

# PREPARATION AND PROPERTIES OF STARCH MODIFIED BY GLUTARALDEHYDE AND CITRIC ACID

by

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## ABSTRACT

The modified starch tannage was prepared by acetalation reaction of degradation starch with glutaraldehyde (GA) and citric acid (CA) in turn. The conditions of modified starch were investigated. The results showed that the suitable degradation starch was obtained by mixing of 22.5g starch, 1g ammonium persulfate (APS) and 127.5g water at 95°C for 1h. The optimum modified starch tannage was obtained by acetalation reaction of degradation starch with 4 mol/AGU GA and CA at 85°C for 5h in turn, respectively. The shrinkage temperature ( $T_s$ ) of tanned leather by the modified starch increased from 41.3°C to 83.8°C. The modified starch can be used as tannage for making leather. Meanwhile, the chemical structure of the starch tannage was characterized by FTIR and NMR, which provided the evidence that GA and CA were bonded on the repeat unit of starch through substituted reaction.

## RESUMEN

El curtido por medio de almidón modificado fue preparado por la reacción degradando el almidón por acetilación con glutaraldeído (GA) y a su vez con ácido cítrico (CA). Las [resultantes] condiciones del almidón modificado fueron investigadas. Los resultados demostraron que una apropiada degradación del almidón resultó de mezclar 22,5 g de almidón, 1 g de persulfato de amonio (APS) en 127,5g de agua a 95 °C durante 1 hora. El curtido óptimo con el almidón modificado resultó por reacción de degradación por acetilación cuando se utilizó 4 moles del GA acuoso seguido por el CA a 85 °C a su vez por 5 horas respectivamente. La temperatura de contracción ( $T_s$ ) del cuero obtenido por medio del almidón así modificado se incrementó de 41.3°C a 83.8 °C. El almidón modificado entonces sirve como curtiente para fabricar cuero. La estructura química del curtiente al almidón se caracterizó por medio FTIR [Transformación de Fourier del Espectro Infra-rojo] y NMR [Resonancia Magnética Nuclear], lo que produjo evidencia que el GA y el CA se fijaron en cada unidad de repetición del almidón glucosídica por reacción de sustitución.

## INTRODUCTION

In recent years, the serious environmental pollution produced by leather chemicals, especially chrome tannage, has restricted development of leather industry around the world.<sup>1</sup> The main reason is that Cr(III) existed in the chrome-tanned leather in use process can be oxidized into Cr(VI), which is easy aborted by living cells and resulted in cancer.<sup>2,3</sup> Consequently, development of green and eco-friendly leather chemicals originated from natural biopolymer has drawn considerable attention.<sup>4</sup> A tanning agent is a type of chemical material that can convert the skin or hide into leather, which will not putrefy and is suitable for a wide variety of application. In the past, whether the materials can be chosen as a tannage depends chiefly on  $T_s$  (shrinkage temperature) of tanned leather. But now, the requirements of tanneries for leather tannages is not only hold excellent tanning effects but also environmentally-friendly in application.<sup>5</sup> Moreover, conventional tannages are usually originated from metallic mineral resources and petroleum resources. The widespread use of these resources has caused serious environmental problems and also leads to development of increasingly depleting of these resources. Thus, the preparation of green tannages using renewable and environmentally friendly natural materials has been paid more attention than ever.<sup>6</sup>

Starch is a kind of biopolymer with prospect of wide development and utilization in many fields such as degradable plastics, agriculture, medicine, adhesives, textile sizes, paper-making and food thickeners.<sup>7</sup> Starch is composed of long chains including anhydro-D-glucopyranose units (AGU). Each AGU has three hydroxyl groups except terminal ends. Raw starch cannot be directly applied in these fields and need chemical modified prior to application.<sup>8</sup> The purpose of chemical modification is to introduce some functional groups on starch molecules in order to improve its applied properties. The typical modification reactions are derivatization (esterification, etherification, cross linking, oxidation and grafting) and decomposition. The schematic diagrams of chemical modified starch are shown in Figure 1.<sup>9-14</sup> Owing to biodegradability, low cost and renewability, starch is considered as a promising candidate for developing green materials.<sup>15,16</sup> However, the modified starch designed to replace

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standard tannages has been reported on very little. In this paper, the preparation and properties of modified starch by acetalation reaction of degradation starch with GA and CA were reported.

