by Size-exclusion chromatography (Malvern 270 max, Malvern Instruments, UK), equipped with a TSK-gel GMPWXL column (7.8 mm × 300 mm, Tosoh, Japan). Aqueous solution of CMC (2 mg/mL) and DCMC (5 mg/mL) were filtered through a 0.22 μm pore membrane to eliminate dust particles. The injection volume of sample was

100 µL. The eluent was 0.1 mol/L $NaNO_3$ at a flow rate of 0.6 mL/min under 30°C elution temperature. Molecular weight of samples was calculated using OmniSEC 4.7 software with a dn/dc value of 0.136 mL/g by the comparison to Shodex pullulan standard P-20 (2 mg/mL, Mw= 34.4×10^4 for CMC and Mw= 10.7×10^4 for DCMC, Showa Denko K.K., Japan)[9].

2.4 Nuclear magnetic resonance (NMR) spectroscopy

The ^1H NMR spectra of CMC and DCMC were acquired on a Bruker Avance II-400 spectrometer (Bruker, Germany) using D_2O as solvent at a concentration of 50 mg/mL.

2.5 Fourier transform infrared (FT-IR) spectroscopy

CMC and DCMC samples were lyophilized using LGJ-30F freezer dryer (XinYi, China). Then their FT-IR spectra were recorded by a FT-IR spectrophotometer (Thermo Scientific Nicolet IS10, USA). The discs containing sample and potassium bromide (KBr) were measured in the wavenumber region 500-4000 cm^{-1} at room temperature, using 32 scans and a resolution of 4 cm^{-1}.

2.6 Determination of aldehyde group content

The aldehyde group content of DCMC was determined by hydroxylamine hydrochloride method[10]. 0.1 g dried DCMC was dissolved in 25 ml distilled water. The pH of the solution was adjusted to 5.0 with 0.1 mol/L NaOH solution. 20 ml of 0.25 mol/L hydroxylamine hydrochloride (pH = 5.0) was added into the DCMC solution and the mixture was stirred for 4 h in the thermostated water bath at 40°C. Then 0.05 mol/L NaOH standard solution was used to titrate with the hydrochloric acid produced in the mixture and the consumption of NaOH solution was obtained. Thus, the aldehyde group content of DCMC was calculated via equation (1):

$$\text{Aldehyde group content}(\text{mmol/g}) = \frac{V_{NaOH}\times M_{NaOH}\times 0.001}{m} \quad (1)$$

where V_{NaOH} is the consumption of NaOH solution, M_{NaOH} is 0.05 mol/L and m is the dry weight of DCMC sample. Measurements were made in triplicate.

2.7 Determination of formaldehyde content

The determination of the formaldehyde content in DCMC aqueous solution was performed following ISO 27587-2009[11] with some modifications. 0.2 mL of 50 g/L DCMC solution was put into the U-tube and was incubated at 90°C. The released free formaldehyde in the sample was continuously purged by nitrogen gas and was collected by DNPH absorption solution. After 30 min, the DNPH absorption solution was kept in dark for 30-150 min and then filtrated through a 0.45 µm membrane filter. High Performance Liquid Chromatography (HPLC, 1260 Infinity II, Agilent, USA) with a CAPCELL PAK C18 MG II column (4.6mm × 150mm, Shiseido, Japan) was used to analyze the formaldehyde in DNPH absorption solution. The injection volume of sample was 20 µL. The eluent was the mixture of acetonitrile and distilled water (60%: 40%, v/v) at a flow rate of 1.0 mL/min under 30°C elution temperature. Then the target substance (formaldehyde phenylhydrazone) was detected by Diode Array Detector (DAD) at 360 nm. The formaldehyde content was calculated according to the standard calibration curves obtained by using formaldehyde standard solution with different concentrations.

2.8 DCMC tanning trials

Pickled cattle pelt was cut along the backbone into matched pieces. Then they were tanned with 4wt% DCMC of different DS (based on twice the weight of pickled pelt) at 25°C, respectively. The

initial tanning pH was 3.0. After penetration of DCMC for 4 h, the pH of tanning bath was increased to 7.8-8.0 by the controlled addition of sodium bicarbonate. Then the drum kept running for 4 h at 40°C and then left overnight. After running for 30 min next morning, the tanned leather was washed by water at 25°C for 10 min and then horsed up for 24 h.

Two small pieces of each group of leather were sampled for shrinkage temperature (Ts) test using a digital leather shrinkage temperature instrument (MSW-YD4, Shanxi University of Science and Technology, China).

