

# Tanning with Aluminum-Gallic Acid Complex: A New Way to Improve the Tanning Effect of Aluminum Salts

by

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## Abstract

To figure out how polyphenol compounds with a low molecular weight helped in aluminum tannage, a complex of gallic acid and aluminum as well as its application to the tanning of hide powder was studied in this paper. Precipitation points of aluminum chloride solution with different concentrations of gallic acid were measured to guide the basification in hide powder tannage. UV-Visible spectra showed that gallic acid and aluminum would form soluble complexes in aqueous solution and the complexation reaction was pH reliable. Through stoichiometry studies, generations of the 1:2 complex under pH 4.0 and 2:3 complex under pH 4.5 were discovered. Results of stoichiometry studies and Fourier Transform Infrared Spectroscopy (FTIR) spectra confirmed that aluminum-gallic acid complex played the role of links which connected collagen molecules rather than gallic acid or aluminum forming individual bridges with collagen. According to the results of differential scanning calorimetry (DSC) and thermal gravity analysis (TGA), denaturation temperature ( $T_d$ ) of hide powder tanned with different methods, such as aluminum, gallic acid-aluminum combination or aluminum-gallic acid complex, was 76.1°, 82.8° and 85.5°C respectively, and the initial decomposition temperature for the aluminum-gallic acid complex tannage was 300.7°C, also higher than those for another two methods. Furthermore, the results of inductive coupled plasma emission spectroscopy (ICP) showed that after washing for 12 h, the  $Al_2O_3$  content in hide powder tanned with complex could be maintained at 93.42% of that in unwashed samples, which was the highest among three tanning methods.

## Introduction

Aluminum tannage, a long-involved metal tanning method in leather manufacture history,<sup>1</sup> transforms pickled pelt into white, soft, fine and tight, bright and stretchable leather whose grain surface is as fine as woolen cloth.<sup>2</sup> However, a moderate shrinkage temperature (about 75°C) of tanned leather and the weak link between aluminum and collagen molecule<sup>3</sup> limit the solo application of aluminum salts in leather making. Therefore, various combination tannage

methods were carried out, such as chrome-aluminum tanning, vegetable-aluminum tanning, titanium-aluminum tanning<sup>4</sup> as well as aluminum used in conjunction with other compounds, like glutaraldehyde,<sup>5</sup> genipin,<sup>6</sup> some polymers<sup>2</sup> and syntans<sup>7</sup> to improve the properties of tanned leather. Among these methods, vegetable-aluminum tannage is considered as a potential replacement for chrome tannage since it results in the similar thermal stability of leathers to that of chrome tanned leathers,<sup>5, 8</sup> increasing shrinkage temperature of hides and skins to near 100°C.<sup>6, 9-11</sup> Note that vegetable tanning also limits the denaturation temperature to 85°C,<sup>12</sup> thus it is worth pondering why combination tannage of aluminum and vegetable tannins can significantly improve the hydrothermal stability of hides and skins.

Many studies have been done by leather chemists to figure out how polyphenols coupled with aluminum synergistically work on increasing shrinkage temperature and resulted in some meaningful conclusions. According to the reduction on pH value of aluminum sulphate after the addition of polyhydroxy compounds, Sykes *et al.*<sup>13</sup> inferred the formation of the complex without other specific evidence. Both of pyrogallol and catechol could inhibit the precipitation of aluminum, but the dosage of catechol would be twice pyrogallol, which emphasized the importance of the location of the hydroxy function on the benzene ring. By comparing shrinkage temperatures of tanned pelts, they also found that the essential condition for a satisfactory masking or pre-tanning agent should be either a higher molecular weight or the presence of tri-hydroxy groups. In research by Sykes *et al.*,<sup>14</sup> the authors revealed the presence of polyphenolics would reduce the rate of deuterium exchange of gelatin films treated by polyphenols, implying the generation of the hydrogen bond between polyphenols and gelatin. Moreover, the addition of aluminum to pyrogallol or catechol had insignificant effect on the exchange rate, which might suggest that aluminum was not attached to gelatin directly. According to the transmission electron micrographs of aluminum tanned and vegetable-aluminum tanned collagen fibrils, Hernandez<sup>15</sup> observed that aluminum was completely distributed over the fibrils after the combination tannage. It appeared that aluminum had no specific reaction with polar zones of collagen in combination tannage,

