Oxidized Maltodextrin: A Novel Ligand for Aluminum–Zirconium Complex Tanning

by

Xueru Guo,[1] Yue Yu,[1,1*] Ya-nan Wang[1,2,**] and Bi Shi[1,2]
[1]*National Engineering Research Center of Clean Technology in Leather Industry,*
Sichuan University, Chengdu 610065, China
[2]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education,*
Sichuan University, Chengdu 610065, China

Abstract

Hydrogen peroxide (H_2O_2) oxidized maltodextrin was prepared as the ligand for aluminum–zirconium complex tanning. The effects of catalyst dosage, initiation temperature, and H_2O_2 dosage on maltodextrin oxidation were investigated. FT-IR analysis demonstrated that carboxyl groups were successfully introduced into oxidized maltodextrin. The carboxyl content and degradation degree of oxidized maltodextrin increased with the increase of H_2O_2 dosage. Maltodextrin oxidized by 40% H_2O_2 and 0.015% Cu–Fe catalyst at an initiation temperature of 70°C (OD-40) with moderate carboxyl group (6.75 mmol/g) and molecular weight (M_w 450) promoted the penetration and fixation of aluminum–zirconium salts in leather and showed better tanning performance, such as hydrothermal stability and porosity of leather, than traditional citric acid ligand.

Introduction

Developing effective chrome-free tannages to eliminate chrome discharge from the source is one of the key tasks of sustainable development of leather industry.[1-4] Aluminum and zirconium salts have been regarded as alternatives to chrome tanning agent for a long time due to their similar tanning effects with chrome salts.[5-7] However, aluminum and zirconium salts possess relatively high hydrolysis and olation ability,[8] thereby resulting in their fixation on leather surface and uneven distribution through the cross-section. As a result, leather tanned with aluminum/zirconium salts commonly shows unsatisfactory physical and organoleptic properties such as rough and stiff handle.

There are two possible ways to solve the problem. The first one is to combine aluminum and zirconium salts together and form a heteronuclear complex tanning agent.[9] The second one is to introduce ligands (masking agents for tanning) into the complexes.[10] These modifications aim to slow down the reactivity and raise the alkali resistant ability of Al(III)/Zr(IV). Thus, hydrolysis and olation of aluminum/zirconium salts will be inhibited to some extent and tanning performance is expected to be improved.[8] Some hydroxy carboxylic acids, such as lactic acid, citric acid, malic acid and tartaric acid, were reported as ligands of aluminum/zirconium complexes before.[9,10] However, limited enhancement to the tanning performance was achieved and few practical examples of industrial scale were performed. This result should be attributed to the inappropriate coordination ability and molecular size of the present ligands. Therefore, it is necessary to seek new ligands and clarify their structure-property relations in the development of metal complex tannage.

Our previous work reported a type of highly-oxidized starch (HOS) prepared using H_2O_2 and its application as ligand for zirconium and aluminum-zirconium complex tanning.[11-14] The multiple hydroxyl groups on the anhydroglucose unit of starch were oxidized into carboxyl groups by H_2O_2, accompanied by the degradation of starch. An optimized HOS ligand with proper carboxyl content and molecular weight was obtained through regulating oxidation degree and the complex tanning performance was proven to be upgraded when HOS was introduced into the tanning system. The major difficulty of this technology occurred in the preparation of HOS. Starch, as a natural polymer, was in high viscosity and low concentration when dissolved in water,[15] thereby leading to severe oxidation conditions and high dosage of H_2O_2 during production. In addition, the product quality was hard to control.

Maltodextrin, produced from starch by enzymatic hydrolysis, exhibits lower molecular weight and higher solubility than starch,[16] which may favor the control of the oxidation reaction and industrial production of high-solid-content ligand. In this study, oxidized maltodextrin ligand using H_2O_2 was prepared under relatively mild oxidation conditions. Effects of catalyst dosage, initiation temperature and H_2O_2 dosage on maltodextrin oxidation were investigated. The relationship between the structure of oxidized product and the tanning performance of aluminum–zirconium–oxidized maltodextrin complexes was explored. We hope this work will provide a promising and practical chrome-free tannage for sustainable development of leather industry.