Thickness of pickled pelt and leathers tanned by DCMC was measured using a digital display thickness gauge (MY-3130-A2, Ming Yu, China). The thickening rate was calculated by the equation (2):

$$\text{Thickening rate } (\%) = \frac{T_a - T_b}{T_a} \times 100 \quad (2)$$

where T_a represents the thickness of DCMC tanned leather and T_b is the thickness of pickled pelt.

2.9 Constituents analysis of DCMC

Constituents analysis of DCMC was performed by HPLC (1260 Infinity II, Agilent, USA) using an Aminex column (model HPX-87H, 300 mm × 7.8 mm, Bio-Rad) and a RI detector. 5 mmol/L H_2SO_4 solution was used as the mobile phase at a flow rate of 0.6 mL/min. The temperature of column and RI detector was maintained at 50°C[12]. The components in DCMC were quantified by comparison with standard calibration curves obtained by using authentic chemicals with different concentrations. The yield of products was calculated following equation (3):

$$\text{Yield (wt\%)} = \frac{\text{Weight of products}}{\text{Weight of raw material}} \times 100\% \quad (3)$$

3 Results and discussion

3.1 Molecular weight

The molecular weights (M_w and M_n) and polydispersities (M_w/M_n) of CMC and DCMC (DS=0.7, 0.9 1.2) are shown in Table 1. The molecular weight decreased remarkably after periodate oxidization owing to the concomitant degradation during oxidization of CMC. In addition, DS of CMC had little impact on molecular weight of DCMC for Mw of the three samples were all around 12000-16000.

Table 1. The molecular weights of CMC and DCMC

DS	Sample	M_w	M_n	Mw/Mn
0.7	CMC	419540	200257	2.095
	DCMC	12319	2931	4.202
0.9	CMC	225461	64346	3.504
	DCMC	15572	2594	6.003
1.2	CMC	255047	127352	2.003
	DCMC	13594	2878	4.722

3.2 ^{1}H NMR

The successful preparation of DCMC was confirmed by ^{1}H NMR as given in Fig 2. Three new chemical shifts were obtained in the ^{1}H NMR spectra of DCMC compared with that of CMC. The most

pronounced peak at δ=8.38 ppm was considered as aldehyde group[13,14]. The aldehyde group was also present as the hemiacetal form as judged by chemical shift at δ=4.8-5.5 ppm[15,16]. The intramolecular hemiacetal was formed between the dialdehyde groups and hydroxyl groups of neighboring unoxidized AGU [17]. Moreover, the assignment of δ=9.20 ppm to aldehyde proton was consistent with a typical ^{1}H-chemical shift region of aldehydes[18].

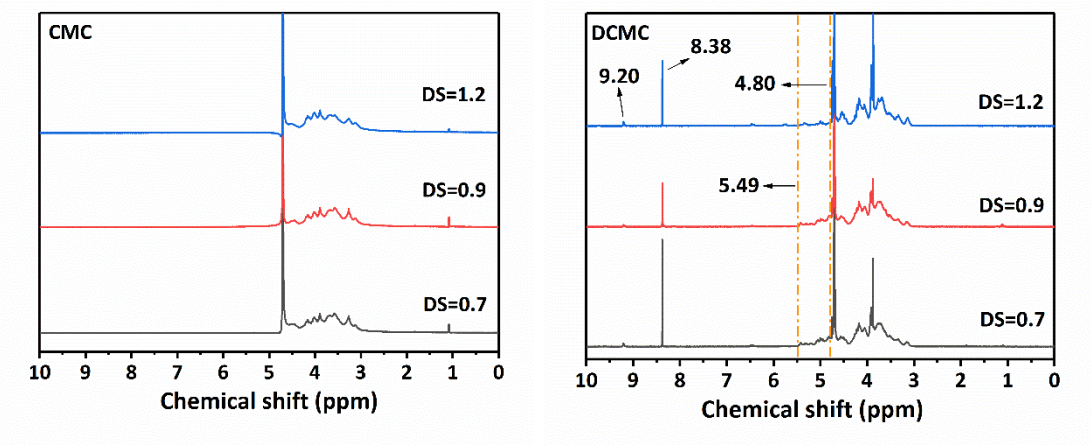

Figure 2. ^{1}H NMR spectra of CMC and DCMC.

