# Hydrogen Peroxide-oxidized Soybean Polysaccharides as Novel Masking Agents for Zirconium Tanning

by

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## Abstract

A series of hydrogen peroxide-oxidized soybean polysaccharides (HPS) were prepared using $H_2O_2$ and copper catalyst, which were then used as novel masking agents for zirconium tanning. The HPS samples were characterized by Fourier transforms infrared (FT-IR) spectroscopy, dynamic light scattering (DLS), and X-ray diffraction (XRD). FT-IR suggested the formation of carbonyl and carboxyl groups after hydrogen peroxide oxidation. DLS indicated that the HPS particle size decreases with increasing the $H_2O_2$ dosage. HPS with carbonyl and carboxyl groups and medium particle size was able to coordinate with zirconium to remarkably facilitate the tanning process. The shrinkage temperature of the tanned leather reached 92°C. Meanwhile, the fullness, softness, and mechanical properties of the leather were greatly improved by the tanning. The function of HPS and its interaction with zirconium were studied by FT-IR, XRD, and it was found that the triple helical structures of collagen fiber were not changed greatly. Scanning electron microscopy (SEM) showed that collagen fibers were dispersed and tanning agents were evenly distributed in collagen fibers. A new strategy for chrome-free tanning is suggested and a strong support for the application of zirconium tanning is provided.

## Introduction

The soybean curd residue is the main surplus material, which is usually discharged as solid waste.[1] In order to reduce the cost and energy waste, it is widely reused to obtain polysaccharides.[2] Soluble soybean polysaccharide (SSPS) is an acid polysaccharide like pectin, composed of D-galactose, L-arabinose, D-galacturonic acid, and L-rhamnose. It has found a wide application in the food industry due to its excellent water solubility, oxidation property, good film-forming ability, emulsifying property, and nutritional value.[3] For example, SSPS has been used for yogurt dispersion and food packing.[4] After being oxidized by sodium periodate, dialdehyde polysaccharides can be used as a crosslinker for stabilizing collagen in leather.[5, 6]

Nowadays, the leather industry is faced with rigorous environmental pressure due to the use of chrome tanning agent.[7] The wet blues, chrome-contained wastewater, and solid waste may pose a potential harm to the environment because the Cr(III) may be converted into more toxic Cr(VI).[8] Therefore, the development of sustainable chrome-free tanning agents has become one of the focuses of researchers both in academia and in industry.[9,10]

Zirconium-tanned leather has higher shrinkage temperature, pure white color, fullness and tightness, good wear resistance, as well as high resistance to aging, sweat, and mold.[11-13] However, such shortcomings as poor tear strength, low permeability, and weak water absorption do exist for zirconium-tanned leather, compared to the chrome-tanned one.[14] A generally accepted reason is that the zirconium tanning takes place at low pH with fast hydrolysis of zirconium salt to form multimer, which destroys the collagen structure, resulting in the decrease of mechanical properties of the zirconium tanned leather.[11] On the other hand, the zirconium salt is very active to react with collagen at the initial stage of tanning, leading to the precipitation on both sides of grain and flesh, and uneven distribution of zirconium in the cross section of leather, and poor tanning performance.

Small molecular ligands with carboxyl groups, such as lactic acid, citric acid, and sulfamic acid are usually used as masking agents to coordinate with zirconium to reduce the reactivity of zirconium.[12] However, the improvement of organoleptic properties of leather is still limited. Highly-oxidation starch (HOS) was used in zirconium tanning, which effectively slowed down the hydrolysis of zirconium and improved the penetration of zirconium, with the amounts of 4.8% HOS and 6% zirconium of the pickled cattlehides in weight.[12] Unfortunately, the HOS was prepared by conventional oxidation and alcohol-precipitation process, causing a great waste of resources. Sulfonated tetraphenyl calix[4] resorcinarene (STCR) was used as a ligand in zirconium-tanning, in which STCR inhibited the hydrolysis and promoted the penetration of zirconium, which obviously reduced the zirconium consumption and improved the organoleptic properties of the zirconium tanned leather.[13]

There are abundant hydroxyl groups in soluble soybean polysaccharides, primarily in C-2, C-3, and C-6 positions of glucose unit,[15] which could be transformed into carbonyl and carboxyl groups by oxidation to form stable hydrogen bonds and metal chelation with the zirconium complexes. A potential tanning agent should have suitable viscosity for effective flow and

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penetration to achieve uniform distribution in leather. Meanwhile, the molecular weight of oxidized soluble soybean polysaccharides could be regulated by oxidation through controlling the rupture degree of (1-4) glycosidic bond. Polysaccharides with appropriate molecular weight distribution could effectively affect the penetration of tanning agent in leather. Therefore, oxidation soluble soybean polysaccharide should be an excellent choice for the ligand of zirconium complex due to its variable coordination group, suitable viscosity, and molecular size. Moreover, compared with synthetic organic ligands, the polysaccharide-based ligand is more environment-friendly, sustainable, and economic because of the biodegradability, renewability, and cheapness of soybean polysaccharides.