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which was contrary to the results of the aluminum tannage. Thus, Hernandez concluded that it was two tannin molecules which were linked together by one aluminum molecule that acted as the bridge between two polypeptides, and this linkage was expressed as "P-Tannin-Al-Tannin-P" (P stood for protein). Madhan *et al.*<sup>8</sup> concluded the shrinkage temperature of the leather tanned with vegetable followed by aluminum was much higher than the reverse order one, which could be explained by the view that following aluminum treatment to pelts pretanned by vegetable tannins would lead to the formation of another matrix in which aluminum is crosslinked between vegetable tannins therefore resulted in a higher hydrothermal stability of the tanned leathers. Theories above gave an insight into mechanism of the aluminum-vegetable tanning system and showed the important role of vegetable tannins in aluminum tannage, but there's still not specific research on how low molecular weight polyphenols and their complexes with aluminum donate to the properties of leather or other collagen-based materials.

Herein, hide powder, gallic acid and aluminum chloride was used to investigate how collagen, polyphenols and aluminum are interacting with each other. Aluminum tannage, gallic acid-aluminum tannage and aluminum-gallic acid complex tannage were applied to study the tanning effect of different tanning methods. First of all, the precipitation points of the different concentrations of the complexes were measured by pH titrations. The conformation of the reaction between gallic acid and  $Al^{3+}$  and how pH impacts the interaction was detected by ultraviolet-visible spectrophotometer. The coordination number of the aluminum-gallic acid complex was calculated by Job's Method.<sup>16</sup> The structural characteristics of varieties of the complexes and the binding modes between collagen and tanning agents in different tanning methods were explored by Fourier transform infrared spectroscopy (FTIR). Moreover, the thermal stability of hide powder was evaluated by differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TGA). Inductive coupled plasma emission spectrometer (ICP) was used to determine the washability of hide powder after tanning. Through this study, we hope to find out the specific interaction among aluminum, polyphenol and collagen thus providing an idea for broadening the application field of the tannage by aluminum-polyphenol complexes.

## Experimental

### Materials

Hide powder was obtained from grinding pickled pelt (made by cattle hide) and dehydrating with acetone and ethanol. Gallic acid ( $C_7H_6O_5 \cdot H_2O$ , AR) and aluminum chloride ( $AlCl_3 \cdot 6H_2O$ , AR) were purchased from Jinshan Chemical Test (Chengdu, China). Glycine (AR) came from Chron Chemicals (Chengdu, China). Aluminum standard solution in water (1000 mg/L, containing 5% nitric acid

and 0.4% hydrochloric acid) was gained from TMRM Quality Inspection Technology Co., Ltd. (Beijing, China). Polycaprolactam ( $[-NH(CH_2)_5CO-]_n$ , 60-90 mesh) was provided by Macklin Reagent (Shanghai, China). All reagents were used as received.

### pH Titrations of Aluminum Chloride and Gallic Acid Mixed Solutions

The precipitation points of the different concentrations of the complexes were determined by pH titration under room temperature ( $22^\circ\sim 25^\circ C$ ). Firstly, gallic acid was dissolved in the equimolar  $NaHCO_3$  solutions to achieve different concentrations of 1, 2, 3, 4, 5, 6 and 7% (w/w), respectively. Alkaescent condition created by  $NaHCO_3$  would improve the solubility of gallic acid. Then gallic acid solutions were mixed with equivalent volume of  $AlCl_3$  aqueous solution (containing 3%  $Al_2O_3$ , by weight). After stirring for 4 h, these mixed solutions were titrated with 0.5 mol/L NaOH solution at a speed of 0.25 mL/min with a HL-2 constant flow pump (Jiapeng Tech, Shanghai, China). Finally, the pH values at which the precipitation firstly appeared would be recorded as the precipitation of the complex solutions. At the endpoint of the titrations, the contents of  $Al_2O_3$  in solutions would be from 1% to 1.5% (by weight).