Corresponding author emails: *yuyue@scu.edu.cn, **wangyanan@scu.edu.cn
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Experimental

Materials

Maltodextrin (DE value of 19) and hydrogen peroxide (50 wt%) were of commercial grade and provided by a leather chemical company. Pickled cow hides were supplied by a tannery in Jiangsu Province, China. Amberlite IR120 strong-acid cation exchange resin was purchased from Sigma-Aldrich LLC. The other chemicals used for analysis were of analytical grade. The chemicals used for leather processing were of industrial grade.

Preparation of Oxidized Maltodextrin

Four hundred grams of maltodextrin was dissolved in 267 g water. Different amounts (0.005%, 0.010%, 0.015% and 0.025%, based on the weight of maltodextrin, the same below) of catalyst ($CuSO_4 \times 5H_2O$ and $FeSO_4 \times 7H_2O$ in a mass ratio of 2:8) were introduced, and then a certain amount of H_2O_2 (20%, 30%, 40%, 50% and 60%, respectively) was dropwise added under stirring at different temperatures (60, 70, 80 and 90°C). After the addition of H_2O_2, the oxidation proceeded at 90°C for another 1 h to obtain the product. During this period, samples were collected at 0, 15, 30, 45 and 60 min for measuring decomposition rate of H_2O_2, carboxyl content and colority. The products oxidized by different amounts of H_2O_2 were marked as OD-20 (oxidized by 20% H_2O_2, similarly hereinafter), OD-30, OD-40, OD-50 and OD-60.

Determination of Decomposition Rate of H_2O_2

Iodometric titration method was used for determining the decomposition rate of H_2O_2.[11] In brief, oxidized maltodextrin samples were mixed with sulfuric acid, potassium iodide and ammonium molybdate, kept in a dark place for 10 min, and then titrated with sodium thiosulfate. Maltodextrin solution was used for the blank titration. The concentration of H_2O_2 in the samples was calculated. Decomposition rate of H_2O_2 was then calculated by the initial and the final H_2O_2 concentrations of the reactant/product.

Determination of Carboxyl Content

Acid-alkali titration method was used for determining the carboxyl content of oxidized maltodextrin samples.[11] In brief, the sample was loaded on a column (3.0 cm × 75 cm) filled with strong-acid cation exchange resin, and then eluted with ultrapure water. The eluate was titrated with sodium hydroxide using phenolphthalein as indicator. Maltodextrin solution was used for the blank titration. The carboxyl content of sample was calculated.

Determination of Colority

Platinum-cobalt colorimetric method was used for determining the colority of oxidized maltodextrin samples.[17] The sample solution was diluted 25 times with ultrapure water, and then the colority of diluent was measured by a Pt-Co colorimeter (EC 2000, Loviband, UK). Ultrapure water was used for the background correction.

Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

The FT-IR spectra of maltodextrin and oxidized maltodextrin samples were obtained using a FT-IR spectrometer (Nicolet 6700, Thermo Scientific, USA). Oxidized maltodextrin samples were lyophilized using a freezer dryer (LGJ-30F, Xinyi, China). The mixture of sample and potassium bromide was pressed into a thin disk before analysis.

Determination of Molecular Weight and Particle Size

The weight-average molecular weight (M_w) of maltodextrin and oxidized maltodextrin samples were measured by gel permeation chromatography (Viscotek 270maxGPC, Malvern, UK).[11] The sample solution with a mass concentration of 10 mg/mL was filtered through a 0.25 μm microporous membrane. Then, 100 μL filtrate was injected into a column (7.8 cm × 30 cm, TSK-gel GMPWXL, Tosoh, Japan) and eluted by 0.1 mol/L $NaNO_3$ at a flow rate of 0.6 mL/min under 40°C. The Shodex pullulan standard P-5 (2 mg/mL, M_w 6.1×10^3, Showa Denko K.K., Japan) was used for reference. The calculation of molecular weight of the sample was performed using OmniSEC 4.7 software with a dn/dc value of 0.146 mL/g. The particle size of samples (200 mg/mL) was determined using a particle size analyzer (Nano Brook Omni, Brookhaven, US) with a test temperature of 30°C and an equilibration time of 3 min.