In this work, HPS was prepared using hydrogen peroxide without alcohol precipitation, which was then employed in tanning as a ligand for zirconium complexes. The structures of HPS were characterized by Fourier transform infrared (FT-IR) spectroscopy, dynamic light scattering (DLS), and X-ray diffraction(XRD). The mechanical properties of leather tanned by HPS and zirconium (HPS-Zr) were studied. Then the performance of HPS as a ligand in zirconium tanning was evaluated. The synergy between HPS and zirconium was studied by FT-IR, thermogravimetric analysis (TGA), and scanning electron microscope (SEM). The possible mechanism of the tanning process was proposed and discussed.

## Materials and methods

### Materials

Pickled sheepskin was kindly provided by Henan Prosper Skin & Leather Enterprise Co., Ltd, China. SSPS was kindly provided by Jinjing Bio. Co. Ltd. (Pingdingshan City, Henan, China). $H_2O_2$ (30%), $CuSO_4{\cdot}5H_2O$, $Zr(SO_4)_2{\cdot}4H_2O$ were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China) Aladdin Reagent Co.Ltd. (Shanghai, China). The other chemicals used in tanning were of analytical grade.

### Preparation of HPS

The oxidation process was carried out according to the reported work by Yu et al. with slight modifications.[12] In the 100 g/L soluble soybean polysaccharides solutions, 0.1% $CuSO_4{\cdot}5H_2O$ was added to act as catalyzer (based on the weight of soybean polysaccharides, the same below), and 30%, 60%, and 90% hydrogen peroxide of the SSPS in weight were drop-wisely added, respectively. The mixtures were allowed to react at 120°C for 2 hours to yield HPS solutions containing aldehyde and carboxyl groups, which were collected and directly used for zirconium tanning.

### Tanning process

Table I shows the zirconium tanning process of pickled sheepskin. Leather tanned by pure zirconium tanning agent was used as the control, noted as "a". Leathers tanned by HPS-30, HPS-60 and HPS-90 were the b, c, and d, respectively.

### Characterization of HPS

#### Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared (FT-IR) spectra of SSPS and HPS were recorded using a FT-IR spectrometer (Nicolet iS10, Thermo Scientific, USA). Samples were pressed with KBr pellet and scanned in the range of 400-4000 $cm^{-1}$ at room temperature, with an accumulation of 32 scans and a resolution of 4 $cm^{-1}$.

#### X-ray Diffraction (XRD)

X-ray diffraction patterns of the SSPS and HPS were recorded using a Cu-Kα wide-angle X-ray diffractometer (XRD, PANalytical B.V., Netherlands). The scattered radiation was detected in the angle range of 5-90° (2θ) at a scanning rate of 0.3°/s.

#### Particle size analysis

Particle size analysis of samples was performed by a dynamic light scattering instrument (Nanostar, Wyatt). All the experiments were conducted at 25°C. The concentration of polysaccharide solution was 10 g/L.

**Table I**

**The zirconium tanning process of pickled sheepskin**

| Process | Chemicals | Quantity/% | Duration/min | Temperature/°C | pH |
|---|---|---|---|---|---|
| Tanning | Water | 300 | | 25 | |
| | NaCl | 6 | 10 | | |
| | $Zr(SO_4)_2{\cdot}4H_2O$ | 5 | 240 | | |
| | HPS | 5 | 120 | | |
| | Sodium bicarbonate | 2 | 3*30+60 | | 3.8-4.0 |
| Fixation | Water | 300 | 240 | 40 | |
| Washing | Water | 1000 | 30 | 25 | |

### Characterization of leather

### Thermal properties

Shrinkage temperature of leather is an important index to evaluate the tanning effect of a tanning agent, which was recorded using a digital leather shrinkage temperature instrument (MSW-YD4, Shaanxi University of Science and Technology, China). The heating rate was 2.0±0.2°C/min.

The thermogravimetric analysis was carried out using TGA (METTLER TOLEDO, Switzerland) with the nitrogen flow of 40 mL/min. The 5-7 mg sample was put in an open aluminium crucible and heated from 30 to 600°C at the heating rate of 10°/min.

### Mechanical properties

The tanned leathers were cut into the shape of dumbbell (GB/T-528II, Kunshan Creator Testing Instrument Co. Ltd., China). After being air conditioned at Relative Humidity 60±5% for 48h, the samples were stretched to calculate the tensile strength and elongation at break with SMSTA.XT Plus Texture analyzer (Lotun Science Co. Ltd., British)[16].

### Thickening rate

The thickness of leathers before and after tanning was measured by thickness gauges. The thickness of the sheepskin was the $a_0$ (mm), and that of the tanned leather was the $a_1$ (mm). Thus, P (thickness rate) was calculated by equation (1).

$$P/\% = \frac{a_1 - a_0}{a_0} \times 100\% \tag{1}$$

### Color

The color of different leathers was determined by a digital chromatic aberration instrument (CR-10plus, Japan). L* stands for brightness, a* stands for red and green, while b* stands for yellow and blue (L*=99.29, a* =-0.15, b* =1.34). The calculation formula of the total color difference of leather is according to equation (2).

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \tag{2}$$

Where ΔE stands for total chromatic aberration, L, a, and b are the parameters of the sample. All the leather samples were measured on the standard plate.