### Preparation of Aluminum-Gallic Acid Complex

Various molar ratios of gallic acid :  $Al^{3+}$  were prepared (1:0.1, 1:0.5, 1:1, 1:2, 1:3 and 1:4) in aqueous solution (pH 4.0, adjusted by HCl and NaOH solution) and concentration of gallic acid in blend solutions was kept constant at 0.1 mM. The solutions were incubated for 3 h at  $40^\circ C$  in a SHA-BA constant temperature water bath oscillator (Hongke Instruments, Nanjing, China) at 200 rpm. In addition, the reaction between gallic acid and aluminum chloride at under different pH values (3.5, 4.0, 4.5, adjusted by HCl and NaOH solution) were executed. Concentration of gallic acid and aluminum chloride was fixed at 0.01 mM and the solutions were incubated under the same condition described above. Finally, UV-visible spectra (from 200 to 400 nm) of solutions with different molar ratios and solutions under different pH values were obtained using a UV-1900 spectrophotometer (Jinghua Instruments, Shanghai, China) to verify the formation of aluminum-gallic acid complex and explore the influence of pH on the complexation.

### Determination of Stoichiometry of Aluminum-Gallic Acid Complex under Different pH Values

Job's Method<sup>16</sup> was used to determine stoichiometric coefficients for the complexes at pH 4.0 and 4.5. The mixtures contained a total of 0.2mM of reactants composed of various ratios of aluminum chloride and gallic acid. Each experiment was repeated three times. The UV-visible spectra of complex solutions were recorded as described above. Averages of three determinations were fitted using Origin 8.5 to identify the mixture composition value that yielded maximum absorbance at a wavelength characteristic of the aluminum-gallic acid complex.

Table I  
Types and Dosages of Materials in Different Systems

Group	Binary System						Ternary System						
	a		b		c		d		e		f		
Reactant	GA*	Al**	Gly***	Al	Gly	GA	N6****	Al	N6	GA	GA	N6	Al
Dosage	2mM	2mM	2mM	2mM	2mM	2mM	0.1g	0.2mM	0.1g	0.2mM	0.2mM	0.1g	0.2mM
Volume	100 mL						20 mL						

\*GA: gallic acid; \*\*Al: aluminum chloride; \*\*\*Gly: glycine; \*\*\*\*N6: polycaprolactam.

#### Preparation of Different Binary and Ternary Compounds

Types and dosages of the reactants used in preparing different binary and ternary compounds are shown in Table I. Each set of the experiments carried out at 40°C for 3 h under constant stirring at 150 rpm. When the reactions were terminated, solutions were poured into petri dishes, respectively, and then were lyophilized to get solid complexes for FTIR measurements. Reactions containing glycine were designed to explore how gallic acid and aluminum chloride react with carboxyl and amino groups, while the polycaprolactam was used to imitate the amido bond of collagen.

#### Tanning of Hide Powder

Hide powder was tanned by gallic acid and aluminum chloride after it was soaked for 2 h and drained. The detailed dosages of the tanning agents are displayed in Table II. In Group A, hide powder was only tanned by aluminum chloride for 3 h. The difference between Group B and Group C was the way of adding gallic acid and aluminum chloride. In Group B, aluminum chloride was added after hide powder reacting with gallic acid for 1.5 h. In Group C, gallic acid and aluminum chloride were first mixed to generate the complex under pH 4.0, and then hide powder was added to the complex solution. When tanning time reached 3 h, each group would get a basification with 10% of NaHCO<sub>3</sub> solution in 1 h to reach pH 4.0 and continued reacting for another 1 h. Finally, hide powder tanned by different methods was filtered and dried at 40°C in air. Samples were preserved in a desiccator filled with silicone particles for two days before various measurements.

#### Fourier Transform Infrared Spectroscopy (FTIR)

All binary and ternary compounds as well as tanned hide powder samples were ground with potassium bromide (KBr) by a ratio of 1:100 and the mixtures were made into round slices under a pressure of 15 MPa. The FTIR spectra of the samples were recorded by a Nicolet iS10 FTIR spectrometer (Thermo Scientific, Waltham, USA) at a wavenumber ranges between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup> and a resolution of 2 cm<sup>-1</sup> to investigate the structural features.

#### Thermal Analysis

Differential scanning calorimetry (DSC) and thermal gravity (TG) measurements were performed by DSC200PC (Netzsch, Bayern, Germany), TG209-F1 (Netzsch, Bayern, Germany), respectively, to research on the thermal properties of tanned hide powder samples. In the former, the temperature range is from 20° to 200°C at a constant heating rate of 5°C/min, and samples were protected by a 60 mL/min of nitrogen. In the latter, samples were heated from 40° to 700°C at a rate of 20°C/min and protected as above.