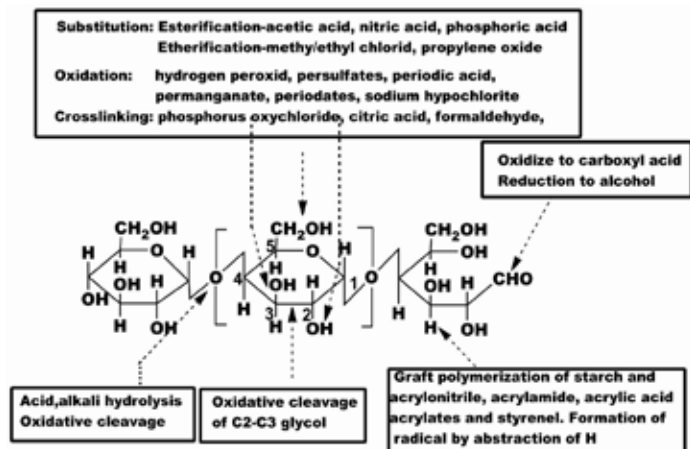


Figure 1. The schematic diagram of chemical modified starch

## EXPERIMENTAL

### Materials

Maize starch was supplied by Xi'an starch factory of China. Glutaraldehyde (GA), bromophenol blue, ammonium persulfate (APS), citric acid (CA), hydroxylamine hydrochloride, concentrated sulfuric acid (98wt%), *p*-toluenesulfonic acid (PTSA), isopropanol and ethyl alcohol were analytical reagents and purchased from Xi'an chemical Company of China. The goat chrome tanned garment leather was selected for the present investigation made by Hongshun Making Leather Factory in Xinji city, Hebei province of China.

### Preparation of modified starch tannage by GA and CA

127.5 mL distilled water, 22.5g maize starch and 1.0g APS were put into a 500 mL three-neck round-bottom flask equipped with a stirrer and a control temperature device. The starch was degraded for 1 h at 95°C and then cooled the degradation starch to 60-90°C. 2g PTSA and 3-6mol/AGU GA were added into the degraded starch. The reaction was implemented at 60-90°C for 5h and the product was GA modified starch. Then added CA with equal molar ratio of GA into the GA modified starch. The reaction was carried out at 85°C for 5h. The final product was modified starch tannage by GA and CA. The schematic diagram of modification starch is shown in Figure 2. The chemical structure of modified starch was characterized by NMR. The results are shown in Figure 3 and Figure 4. The results of NMR were analyzed as follows.

$^1\text{H-NMR}$  (400MHz,  $\text{DMSO-}d_6$ ,  $\delta$ , ppm): 11.86 (m,6H), 5.51 (s,1H), 5.02 (s,1H), 4.80 (s,1H), 4.60 (s,1H), 4.57 (m,2H), 4.38 (s,1H), 4.03 (s,1H), 3.64 (m,1H), 3.36 (m,2H), 2.59 (s,1H), 2.29 (m,4H), 1.73 (m,2H), 1.56 (m,2H), 1.24 (m,2H).