### Morphological analysis

The leather samples were lyophilized after tanning. Both the cross-section and surface of the leather samples were observed using a scanning electron microscope (SEM, S4800, Hitachi, Japan) with an accelerating voltage of 10 kV.

### Organoleptic properties

Organoleptic properties such as fullness, grain tightness, and grain smoothness were assessed and rated by three experts independently, which were rated on a scale of 1-10, with 10 of the best.

### The structures of leather

FT-IR spectra of leathers were obtained using a TENSORII spectrometer (Nicolet iS10, Thermo Scientific, USA) equipped with universal attenuated total reflection (ATR) sampling accessory. For each spectrum, the transmittance was recorded from 400 to 4000 $cm^{-1}$ with an accumulation of 32 scans and a resolution of 4 $cm^{-1}$.

XRD measurements were performed on an Empyrean X-ray diffractometer (PANalytical B.V., Netherlands) at 40 kV, 40 mA, with CuKα (λ = 1.5406 Å) as radiation source. The leather samples were irradiated in the range from 5 to 60° at a scanning rate of 0.3°/s.

## Results and discussion

### Structure of polysaccharides

### FTIR and XRD analysis

The FT-IR spectra of SSPS, HPS-30, HPS-60, and HPS-90 are shown in Figure 1. Two characteristic peaks around 3200-3500 $cm^{-1}$ and 2927 $cm^{-1}$ are attributed to the stretching vibration of –OH and C-H. The intense band at 1640 $cm^{-1}$ is assigned to the bending vibration of water molecules contained in polysaccharides. The characteristic peaks near 1000 $cm^{-1}$ in the fingerprint region are ascribed to the bond stretching of –OH with some contributions from the rhamnogalacturonan moiety in the samples. The new peak at 1740 $cm^{-1}$ which corresponds to the stretching vibration of carbonyl groups was found in both HPS-30, HPS-60 and HPS-90. Furthermore, the intensity of this absorption peak was enhanced with increasing the $H_2O_2$ dosage by oxidation. This result further confirmed that carbonyl and carboxyl groups were introduced in the molecular structure of HPS by the oxidation with $H_2O_2$.

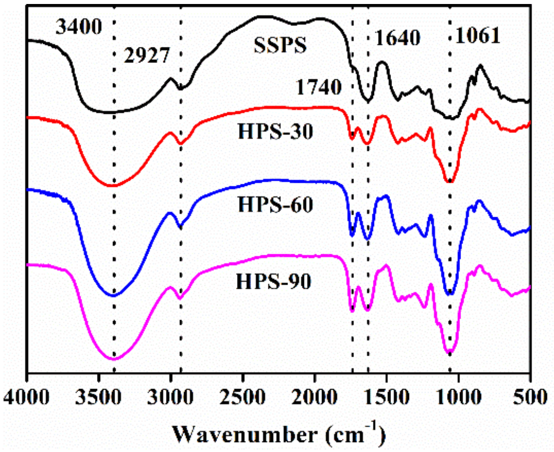

**Figure 1.** FT-IR spectra of SSPS, HPS-30, HPS-60 and HPS-90

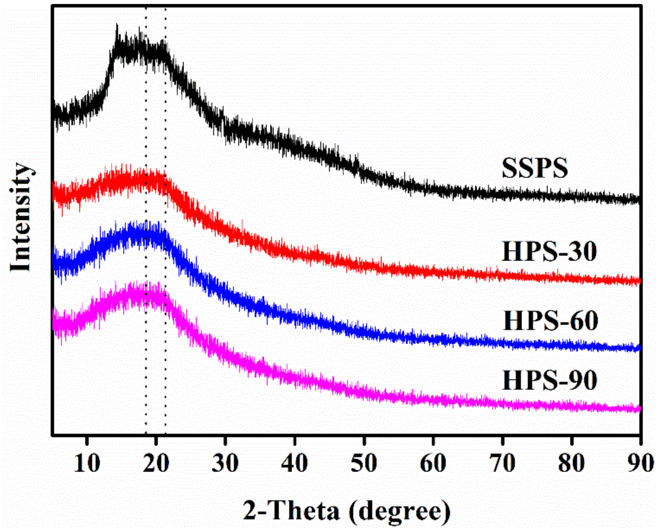

**Figure 2.** X-ray diffraction (XRD) patterns of SSPS, HPS-30, HPS-60, and HPS-90

Figure 2 shows the XRD pattern of soybean polysaccharide before and after $H_2O_2$ oxidation. The obvious diffuse broad peak of SSPS at 19° (2θ) indicated a low crystallinity of polysaccharides with an amorphous structure. The lower crystallinity suggests the lower chain stiffness of polysaccharides. High crystallinity and chain stiffness would affect the accessibility of oxidation agent to the crystal region, and thus the degradation mainly takes place in the amorphous region. XRD patterns indicated that SSPS could be degraded by the oxidation with hydrogen peroxide. For the samples of HPS-30, HPS-60, and HPS-90, obvious diffuse broad peaks at 21° and dispersion broad peaks are basically consistent with those of SSPS, indicating an amorphous structure in the oxidized polysaccharides.