#### Measurements on Washability of Tanned Hide Powder

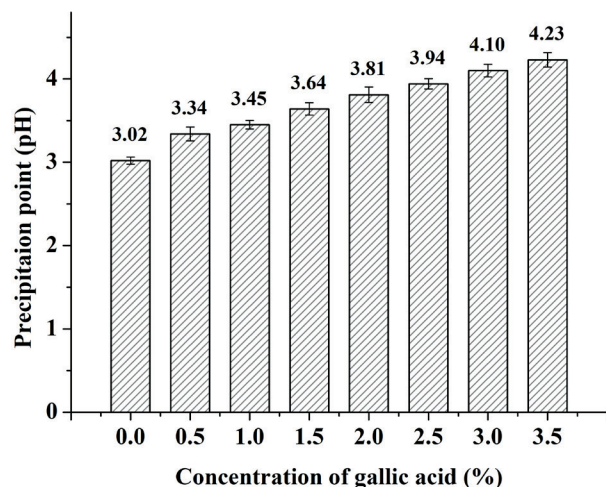
Different groups of tanned hide powder were washed in deionized water at 40°C for 0 h, 4 h, 8 h and 12 h, respectively. 50 mg of tanned hide powder before or after washing was digested in heated nitric acid and hydrogen peroxide, and then the remaining 1-2 mL of the digestion solutions were diluted to 50 mL with deionized water. An Optima 2100DV Inductive Coupled Plasma

Table II  
Dosages of the Materials in Tanning

	Gallic Acid/%	Al <sub>2</sub> O <sub>3</sub> /%	Wet Hide Powder/g	Deionized Water/%	Group
Dosage*	0.0	0.0	10	100	Control**
	0.0	1.0	10	100	A
	3.0	1.0	10	100	B
	3.0	1.0	10	100	C

\* The dosages of materials were based on wet hide powder;

\*\* pH value of control was adjusted to 4.0 by HCl solution.



**Figure 1.** Precipitation points of different concentrations of aluminum and gallic acid mixed solutions. Concentrations of  $\text{Al}_2\text{O}_3$  in initial mixed solutions was 1.5% (w/w)

Emission Spectrometer (Perkin Elmer, Massachusetts, USA) was used to determine the content of aluminum in various solutions and evaluate how the presence of gallic acid would impact the absorption of aluminum by hide powder. Parallel experiments were executed for three times.