Tanning Trials

One pickled cattle hide was cut along the back bone into matching pieces (50 cm × 40 cm) for the tanning trials. They were weighed and tanned with aluminum–zirconium salts (70 wt% $Al_2(SO_4)_3{\cdot}18H_2O$ and 30 wt% $Zr(SO_4)_2{\cdot}4H_2O$) and different ligands (OD-20, OD-30, OD-40, OD-50, and OD-60) as shown in Table I. A group without any ligand was used as control. Another group with citric acid (CA) ligand was performed for comparison. All groups were named after the name of the ligands, except for the control. The shrinkage temperature (T_s) of the wet white was measured using a shrinkage temperature tester (MSW-YD4, Sunshine Electronic Research Institute, China). The wet white was split into three uniform layers and dried to constant weight at 102°C. Metal oxide content (the sum of Al_2O_3 and ZrO_2, based on the weight of dry leather) of each layer and the whole leather were determined using ICP-OES (Optima 8000, PerkinElmer, USA). The metal oxide content in grain layer was named as G, in middle layer was named as M, and in flesh layer was named as F. The distribution uniformity of tanning agent was calculated as: [12]

$$\text{Distribution uniformity (\%)} = \frac{2 \times M}{G + F} \times 100$$

The wet white was lyophilized using a freezer dryer, and its cross-section was observed using SEM (JSM-7500F, JEOL, Japan). The porosity of the wet white was measured by mercury intrusion porosimetry using AutoPore IV 9500 analyzer (Micromeritics, USA).[18]

Table I

Al–Zr complex tanning process for cattle hide

Process	Chemicals	Dosage[a] (%)	Temperature (°C)	Time (min)	Remarks
Tanning	Water	80	25		
	Sodium chloride	5.6		30	
	Aluminum–zirconium salts	8.5			
	Ligand	1.2		240	
Basification	Magnesium oxide	1.2		100	
	Sodium bicarbonate	0.2 × n		15 × n	pH 4.0
	Water	200	40	120	Overnight
Next day run for 30 min and drain → Horse up for 24 h					

[a] The percentage of chemicals in Al–Zr complex tanning was based on limed pelt weight.

Table II

Post-tanning process

Process	Chemicals	Dosage[a] (%)	Temperature (°C)	Time (min)	Remarks
Rewetting	Water	400	35		
	Degreasing agent	0.5		40	
	Water	400 × 2		10 × 2	
Neutralizing	Water	200	35		
	Neutralizing syntan	2			
	Sodium formate	1		30	
	Sodium bicarbonate	0.6 × 2		15 + 60	pH 6.0
	Water	400 × 2		10 × 2	
Fatliquoring	Water	150	50		
	Synthetic fatliquor	15		60	
	Formic acid	0.5 × 4		15 × 4	pH 3.8
	Water	200	25	15	
Horse up overnight → Hang drying → Conditioning → Milling					

[a] The percentage of chemicals in post-tanning was based on shaved wet white weight.

The wet white was wrung and shaved to uniform thickness (1 mm), and then post-tanning was performed as shown in Table II to obtain the crust leather. The crust leathers were conditioned for 48 h at 20°C and 65% RH, and then their physical properties, such as softness, tensile strength, tear strength, and bursting strength were measured.

Results and Discussion

Effect of Catalyst Dosage on Maltodextrin Oxidation

The hydroxyl groups on maltodextrin were oxidized into carboxyl groups by H_2O_2. Salts of Cu–Fe can be used as catalysts in the oxidation.[12] Figure 1 shows the effect of catalyst dosage on maltodextrin oxidation. The oxidation reaction was not conducted efficiently without catalyst, as the decomposition rate of H_2O_2 and carboxyl content of oxidized maltodextrin were both low. The decomposition rate of H_2O_2 was enhanced with the increase of catalyst dosage, thereby resulting in the increase of carboxyl content of oxidized maltodextrin. When the amount of catalyst was 0.015%, H_2O_2 was exhausted in 15~30 min, and the carboxyl content stabilized at around 6.4 mmol/g. Further addition of catalyst dosage and reaction time did not improve the oxidation degree. Thus, the catalyst dosage was set to be 0.015%. It should be noted that the color of product became dark brown gradually once H_2O_2 was exhausted (see colority in Figure 1c), which may give leather unexpected color during tanning. This phenomenon can be explained by the dehydration reaction of sugar and formation of colored substances.[19,20]