## Particle size of HPS

DLS was used to determine the average particle size of SSPS and HPS. Figure 3 shows the particle size distribution of HPS, and the intensity average diameter and intensity calculated from the particle size distribution are shown in Table II. For SSPS, the major set of particles was observed, in which 89.6% had an intensity average diameter of 901.8 nm. The particles of HPS-30 distributed over a larger range with three part sets. The intensity average diameter of the main set (539.0 nm, intensity 74.3 %) was smaller than that of SSPS. With increasing the amount of hydrogen peroxide used in the oxidization, the average particle size of the polysaccharide gradually decreases. The average particle size of HPS is significantly smaller than that of SSPS, indicating that hydrogen peroxide could probably degrade the soybean polysaccharides by destroying the glycosidic bonds of soybean polysaccharides to depolymerize the molecular chains of soybean polysaccharides. So the average particle size of the polysaccharides was reduced. The reduction in average particle size is conducive for the penetration of polysaccharide ligands into leathers. Furthermore, the full-component polysaccharide has a wide particle size distribution, and it could act as a masking agent for zirconium tanning and serve as a good filling agent, which was further confirmed by the results of the thickening rate in Figure 6.

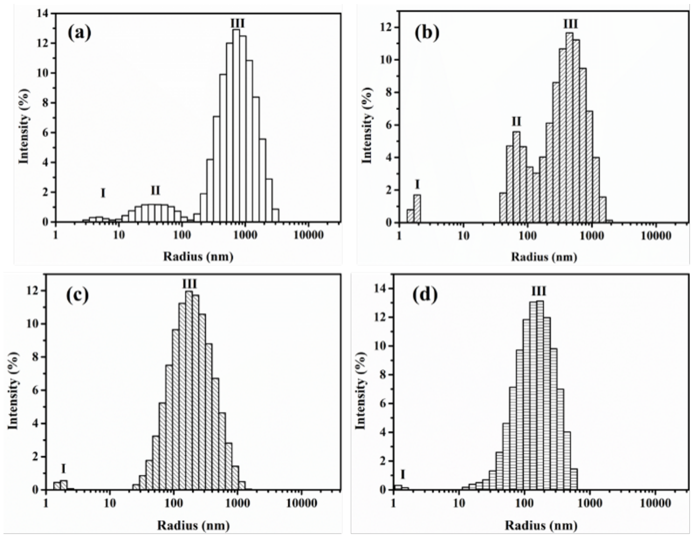

**Figure 3.** Particle size distribution of different polysaccharides (**a:** SPSS; **b:** HPS-30; **c:** HPS-60; **d:** HPS-90)

**Table II**

**Particle size distribution (A-intensity average diameter, B-intensity) of HPS.**

| | SSPS | | HPS-30 | | HPS-60 | | HPS-90 | |
|---|---|---|---|---|---|---|---|---|
| | A/nm | B/% | A/nm | B/% | A/nm | B/% | A/nm | B/% |
| I | 5.0 | 1.1 | 1.8 | 2.5 | 1.8 | 1.1 | 1.2 | 0.7 |
| II | 43.4 | 9.3 | 80.8 | 23.2 | - | - | - | - |
| III | 901.8 | 89.6 | 539.0 | 74.3 | 243.7 | 98.9 | 176.2 | 99.3 |

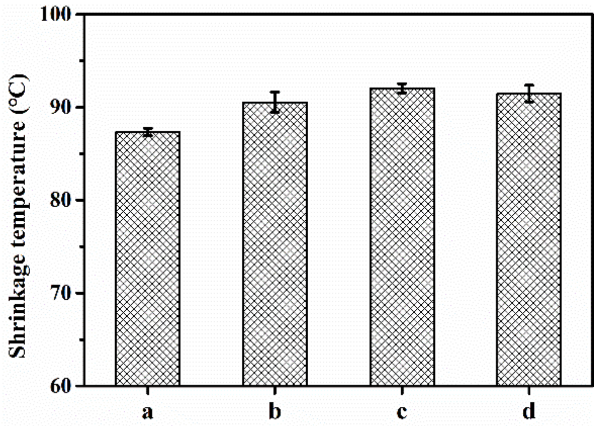

**Figure 4.** Shrinkage temperature of samples for different tanning processes

(Note: **a**-Zirconium-tanned leather; **b**-HPS-30-zirconium-tanned leather; **c**-HPS-60-zirconium-tanned leather; **d**-HPS-90-zirconium-tanned leather)

## Structure and properties of leather

### Thermal properties of leather

The shrinkage temperature ($T_s$) of leathers is usually used to evaluate the hydrothermal stability and performance of leathers.[17] High shrinkage temperature of leather means good hydrothermal stability and good tanning effect. The shrinkage temperature of leathers is closely related to the degree of tanning. Figure 4 shows the shrinkage temperatures of leather samples tanned by different zirconium tanning processes. The shrinkage temperature of the tanned leather was 87°C for the control, which reached the highest of 92°C with HPS-60. So the HPS with medium oxidation degree and particle size does good in zirconium tanning. This could be ascribed to the better penetration, distribution, and crosslinking of HPS-Zr complexes in the collagen fiber network of leather. So the introduction of HPS-60 could significantly improve the hydrothermal stability of leather.