3.3 FT-IR

FT-IR analysis was used to further support the formation of aldehyde groups in DCMC (Figure 3). A new IR band appeared at 1737 cm^{-1} region in DCMC, which was attributed to the stretching vibration of aldehyde group[19]. The absorption peaks at 1606 and 1424 cm^{-1} were assigned to the asymmetric and symmetric stretching vibration of carboxylate group, respectively[20]. The absorption peak at 896 cm^{-1} indicated the presence of the hemiacetal bond between aldehyde group and neighbor hydroxyl group, which was in correspondence with the result of ^{1}H NMR[21]. A broad band occurred at 3434 cm^{-1} was assigned to the stretching vibrations of hydroxyl group[21]. The number of hydroxyl group in DCMC declined notably compared with those in CMC because the hydroxyl groups were mostly oxidized. In addition, the absorption bands at 2915 cm^{-1} and 1326 cm^{-1} were attributed to CH stretching, CH_2 stretching respectively[21,22].

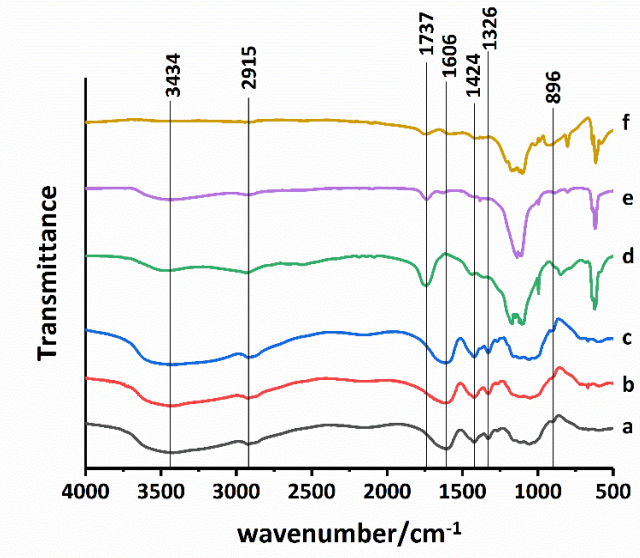

Figure 3. FT-IR spectra of CMC and DCMC. a) CMC (DS=0.7); b) CMC (DS=0.9); c) CMC(DS=1.2); d) DCMC (DS=0.7); e) DCMC(DS=0.9); f) DCMC (DS=1.2).

3.4 Aldehyde group and formaldehyde in DCMC

The aldehyde group content and formaldehyde content of DCMC are shown in Figure 4. The aldehyde group content declined along with the increased DS, which may result from the decreased number of adjacent hydroxyl group in CMC since the hydroxyl group in C2 tended to be substituted by carboxymethyl group. Surprisingly, formaldehyde was detected in DCMC. The formaldehyde content also decreased with the increased DS. The reason for formaldehyde formation will be explored in the following section.

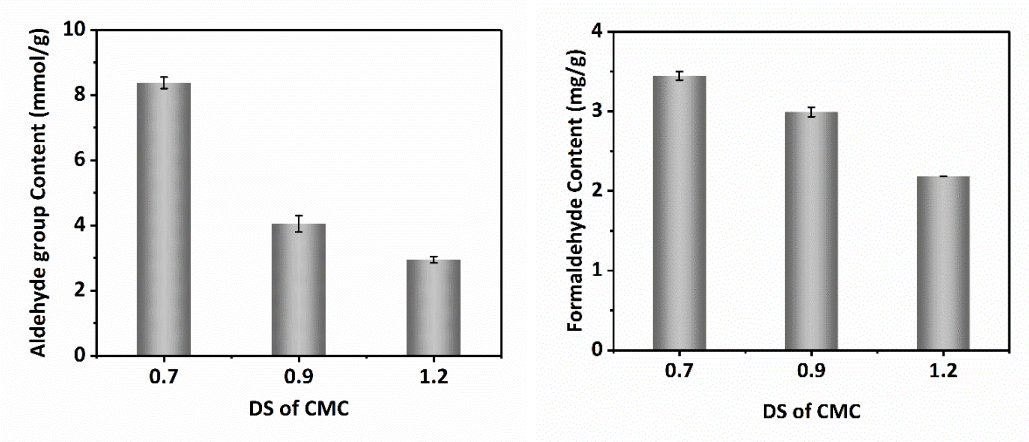

Figure 4. The content of aldehyde group and formaldehyde of DCMC.