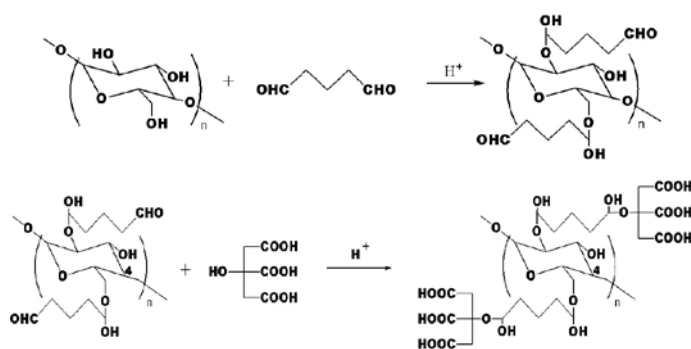


Figure 2. Schematic diagram of modified starch by GA and CA

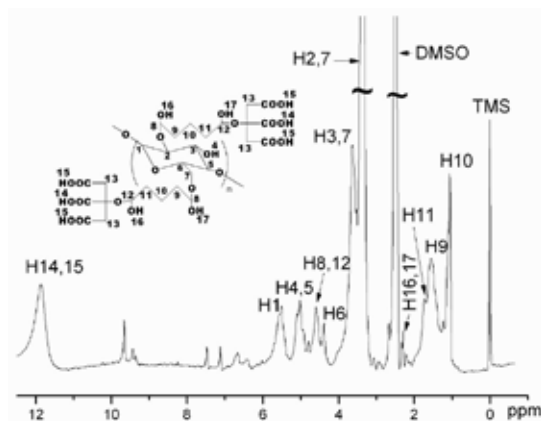


Figure 3. The  $^1\text{H-NMR}$  of modified starch by GA and CA

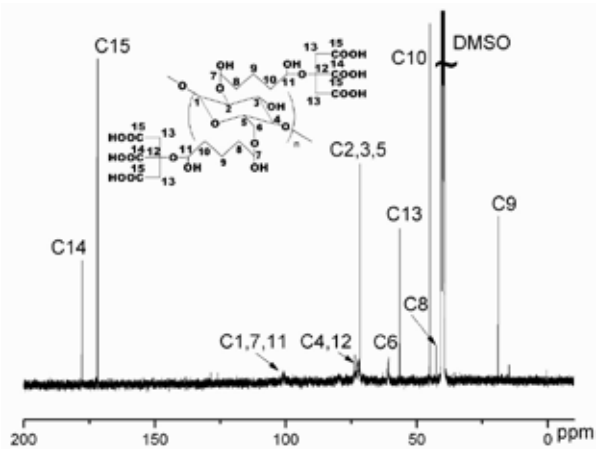


Figure 4. The  $^{13}\text{C-NMR}$  of modified starch by GA and CA

$^{13}\text{C-NMR}$  (400MHz,  $\text{DMSO-}d_6$ ,  $\delta$ , ppm): 177.79 (C14), 101.15 (C1,C7,C11), 73.67 (C4, C12), 71.74 (C2,C3,C5), 60.76 (C6), 56.28 (C13), 45.31 (C10), 42.85 (C8), 18.89 (C9).

### Application of modified starch tannage

The application of modified starch used as tannage was carried out with goat pickling pelt for garment leather. After application, the properties of retanned goat garment leather were evaluated by measuring its shrinkage temperature ( $T_s$ ) and mechanical properties such as tensile strength, elongation

ratio, and tear strength. The tanning and retanning processes are shown in Table I.

### Test and measurements

The FTIR spectra were carried out by FTIR Spectrometer of VECTOR 22 (BRUKER, German) using conventional KBr tablets. The  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were obtained by an INOVA-400MHz spectrometer (AVANVE III, Swiss) with deuterated dimethyl sulphoxide ( $\text{DMSO-}d_6$ ) as sample's solvent referenced to tetramethylsilane [TMS] internally.

The relative molecular mass was characterized by GPC of model 2414 instrument (Waters, USA). Two columns set (Ultrahydrogel 250 and 120, 7.8×300mm, Waters, USA) were used in series. The mobile phase consisted of a solution of 0.10mol/L sodium nitrate, its flow rate was 0.42mL/min, test temperature was 50°C, and the standard sample was polyethylene glycol. The viscosity of starch degraded for different time was tested with NDJ-5S digital rotational viscometer (Shanghai, China). The degradation starch solution was poured into a special container designed for determination of rotational viscosity which immersed in 25°C water bath. A suitable cylinder was chosen according to the viscosity of degraded starch and put into the degradation starch. The temperature of the starch solution kept constant at 25°C during the test.