Thermogravimetric analysis (TGA) and differential thermal gravity (DTG) analysis could be used to characterize the thermal stability of leather samples.[18] The TGA and DTG curves of the samples by different tanning processes were shown in Figure 5. Similar three stages exist in the TGA curves of the four samples. The first weight loss at 30-100°C was approximately 10% by the volatilization of free water and bound water in leathers. There are a large number of hydrogen bonds in the collagen fibers, which play an important role in stabilizing the collagen fiber and the whole structure of leather. At 100-400°C, some hydrogen bonds might be damaged and the triple helical structure of the collagen fibers might be unwound, resulting in the breakage of the polypeptide chain of collagen in leathers. On the other hand, tanning agent could react with collagen fibers by van der Waals forces, covalent bonds,and hydrogen bonds to form crosslinking and increase the thermal stability of leather. At high temperatures, great damage will take place for collagen fiber, and the weight fell sharply to 33% of the original weight. Finally, at a temperature above 400°C, the TGA curve turns smooth, mainly by the degradation of carbide slag at high temperatures.

The maximum weight loss rate temperature ($T_{max}$) of the leather sample reflects the structural stability of leather. The higher the maximum weight loss rate temperature means the better thermal stability of leather. By comparing the $T_{max}$ in the second stage of the four samples, the ones of HPS-Zr tanned leathers are higher than that of Zr-tanned leather, indicating that HPS with medium size and a moderate degree of oxidation could improve the thermal stability of leather. This should be ascribed to the good penetration, distribution, and crosslinking of HPS-Zr complexes in the fiber network of leather.

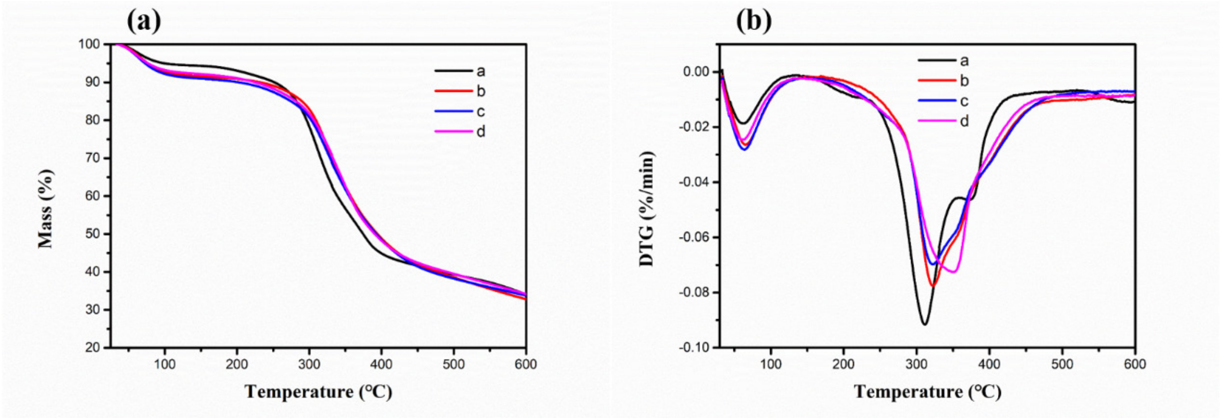

**Figure 5.** TGA **(a)** and DTG **(b)** curves of leather samples for the different tanning process

(Note: **a:** pickled sheepskin, **b:** zirconium-tanned leather, **c:** HPS-30-zirconium-tanned leather, **d:** HPS-60-zirconium-tanned leather)

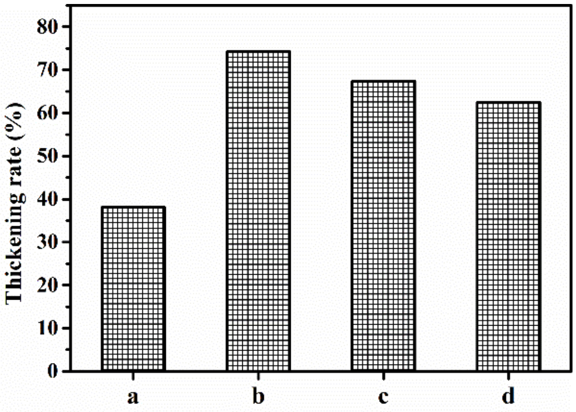

**Figure 6.** Thickness rate of leather samples for different tanning processes

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

### Filling effect of leather

The thickness rate suggests the filling properties of polysaccharides for leather.[12] The higher the thickening rate, the better the filling ability of the polysaccharides. The thickness rate of leathers with different tanning processes is shown in Figure 6. The thickness rates of zirconium, HPS-30, HPS-60, and HPS-90 were 38.1%, 74.2%, 67.35%, 62.46%, respectively. Compared with that of the control, the one with pure zirconium tanning, the thickness rates of all the other samples with HPS are greatly increased, with the highest for the HPS-30. So the filling effect with oxidized polysaccharide as masking agent of zirconium tanning is very good. It could be explained by the particle size of oxidized polysaccharides, which is suitable for the penetration in leather and conductive to the absorption by collagen fibers. All the components were kept in HPS solution, which was directly used in the tanning process. The wide particle size distribution provided the oxidized polysaccharide solution with a very good filling effect.