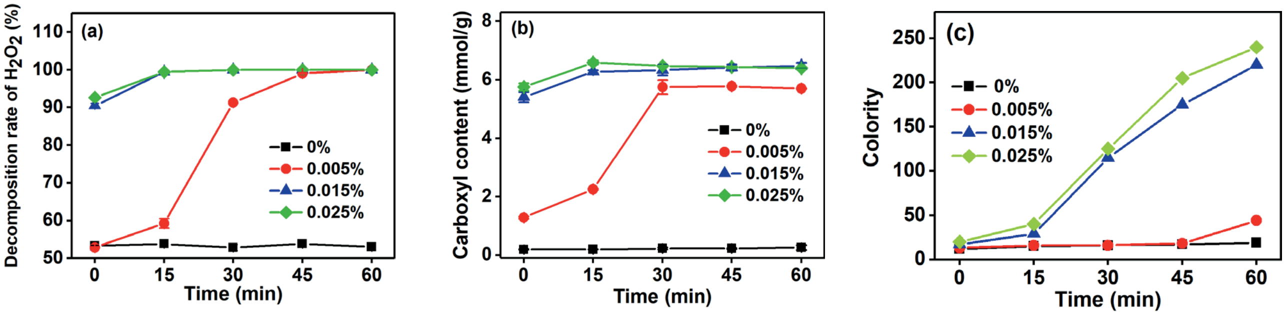

Figure 1. Effects of catalyst dosage on decomposition rate of H_2O_2 **(a)**, carboxyl content **(b)** and colority **(c)** of oxidized maltodextrin (H_2O_2 dosage 40%, initiation temperature 70°C).

Effect of Initiation Temperature on Maltodextrin Oxidation

Oxidation by H_2O_2 under acidic condition follows a free-radical mechanism in presence of Cu–Fe salts. The formation of hydroxyl free radicals may be influenced by the initiation temperature. Figure 2 shows the effect of initiation temperature on maltodextrin oxidation. The decomposition of H_2O_2 was almost complete when the initiation temperature ranged from 60 to 90°C. The carboxyl content (representing oxidation degree) reached a peak at the initiation temperature of 70°C. Further raising the initiation temperature resulted in a slight decline of the carboxyl content. This result may be attributed to the higher risk of ineffective decomposition of H_2O_2 into water and oxygen under higher temperature.[21] The colority of product showed a small growth with the increase of initiation temperature. Thus, the initiation temperature was set to be 70°C in consideration of oxidation degree and energy consumption.

Effect of H_2O_2 Dosage on Maltodextrin Oxidation

The effect of H_2O_2 dosage on maltodextrin oxidation is shown in Figure 3. In 30 min H_2O_2 was almost exhausted for each group, and the carboxyl content of oxidized maltodextrin formed a plateau from this point on. Then the colority of product rose sharply. The carboxyl content of product had a positive correlation with the H_2O_2 dosage, indicating a gradual growth of oxidation degree with the increase of H_2O_2 addition.

FT-IR spectra (Figure 4) also show that a new peak at 1733 cm^{-1} is found in each of the oxidized maltodextrin compared with the spectrum of maltodextrin. This peak is assigned to the stretching vibration of carbonyl groups,[22] demonstrating that carboxyl groups were introduced into oxidized product. The intensity of the peak is enhanced with the increase of H_2O_2 dosage, which is in accordance with the carboxyl content shown in Figure 3b. Moreover, Peaks