The degree of substitution (DS) of modified starch was determined by titrating unreacted GA according to the

reference.<sup>17</sup> 10mL washing liquid, 0.5mL 0.5mol·L<sup>-1</sup> bromophenol blue solution and 50mL distilled water were put into a 150mL Erlenmeyer flask. Then added 0.5mol·L<sup>-1</sup> dilute sulfuric acid was added dropwise into the Erlenmeyer flask until the color changed from blue to colorless. Then 25mL of a mixture of 100g triethanolamine and 20g hydroxylamine hydrochloride was added via pipette into the Erlenmeyer flask. After the reaction for 1h, the solution of the Erlenmeyer flask was titrated to colorless with standard sulfuric acid solution. The DS was calculated by the following Equation (1) and Equation (2).

$$N_{\text{reacted glutaraldehyde}} = \frac{W_0 - V_{\text{waste}} \times C_{\text{sulfuric acid}} \times (\bar{V} - \bar{V}_0) \times 1.001}{M_{\text{glutaraldehyde}}} \quad (1)$$

$$DS = \frac{N_{\text{reacted glutaraldehyde}} \times M_{\text{starch}}}{W_{\text{starch}}} \quad (2)$$

Where:  $W_0$  is mass of GA used for modified starch (g).

$V_{\text{waste}}$  is the volume of the washing samples liquid (L).

$C_{\text{sulfuric acid}}$  is the concentration of standard sulfuric acid solution (mol·L<sup>-1</sup>).

$\bar{V}$  and  $\bar{V}_0$  are average volume of consumed sulfuric acid titrated sample and blank (L).

$M_{\text{glutaraldehyde}}$  is molar mass of glutaraldehyde (100.12g·mol<sup>-1</sup>).

**TABLE I**  
**The tanning process of modified starch tannage**

Process	wt%	Product	Time	Remarks
Goat pickling pelt garment leather, weighed				
Neutralization	100	Water, 35°C		Test $T_s$
	1	Sodium acetate and		
	0.8	Sodium bicarbonate	60min	pH:5.0
Tanning	10	Modified starch tannage	600min	Stop rotating 300min
	2	Sodium bicarbonate	60min	pH:6.5
	2	Sodium bicarbonate	60min	pH:7.5
Washing	300	Water, 35°C	20min	Drain, Test $T_s$
Fatliquoring	150	Water, 50°C		pH:7.0
	12	Fatliquor	60min	
	1.0	Formic acid (10wt%)	20min	
	1.5	Formic acid (10wt%)	20min	pH:4.5
Washing	300	Washing	20min	
Drying	Dried in air through hanging up at room temperature			

$N_{\text{reacted glutaraldehyde}}$  is mole number of GA reacted with starch (mole).

$M_{\text{starch}}$  is molar mass of starch ( $162\text{g}\cdot\text{mol}^{-1}$ ).

$W_{\text{starch}}$  is weight of starch (g).

The shrinking temperature ( $T_s$ ) of the skin and leather were determined on a Digital Display Shrinkage temperature meter MSW-YD4 (Xi'an, China) in water at a heating rate of  $2^\circ\text{C}/\text{min}$ . The mechanical properties of tanned leather, including tensile strength, tear strength, elongation at set strength and elongation at break, were evaluated by strain rate of  $100\text{mm}/\text{min}$  on Tensile Machine TS2000-S (Taiwan, China).

## RESULTS AND DISCUSSION

### Effect of degradation degree on property of modification starch

Figure 5 shows the effect of degradation time on viscosity of starch when 15g starch in 85g water was degraded using 0.15g APS as catalyst at  $95^\circ\text{C}$  for a certain time. The starch tannage was obtained by degraded starch reacted with  $4\text{mol}/\text{AGU}$  GA and  $4\text{mol}/\text{AGU}$  CA at  $80^\circ\text{C}$  for 5h in turn, respectively. The Table II shows the relation between viscosity and molecular mass ( $\bar{M}_w$ ) and effect of viscosity and molecule mass on  $T_s$  of tanned leather. It can be seen from Figure 5 and Table II that the viscosity of degradation starch decreased rapidly between 10 and 60 minutes, and  $T_s$  increase with decreasing of starch's viscosity and molecule weight. The results demonstrate that the permeability of modified starch tannage into leather fibers is key for modified starch tannage. The reason is that raw starch is a kind of natural macromolecule with relative molecular mass ( $\bar{M}_w$ ) between 25,000 and 7,000,000. The raw starch has poor water-soluble and penetrability in skin and leather fibers. So original starch should be first degraded in order to decrease molecular size and increase its penetration in skin fibers. The lower the molecular mass, the better the penetration into leather. So the optimum degradation time is no less than 60 minutes.