### Mechanical properties

Tensile strength and elongation at break are important for leathers, which are commonly used to evaluate the mechanical properties of leather.[5, 10] Table III shows the mechanical properties of leather tanned by different processes. The tensile strength of the leather with HPS-60 is the best. Compared with the one with pure zirconium tanning, the tensile strength of HPS-60 was increased from 13.23 MPa to 18.9 MPa. However, the tensile strength of HPS-90 is only 9.83 MPa, the possible reason is that the smaller ligands are not enough to coordinate and stabilize the Zr complexes. Furthermore, Zr complexes may be too small to sufficiently crosslink the collagen fibers, resulting in decreased tensile strength and increased elongation at break. By the addition of oxidized polysaccharide, the aldehyde and carboxyl group are introduced to bind with collagen fiber and zirconium tanning agent, and the crosslinking degree is increased, resulting in an increased tensile strength.

### Color and area yield

For zirconium tanned leather, generally called wet-white, the whiteness is important because good whiteness is preferable for tanners to make either natural color or light colored products.[6] Thus, the colorimetric values of pickled sheepskin and different tanned leathers were measured to evaluate the whiteness, with the results shown in Table IV. The total color difference (ΔE) value was calculated

**Table III**

**Mechanical properties of leather samples for different tanning processes**

| Sample | Tensile Strength (MPa) | Standard (MPa) | Elongation (%) | Standard (%) |
|---|---|---|---|---|
| a | 13.23±1.2 | ≥12 | 137.66±11.9 | ≥25 |
| b | 14.65±1.2 | ≥12 | 109.28±8.6 | ≥25 |
| c | 18.90±1.1 | ≥12 | 111.85±11.0 | ≥25 |
| d | 9.83±0.6 | ≥12 | 122.34±1.3 | ≥25 |

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

**Table IV**

**Area yield, chromaticity and color difference of different samples**

| Sample | Area yield/% | L | a | b | ΔE |
|---|---|---|---|---|---|
| sheepskin | 100.0 | 77.1 | 5.3 | 11.6 | 25.0 |
| a | 101.2 | 81.2 | 1.3 | 5.9 | 18.8 |
| b | 103.5 | 83.7 | 3.4 | 13.8 | 20.3 |
| c | 102.8 | 82.7 | 2.9 | 15.6 | 21.1 |
| d | 103.1 | 81.1 | 1.5 | 14.6 | 22.6 |

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

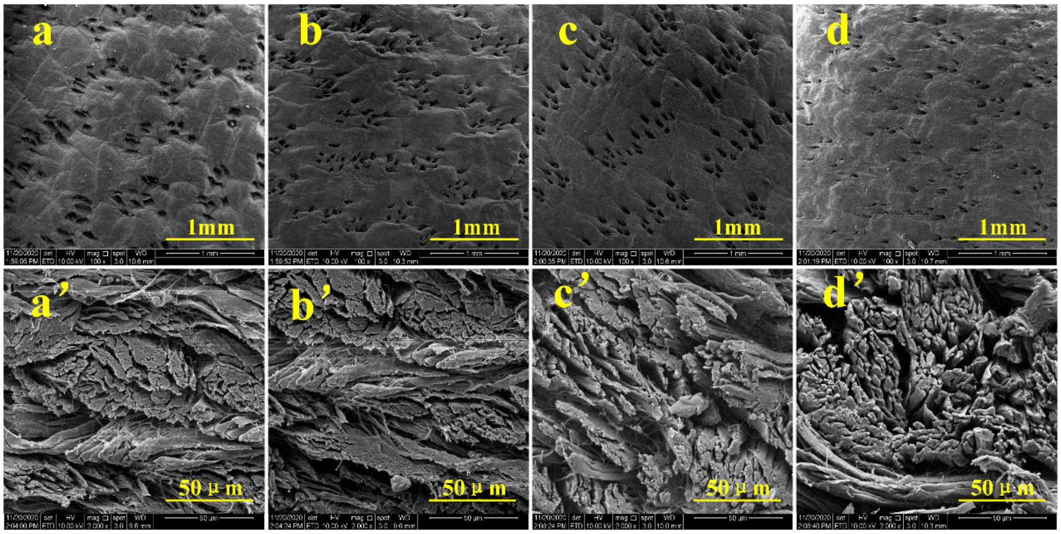

**Figure 8.** SEM images of grain surface **(a, b, c, d,)** and cross-section **(a', b', c', d')** of leathers

(Note: **a** and **a'**: pickled sheepskin, **b** and **b'**: zirconium-tanned leather, **c** and **c'**: HPS-30-zirconium-tanned leather, **d** and **d'** HPS-60-zirconium-tanned leather)

by subtracting the corresponding values for standard white (L=99.29, a =-0.15, B =1.34), and a lower ΔE value means higher whiteness. The ΔE of zirconium-tanned leather with polysaccharides is close to that of pickled sheepskin, indicating that the addition of polysaccharide does not significantly change the whiteness of the leather. As can be seen from Table IV, the introduction of polysaccharide could improve the leather yield of zirconium tanned leather, which is good from viewpoint of economic profits.