3.5 Constituents analysis of DCMC

Figure 6 shows the HPLC spectra of DCMC and a mixed standard solution containing D-(+)-Glucose, D-(-)-Fructose, formic acid and other small-molecule acids. Formic acid (peak c at 13.7min in Figure 5) was detected in DCMC by HPLC with a RI detector. Additionally, formaldehyde was also detected in DCMC (Figure 4). Degradation of CMC with the cleavage of 1-4-glycosidic bond occurred during periodate oxidization[23]. Accordingly, oligosaccharide or even monosaccharide would be generated. If further oxidation is allowed to proceed, the formaldehyde and formic acid which were already monitored in the periodate oxidation products of D-glucose (Table 2) are likely to be produced[24]. Additionally, the content of formaldehyde and formic acid were negatively correlated with DS of CMC as shown in Table 2. The decreasing number of hydroxyl group with the increase of DS leads to the less yield of monosaccharide, which subsequently contributes to the fewer content of formic acid as well as formaldehyde. All in all, it was estimated that the small-molecule degradation products of CMC such as glucose yields formaldehyde since formic acid and formaldehyde are usually the oxidative products of monosaccharide. Nevertheless, glucose was undetected in DCMC by the means of HPLC, which may owe to the low content of glucose in DCMC and the rapid reaction between sodium periodate and monosaccharide so that the glucose was consumed thoroughly within a short time.

Herein, in order to achieve a more drastic degradation of CMC, hydrolysis using concentrated hydrochloric acid was performed on CMC (DS=0.7) before periodate oxidation. Glucose was found in the hydrolysate of CMC (H-CMC). Furthermore, one of the oxidative products of fructose (d at 9.27min in Figure 7), which was in correspondence with the oxidized fructose (B in Figure 7), existed in H-CMC too. Consequently, glucose and fructose were produced during the hydrolysis of CMC. It was found that glucose in H-CMC was entirely consumed after oxidization. At the same time, the substance d (Figure 7) was still remained in H-DCMC and the content of formic acid in H-DCMC was far more than that in H-CMC, as shown in Table 2. A great deal of formaldehyde was produced after oxidization of H-CMC while there was no formaldehyde in H-CMC. Hence, the conceivable sources

of formaldehyde in DCMC were as follows (Figure 8): 1. Glucose produced during oxidation of CMC was oxidized by sodium periodate to form formaldehyde; 2. Glucose was isomerized to fructose, then the periodate oxidation occurred on fructose and formaldehyde was generated[25].

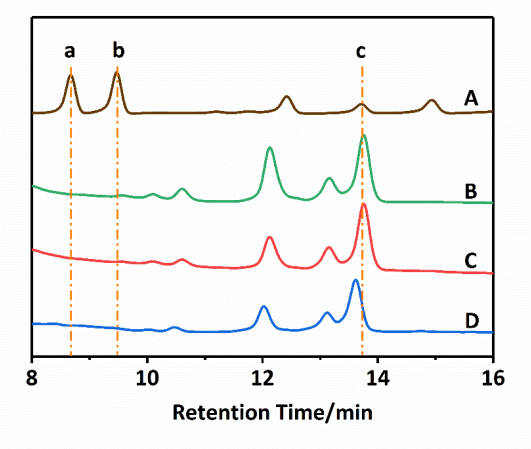

Figure 5. HPLC spectra of DCMC. A) The mixed standard solution; B) DCMC (DS=1.2); C) DCMC (DS=0.9); D) DCMC (DS=0.7); a) D-(+)-Glucose; b) D-(-)-Fructose; c) formic acid.

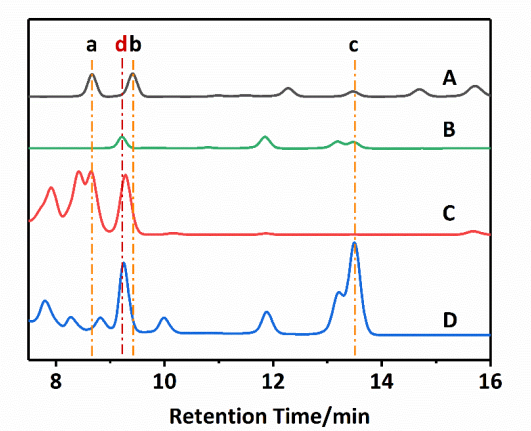

Figure 6. HPLC spectra of H-CMC and H-DCMC A) The mixed standard solution; B) Oxidized fructose (mole ratio of $NaIO_4$/fructose was 5:1); C) H-CMC (DS=0.7); D) H-DCMC (DS=0.7); a) D- (+) -Glucose; b) D- (-) -Fructose; c) formic acid; d) one of the oxidative products of fructose.

Table 2. Yield of formaldehyde and formic acid in oxidized fructose, DCMC and H-DCMC.