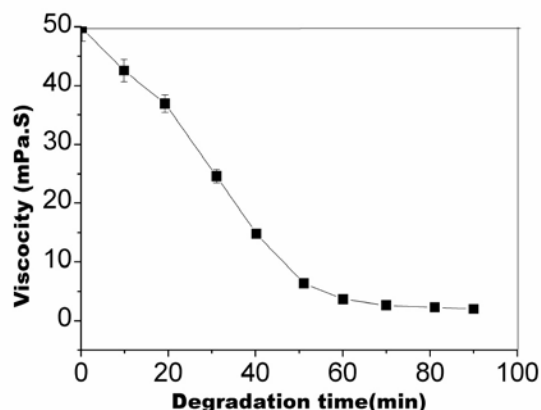


Figure 5. Effect of time on viscosity ( $25^\circ\text{C}$ ) of degradation starch

**TABLE II**  
Effect of degradation degree of starch on  $T_s$  of leather tanned by modification starch tannage

Time [min]	Degraded starch		$T_s$ [ $^\circ\text{C}$ ]	
	Viscosity [mPa.s (250C)]	$\bar{M}_w$	Skin	Leather
20	38.7	45637	42.1	67.3
40	14.8	17891	41.7	73.2
50	6.3	2136	43.2	78.6
60	3.6	1253	41.3	83.8

### The effect of reactant concentration and temperature on DS

The degradation starch was modified with aldolization of GA and CA in turn, respectively. Figure 6 shows the effect of GA dosage on DS, in which the modification reaction was carried out at  $85^\circ\text{C}$  for 5h. It can be seen that DS reached the maximum 2.12 when GA concentration is  $4\text{mol}/\text{AGU}$ . With further increase of GA concentration, DS does not increase but stays level. This means that each AGU unit of starch had two GA grafted on.

Figure 7 shows the effect of reaction temperature on DS of modified starch when the GA concentration was kept  $4\text{mol}/\text{AGU}$ . It can be seen from the result that the DS increases with the increase of reaction temperature from  $60^\circ\text{C}$  to  $85^\circ\text{C}$ , and the DS starts to decrease when the reaction temperature is more than  $85^\circ\text{C}$ . The DS reaches the maximum 2.12 at  $85^\circ\text{C}$ . The result may be that the acetalation products may be decomposed at higher temperature.