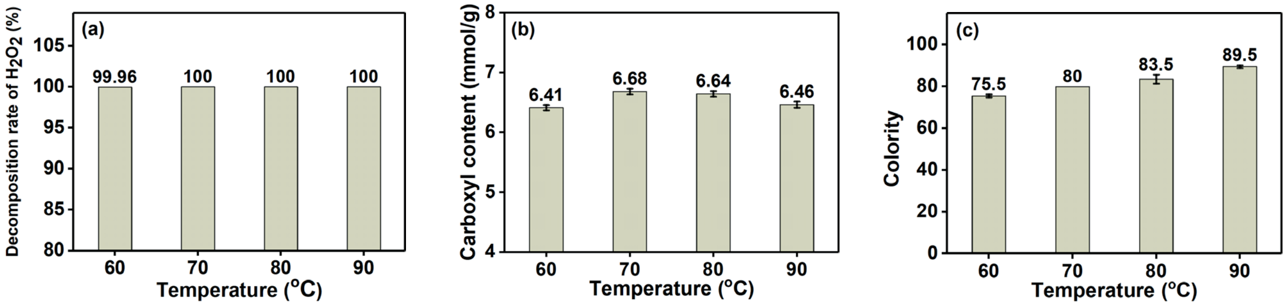

Figure 2. Effects of initiation temperature on decomposition rate of H_2O_2 **(a)**, carboxyl content **(b)** and colority **(c)** of oxidized maltodextrin (H_2O_2 dosage 40%, catalyst dosage 0.015%).

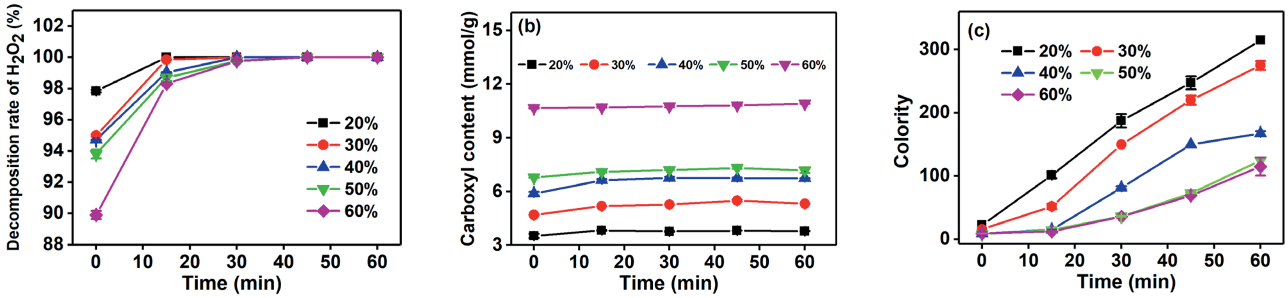

Figure 3. Effects of H_2O_2 dosage on decomposition rate of H_2O_2 **(a)**, carboxyl content **(b)** and colority **(c)** of oxidized maltodextrin (catalyst dosage 0.015%, initiation temperature 70°C).

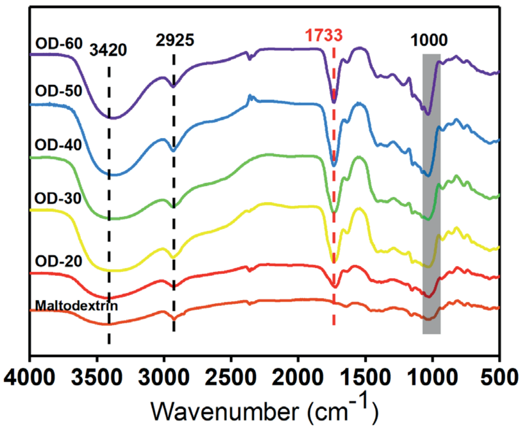

Figure 4. FT-IR spectra of maltodextrin and oxidized maltodextrin with different H_2O_2 dosages.

at 3420 cm^{-1} (stretching vibration of –OH), 2925 cm^{-1} (stretching vibration of C–H) and band around 1000 cm^{-1} in the fingerprint region (C–O and C–C bond stretching) suggest the presence of glucosidic ring structure in the oxidized maltodextrin.[11]

Previous work reported that H_2O_2 can break down the glycosidic bond during oxidation, resulting in the degradation of polysaccharide.[23] The M_w, M_w distribution and average particle size shown in Figure 5 suggest that maltodextrin was also degraded dramatically during oxidation, and the extent of degradation enhanced with the increase of H_2O_2 dosage. In combination of the results in Figure 3, the oxidized maltodextrin with smaller molecular size had higher content of carboxyl groups. To optimize the H_2O_2 dosage and obtain the suitable oxidized maltodextrin ligand for Al–Zr complex tanning, further investigation on the tanning performance will be discussed later.