Sample	Yield (wt%)	
	Formaldehyde	Formic acid
oxidized fructose	11.37	46.81
DCMC-0.7	0.34	1.37
DCMC-0.9	0.30	1.33
DCMC-1.2	0.22	0.53
H-CMC-0.7	0	0.08
H-DCMC-0.7	0.70	15.01

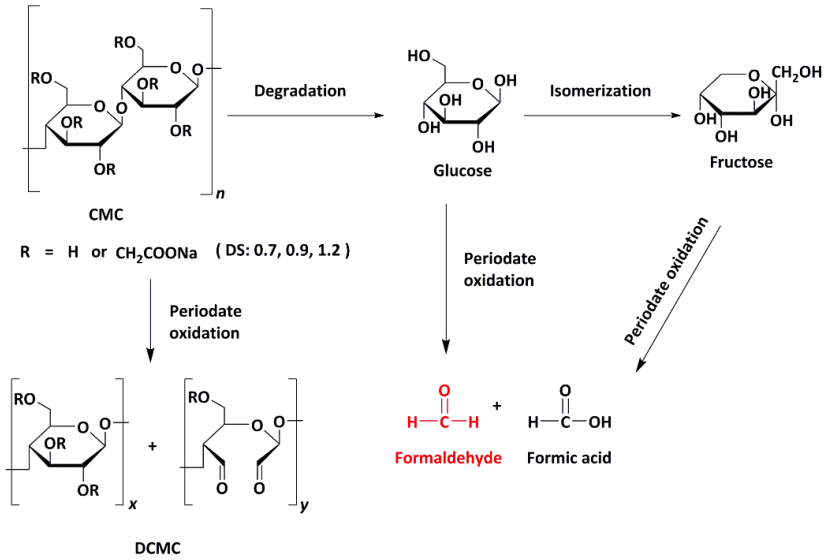

Figure 7. The illustration of the production of formaldehyde accompany with periodate oxidation of CMC.

3.6 DCMC tanning properties

DCMC were used in tanning of leather in order to investigate the effect of DS on tanning performance. Ts is often used to characterize the hydrothermal stability of leather[26]. As shown in Figure 8, an increase in the DS from 0.7 to 1.2 brought about a decrease in the Ts of leathers, which may stem from the descensive aldehyde group content of DCMC. Leather tanned with DCMC-0.7 exhibited highest Ts of 81°C and thickening rate of 76%.

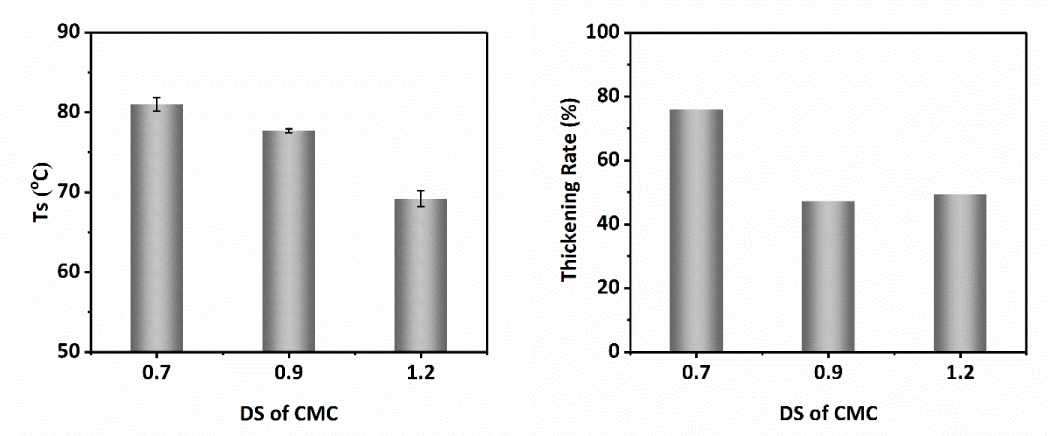

Figure 8. Shrinkage temperature and thickening rate of leathers tanned with DCMC (DS: 0.7, 0.9, 1.2).

4 Conclusion

CMC with DS of 0.7, 0.9 and 1.2 were successfully converted to DCMC. The tanning effect of DCMC was negatively correlated with DS of CMC due to the declined content of aldehyde group of DCMC. Interestingly, formaldehyde was found in DCMC. The mechanism of formaldehyde formation accompany with the periodate oxidation of CMC was investigated. The formaldehyde and formic acid, which are usually the products of periodate oxidation of monosaccharide, were detected in the DCMC. The components of H-CMC were proved containing formic acid, glucose and one of the oxidative products of fructose. After oxidation of H-CMC, formaldehyde was released and the

content of formic acid rose greatly. Simultaneously, the glucose which originally existed in H-CMC was absolutely consumed while one of oxidative products of fructose remained after oxidation. The results suggest that the glucose and its isomer, viz. fructose are the main sources of formaldehyde. The finding about formaldehyde formation is promising and should be validated by the further analysis of dialdehyde polysaccharide.

5 Acknowledgements

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