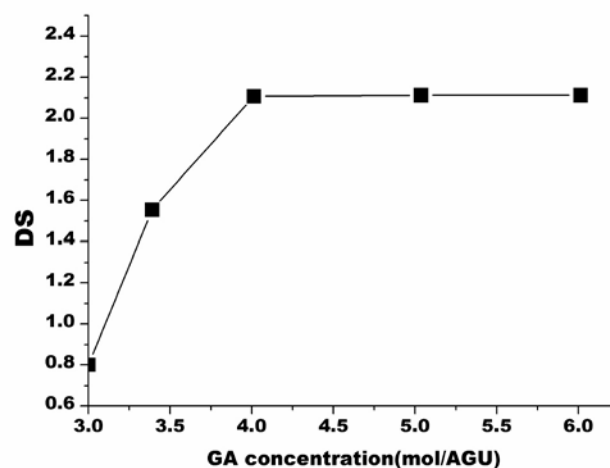


Figure 6. Effect of GA amount on DS of modified starch

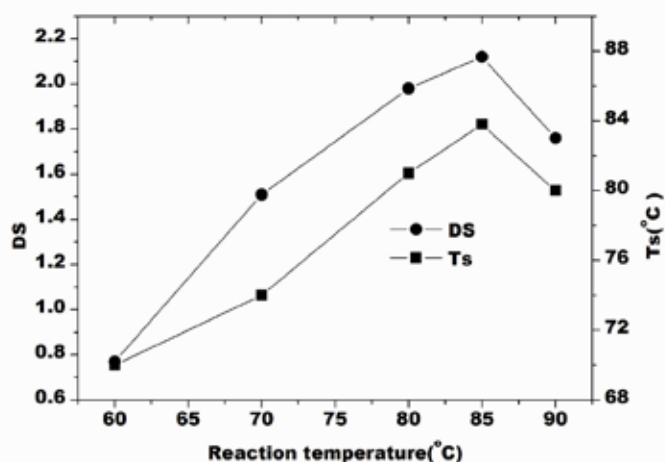


Figure 7. Effect of temperature on DS of modified starch

Figure 7 also shows the effect of DS of modified starch on  $T_s$  of tanned leather. The result shows that the  $T_s$  of tanned leather increases with DS increasing and reaches the maximum 83.8°C when DS is 2.12. The reason is that there is more carboxyl (-COOH) and hydroxyl (-OH) in the modified starch tannage when DS is greater. So the stronger chemical bond can be formed between the starch tannage and skin fibers. The skin fibers consist of very long molecules-collagen, which are twisted and interwoven with one another to give the fibrous structure of the skin. The long molecule is made up of amino acids which are joined together by peptide groups. There are many amino groups (-NH<sub>2</sub>) and hydroxyl groups (-OH) on the skin fibers. Good diffusivity and permeability of modified starch tannage let it permeate easily into skin fibers of each place and form chemical bond between -COOH and -OH of starch tannage and amino-groups (-NH<sub>2</sub>) and -COOH of skin fibers. So  $T_s$  of tanned leather is higher when the DS is greater.

#### The structure characterization of modified starch

FTIR spectra of original and modified starch are shown in Figure 8. The typical absorption peaks of original starch backbone such as  $\nu_{OH}$  3400 $cm^{-1}$ ,  $\nu_{CH_2, CH_3}$  2930 $cm^{-1}$ ,  $\nu_{C=O}$  1640 $cm^{-1}$ ,  $\nu_{CH}$  1410-1350 $cm^{-1}$ ;  $\nu_{C-O-C}$ -six membered ring 1154 $cm^{-1}$  and 1034 $cm^{-1}$ ,  $\nu_{O-}$  890 $cm^{-1}$  can be seen in the FTIR spectra. The characteristic peak of aldehyde groups in 1722 $cm^{-1}$  indicates that GA is successfully bonded on starch. The characteristic absorption peaks of aldehyde groups (1722 $cm^{-1}$ ) in Figure 8 (b and c) have disappeared. Hydroxyl absorption peaks of the composites at 3400 $cm^{-1}$  ( $\nu_{OH}$ ) decreased markedly compared to original starch in Figure 8. The characteristic absorption peaks of  $\nu_{CHO}$ ,  $\nu_{COOH}$  (1722 $cm^{-1}$ , 1730 $cm^{-1}$ , 1640 $cm^{-1}$ ) markedly become stronger. The schematic diagram of the chemical structure of modified starch is shown in Figure 2. The results prove that modified starch was prepared by acetalation of starch with GA and CA.

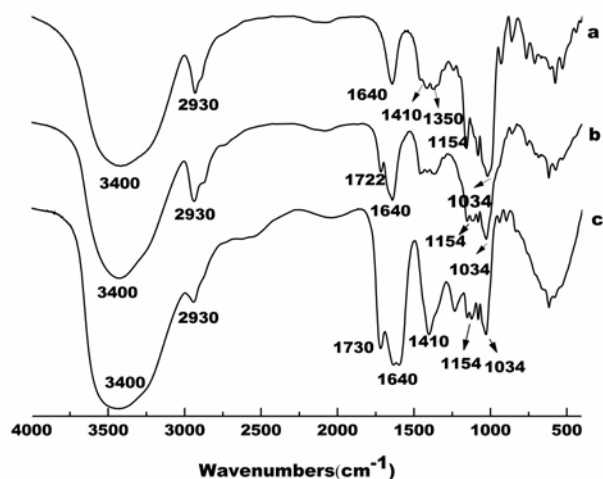


Figure 8. The FTIR of starch (a) and GA modified starch (b) and modified starch tannage (c)

The chemical structure of modified starch with GA and CA was characterized by means of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, which could indicate that modified reaction have successful carried out in starch. It is shown in Figure 3 and Figure 4.