### Morphological analysis

The performance is closely related to the microstructure of leathers.[19] By the changes in the microstructure of samples, we could know the effect of oxidized polysaccharides on the combination, distribution of tanning agent in leather. Leathers dried by different ways were compared for morphological study, and it was found that the SEM images of the lyophilized samples could better explain the degree of collagen fiber dispersion. So the lyophilized samples were used in the study. In Figure 8(a), for the pickled sheepskin before tanning, the collagen fiber bundle is tight and bonded together, with clear grain surface pores. After being tanned with pure zirconium tanning agent, the collagen fiber bundles are better dispersed with clear grain surface pores. In Figure 8(c) and (d), the collagen fiber bundles of leather tanned with zirconium and HPS-30 or HPS-60 were well dispersed with clear surface pores and flatter grain surface. So it can be concluded that the synergism of zirconium and HPS could provide leathers with good fiber dispersion and strong cross linking on collagen fibers, yielding excellent leather.

### Organoleptic properties

The organoleptic properties of zirconium-tanned leathers with and without different HPS are given in Table V, in which the leather tanned with zirconium and HPS-60 exhibited the best organoleptic properties, including softness, fullness, and grain smoothness, compared to those tanned with pure zirconium tanning agent. Generally, compared with vegetable-tanned and aldehyde-tanned leathers, the zirconium tanned leather has better fullness, because of the large polymeric zirconium complex formation. Here in this study, the samples were tanned with zirconium tanning agent with different masking agents of HPS. The fullness evaluation of pure zirconium tanned leather is 5, which is much worse than the 9 of zirconium with HPS-60. Furthermore, the softness and grain smoothness of leather tanned with zirconium and HPS-60 is also 9, indicating that it has good organoleptic properties. The fullness of leather tanned with zirconium and HPS-60 is in accordance with the thickening rate results in Figure 6. The fullness and tightness were found to be enhanced by the introduction of HPS with wide particle size distribution. So the introduction of HPS might provide zirconium tanned leathers with good organoleptic properties.

**Table V**

**Organoleptic properties of leather samples for different tanning process**

| | a | b | c | d |
|---|---|---|---|---|
| Softness | 5 | 9 | 9 | 8 |
| Fullness | 5 | 8 | 9 | 7 |
| Grain smoothness | 5 | 9 | 9 | 8 |

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

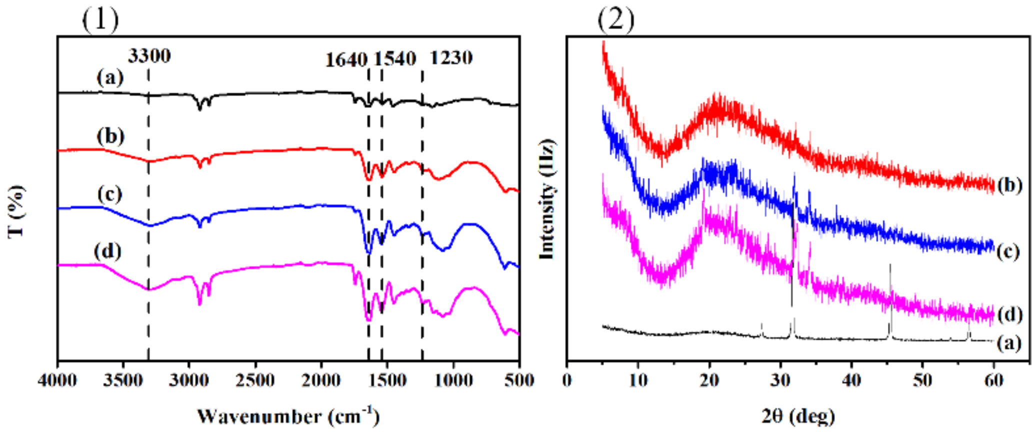

**Figure 9.** **(1)** FTIR and **(2)** XRD of pickled sheepskin **(a)**; zirconium-tanned leather **(b)**; HPS-30-zirconium-tanned leather **(c)**; HPS-60-zirconium-tanned leather **(d)**

## Tanning mechanism

Collagen in leather has a special triple helical structure and is usually characterized by the amide bands in the infrared spectrum. Figure 9(1) shows the infrared spectra of leathers tanned by different tanning processes, which might indicate the tanning mechanism. For the control, the peak at 3300 cm$^{-1}$ was attributed to the N-H stretching vibration in collagen. The bands at 1640 cm$^{-1}$, 1540 cm$^{-1}$, and 1230 cm$^{-1}$ in both the control and tanned leathers using polysaccharide were assigned to the carbonyl stretching vibration (amide I band), C-N stretching vibration (amide II band), and C–N stretching vibration and N-H of the amide group in the peptide bond (amide III band),[20] respectively.