Tanning Performance

Maltodextrin oxidized by varying H_2O_2 dosages was used as ligand of aluminum–zirconium salts for tanning, and thus the relationship between structure (carboxyl content and molecular weight) and tanning performance of oxidized maltodextrin can be elucidated. Here we use shrinkage temperature of tanned leather, distribution uniformity of tanning agent, porosity and morphology of leather fiber network to characterize tanning performance (Table III and Figure 6).

The control group without any ligand exhibited much lower results than the groups with ligand (Table III), which reconfirmed that masking agents can promote the penetration and tanning effects of aluminum–zirconium salts. Among the OD groups, OD-40 with moderate carboxyl content (6.75 mmol/g, Figure 3b) and M_w (450) showed better tanning performance. The hydrothermal stability and tanning agent content (shown as metal oxide content) of leather, and distribution uniformity of tanning agent were all higher than those of the other groups, and the extent of fiber dispersion was greater in terms of porosity and SEM analysis showing the fiber network. OD with more carboxyl groups (also lower molecular weight) possessed a stronger complexing effect with Al and Zr ions, leading to the weaker binding ability of metal complexes to collagen fibers at the beginning of tanning. Thus, more uniform penetration and distribution of tanning agent can be achieved. However, too many carboxyl groups on the ligand tend to occupy all the complexing sites of the metal ions and hinder the coordination of the complexes with collagen fiber. This fact can be proven by the decreased metal oxide content of OD-50 (7.21 mmol/g carboxyl, Figure 3b), OD-60 (10.77 mmol/g carboxyl, Figure 3b) and CA (15.62 mmol/g carboxyl) groups compared with OD-40 group, as shown in Table III.

Sufficient tanning effects are supposed to result in satisfactory physical and organoleptic properties of crust leather.[13] Table IV shows that crust leather from OD-40 group indeed had superior softness and mechanical strengths compared with the other ones. Based on all the results above, OD-40 was chosen as the optimal oxidized maltodextrin ligand for aluminum–zirconium complex tanning.

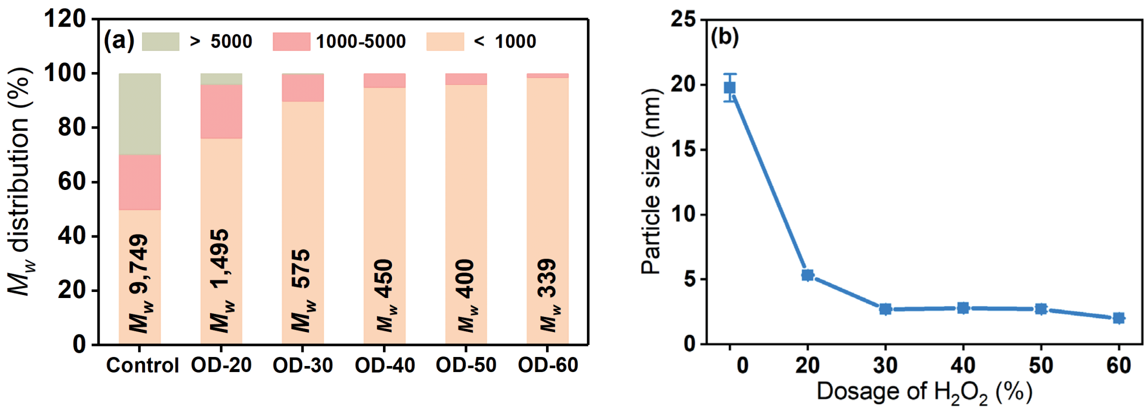

Figure 5. Effect of H_2O_2 dosage on the molecular weight distribution **(a)** and average particle size **(b)**