#### Application properties of modification starch tannage

The modified starch by GA and CA was used as tanning agents in tanning process.  $T_s$  and mechanical properties of tanned leather with differential tannage are shown in Table III. It can be seen from results that the  $T_s$  of tanned goat leather by the modified starch has increased from 41.3°C to 83.8°C. Generally, the tanning materials must make  $T_s$  of leather no less than 80°C, so the modified starch can act as leather tannage. Strength properties for tanned leather by acetalation modified starch and chrome is comparable and meets GB/T22890-2008 (National Standards of the People's Republic of China). The strength properties like tensile and tear strength value are slightly lower than leather tanned by chrome tannage. The reason is that each AGU unit was been bonded two GA. Meanwhile, the modified starch has smaller molecular mass (Table IV) and easily to permeate and distribute through raw skin fibers. So hydroxyls (-OH) and carboxyl (-COOH) can easily permeate into skin fibers and from chemical crosslinking. The modified starch tannage can be used as leather tannage and take the place of chrome tannage. The schematic diagram of the tanning principle of starch tannage is show in Figure 9.

## CONCLUSION

The modification of starch tannage was prepared by acetalation of degradation starch with GA and CA in turn, respectively. The results showed that the modification method is an efficient way to improve tanning properties.  $T_s$  of tanned leather can increase to 83.8°C from 41.3°C. Accordingly, the

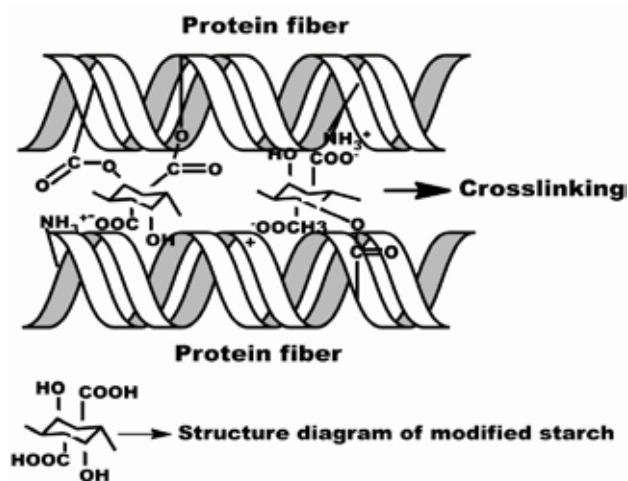


Figure 9. Schematic diagram of the tanning principle of modified starch tannage

modified starch can take the place of chrome tannage and may decrease pollution produced during the tanning process. The chemical structures of modification of starch were characterized by FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , which provided the evidence that GA and CA were grafted on starch by chemical bond. This novel modified method can notably improve tanning property of starch and the future development and application is very promising.

## ACKNOWLEDGEMENT

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### TABLE III

#### The $T_g$ and mechanical properties of tanned leather

Tannage	$T_g$ [°C]		Elongation at break[%]	Tensile strength [N/m <sup>2</sup> ]	Tear strength [N/mm]
	Skin	Leather			
Modified starch by GA and CA	41.3	83.8	61.57	9.73	36.53
Modified starch by AA and AN*	41.8	65.7	38.32	6.65	16.23
Chrome tannage**	41.7	106.5	65.45	14.87	43.41

\*: Modified starch was prepared by copolymerization of degradation starch and acrylic acid (AA) and acrylonitrile (AN).

The mass ratio of starch, AA and AN was 20:10:5.

\*\* : The chrome tannage was supplied by Brother Enterprises Co. Ltd of China

### TABLE IV

#### The relative molecule weight of the modified starch

Sample	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
Modified starch by GA And CA	2421	2874	1.187
Modified starch by AA and AN*	3376	5321	1.576

\*: Modified starch was prepared by copolymerization of degradation starch and AA and AN.

The mass ratio of starch, AA and AN was 20:10:5.

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