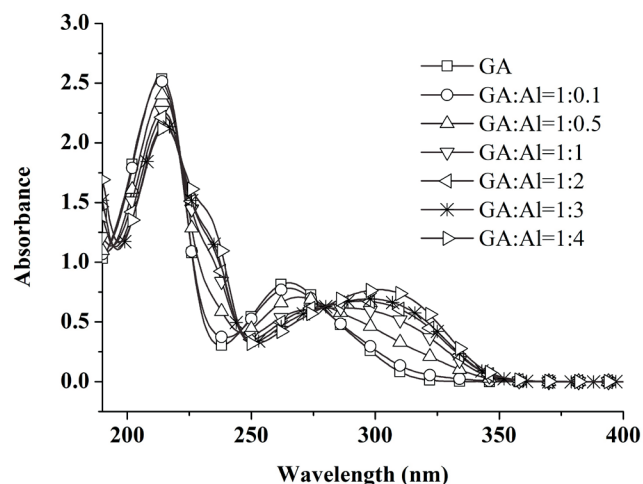
## Results and Discussion

### Precipitation Points of Aluminum and Gallic Acid Mixed Solutions

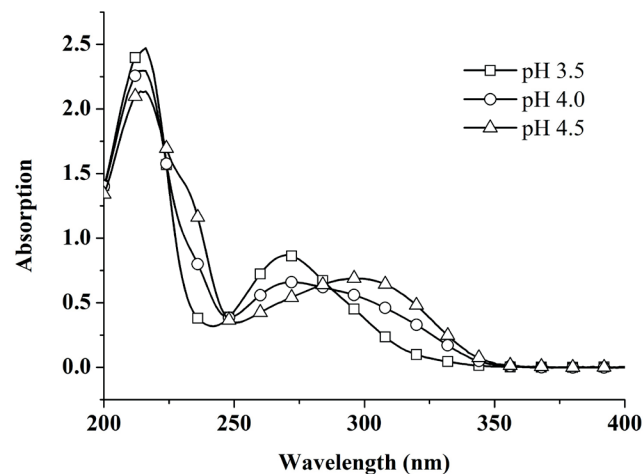
Fig. 1 shows the precipitation points of aluminum and gallic acid mixed solutions. Without gallic acid,  $\text{Al}^{3+}$  would form precipitation with  $\text{OH}^-$  at pH 3.02. As the concentration of gallic acid increased, the alkali resistance of  $\text{Al}^{3+}$  was also improved. When the concentration of gallic acid reached 3.5% in mixed solution, the precipitation point of  $\text{Al}^{3+}$  could be increased to 4.23, which may be resulted by the carboxyl or hydroxyl groups occupying the empty orbital of  $\text{Al}^{3+}$  so that the combination of  $\text{OH}^-$  and  $\text{Al}^{3+}$  was inhibited. Therefore, it could be indicated that complexation took place. Because gallic acid was dissolved in the equimolar  $\text{NaHCO}_3$  solution, to prevent the oxidation of gallic acid in alkaline condition when its concentration was relatively high, the content of gallic acid in the tanning liquid would be chosen at 3% (w/w) during the tanning of hide powder.

### Verification of the Aluminum-Gallic Acid Complexes

The UV-Visible spectra of aluminum and gallic acid mixed solutions with various molar ratios are shown in Fig. 2. Gallic acid shows two characterized absorption peaks at 214 nm and 265 nm. With the increase of the concentration of  $\text{Al}^{3+}$ , the spectra red-shifted incrementally relative to gallic acid and the peak at 265 nm weakened, almost disappeared when the molar ratio of gallic acid and  $\text{Al}^{3+}$  was 1:4. When the molar ratio of gallic acid and  $\text{Al}^{3+}$  was



**Figure 2.** Spectra of gallic acid reacted with different concentrations of aluminum chloride at pH 4.0. Concentrations of  $\text{Al}^{3+}$  were 0.01, 0.05, 0.1, 0.2, 0.3 and 0.4 mM, respectively, and concentration of gallic acid was 0.1 mM.



**Figure 3.** Impact of pH value on complexation of aluminum and gallic acid. Concentrations of gallic acid and  $\text{Al}^{3+}$  were both 0.1 mM.

greater than or equal to 1:1, a new absorption at 303 nm appeared, revealing the generation of the new complex. At pH 3.5, there was no obvious evidence to support the appearance of the new peak in spectrum of gallic acid, indicating the formation of aluminum-gallic acid complex might be restrained by the lower pH (Fig. 3). With the raise of pH value of reaction solution, the variation of the spectra would get more and more evident. When pH reached 4.5, the peak at 265 nm of gallic acid seemed to disappear as it did in a molar ratio of gallic acid and  $\text{Al}^{3+}$  was 1:4 at pH 4.0. This result may be explained by that ionization of tendency of carboxyl groups in gallic acid electronegativity of gallic acid (a nucleophile) could be enhanced by the increase of pH, thus the possibility of gallic acid to attack  $\text{Al}^{3+}$  (a common Lewis Acid) was improved.



### Stoichiometric Studies of Aluminum-Gallic Acid Complex

The stoichiometric ratios at different pH values (4.0 and 4.5) were determined by Job's method. Fig. 4a and 4b show the Job's plots at 303nm for the mixture of gallic acid and aluminum chloride under pH 4.0 and pH 4.5, respectively. Equation (1)<sup>17</sup> was used to calculate the number of gallic acid molecules that attached to each Al<sup>3+</sup>.