Table III

Properties of tanned leather

Group	Shrinkage temperature (°C)	Distribution uniformity of tanning agent (%)	Metal oxide content (%)	Porosity (%)
Control	75.6 ± 3.1	46.6 ± 1.3	2.2 ± 0.5	48.0 ± 5.9
CA	83.2 ± 0.6	62.8 ± 1.7	2.9 ± 0.1	51.9 ± 0.2
OD-20	80.3 ± 0.2	60.3 ± 2.7	3.8 ± 0.2	50.9 ± 2.2
OD-30	81.8 ± 0.4	70.1 ± 4.5	3.9 ± 0.1	51.2 ± 6.4
OD-40	84.4 ± 0.7	79.2 ± 8.6	4.3 ± 1.6	59.4 ± 7.6
OD-50	81.7 ± 0.6	70.4 ± 12.0	4.3 ± 1.0	53.7 ± 2.6
OD-60	80.1 ± 0.1	73.7 ± 17.0	4.0 ± 1.6	52.7 ± 1.8

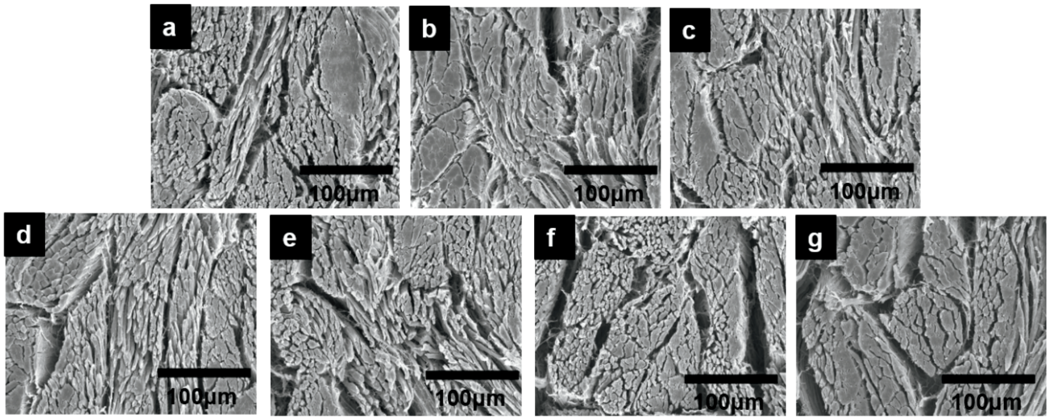

Figure 6. SEM images showing the cross-section of tanned leather (**a** control, **b** CA, c OD-20, **d** OD-30, **e** OD-40, **f** OD-50, **g** OD-60)

Table IV

Physical properties of crust leather

Group	Softness (mm)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Bursting strength (N/mm)
Control	6.9 ± 0.8	13.5 ± 0.1	51.1 ± 4.9	230.6 ± 16.1
CA	6.9 ± 0.8	12.6 ± 1.1	55.3 ± 0.1	246.0 ± 15.7
OD-20	8.2 ± 1.0	13.4 ± 1.0	53.7 ± 4.0	218.7 ± 1.3
OD-30	8.5 ± 0.8	13.3 ± 2.7	57.6 ± 3.6	291.5 ± 11.4
OD-40	9.3 ± 0.3	17.6 ± 3.4	67.2 ± 1.5	300.7 ± 21.2
OD-50	9.1 ± 0.4	16.1 ± 7.6	63.6 ± 4.1	362.2 ± 7.2
OD-60	9.0 ± 0.4	17.2 ± 3.8	69.6 ± 9.2	356.3 ± 7.7

Conclusions

Oxidized maltodextrin with multiple carboxyl groups prepared by H_2O_2 oxidation can be used as a ligand for aluminum–zirconium complex tanning. H_2O_2 dosage played an essential role in the degree of maltodextrin oxidation and degradation. OD-40 (maltodextrin oxidized by 40% H_2O_2) with moderate carboxyl content (6.75 mmol/g) and molecular size (M_w 450) exhibited better tanning performance than traditional citric acid ligand, showing its potential application in chrome-free tanning technologies.

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