The amide I band of collagen is particularly sensitive to the secondary structure of collagen. The amide I band peaks of collagen tanned with pure zirconium tanning agent, HPS-30 with zirconium, and HPS-60 with zirconium, were 1643 cm$^{-1}$, 1640 cm$^{-1}$ and 1642 cm$^{-1}$, respectively. The results showed that the secondary structure of collagen did not change significantly after tanning, suggesting that the triple helical structure of collagen was not destroyed by tanning. Besides, the increase in peak intensity at 1640 cm$^{-1}$ in Figure 9 was contributed to the carbonyl group in the oxidized soybean polysaccharide, demonstrating the existence of HPS in leather.

Figure 9(2) shows the XRD patterns of the samples. Collagen fibers have triple helical structures with good orientation and high crystallinity, which can be characterized by XRD. After tanning, the original two characteristic peaks at 7.6° and 21° were not changed, indicating that the triple helical structure of collagen had not been destroyed in the tanning process. By tanning, the peak at 21° turned broader and the intensity turned weaker, probably because the regularity of collagen fibers was decreased by the interaction between collagen, tanning agent, and HPS. The results showed that both zirconium sulfate and HPS can penetrate into the leather to react with collagen fibers, increasing the distance between collagen fibers and dispersing collagen fibers.

Based on the above results, interaction mechanism in the tanning process of HPS with zirconium was proposed, as shown in Figure 10. The FT-IR spectra and XRD patterns proved that the tanning agent penetrates into the leather and react with the collagen fiber, with the triple helical structure of the collagen not changed. Schiff base reaction could take place between the aldehyde group of HPS and the amino group of collagen.[21] Traditional zirconium tanning had been proven to crosslink with the amino and carboxyl groups of collagen through coordination bonds.[12] HPS and zirconium could form complexes through coordination bonds, by the coordination of zirconium with the carboxyl group of HPS.[11] Therefore, it was speculated that the HPS-Zr tanning agent is bound to collagen through hydrogen bonds, ionic bonds, and coordination bonds.

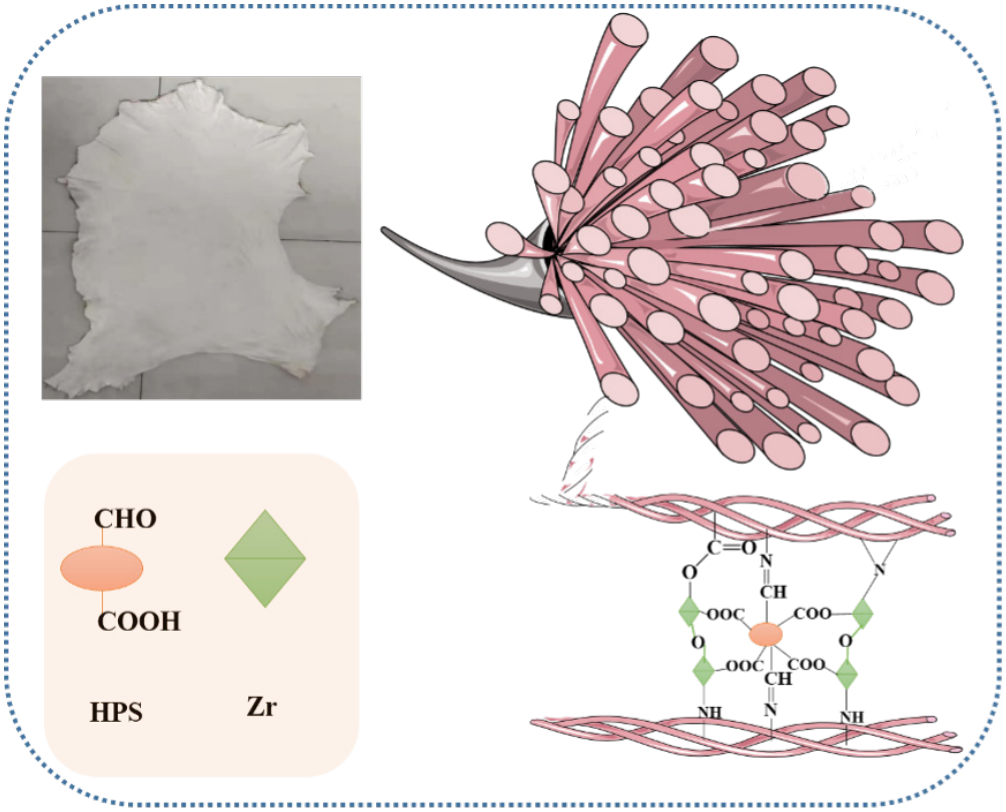

**Figure 10.** Proposed crosslinking reaction between collagen, HPS and zirconium

## Conclusion

By hydrothermal reaction, soybean polysaccharides were oxidized by hydrogen peroxide to yield polysaccharides with aldehyde and carboxyl groups. The oxidized polysaccharide solution was directly used in zirconium tanning. The carboxyl group in the oxidized polysaccharide could act as a ligand with zirconium sulfate to crosslink the collagen fibers to improve the mechanical strength, thermal properties, and organoleptic properties of the leather. With the introduction of HPS, the collagen fibers are dispersed better, which is more beneficial for leather chemicals to penetrate into leathers for efficient tanning. No damage in the triple helical structure of collagen in leathers was found by the HPS and zirconium tanning. The oxidized polysaccharides are suggested a potential application in chrome-free tanning.

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