$$n = \frac{x_{max}}{1 - x_{max}} \quad (1)$$

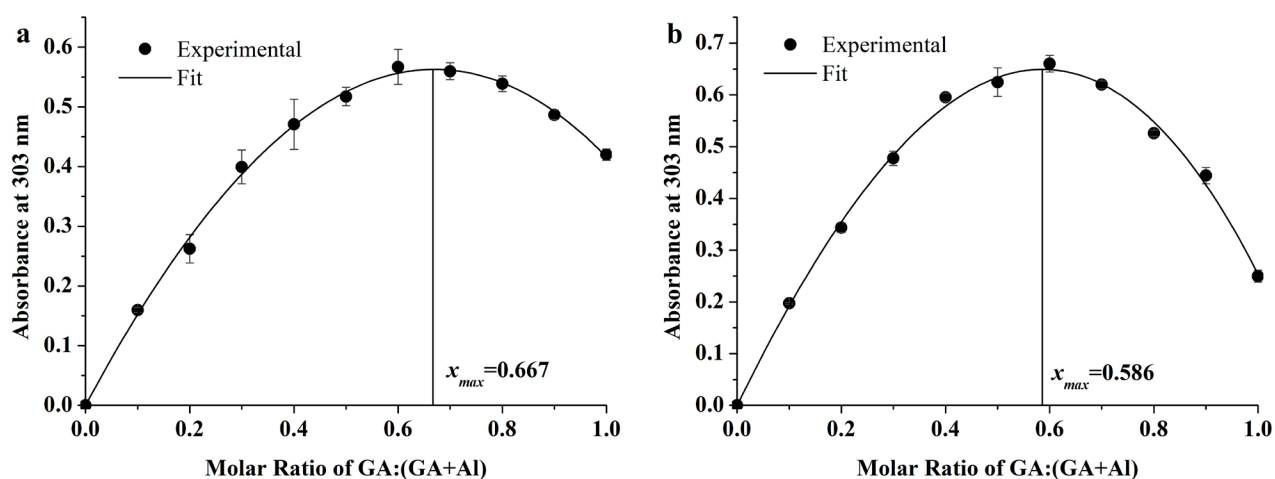
where  $n$  is the number of gallic acid each Al<sup>3+</sup> connects, and  $x_{max}$  is the abscissa of the fitted curves when ordinate gets the maximum. The plots indicated that the gallic acid formed a 1:2 complex at pH 4.0 and a 2:3 complex at pH 4.5. The results suggested that the complexation reaction between gallic acid and Al<sup>3+</sup> was pH reliable. Higher pH value leads to a more complicated complex.

Based on the results, the speculations of the binding mode between gallic acid and Al<sup>3+</sup> under pH 4.0 and 4.5 are given in scheme 1. By raising pH value, a multi-nuclear metal complex is generated.

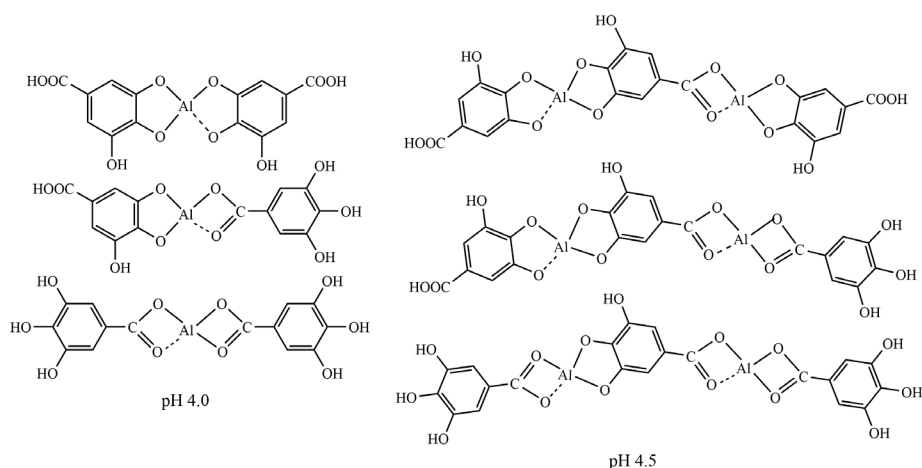
### FTIR Spectra Analysis

The FTIR spectra of gallic acid, gallic acid-aluminum complex and gallic acid-glycine compound are displayed in Fig. 5a, and bands assignment are shown in Table III.<sup>18-20</sup> After reacting with aluminum chloride, absorbance at 3371 cm<sup>-1</sup> shifted to 3386 cm<sup>-1</sup> and peaks at 3286 cm<sup>-1</sup> together with 1703 cm<sup>-1</sup> weakened obviously, demonstrating that both hydroxyl and carboxyl would participate in the complexation with aluminum. Furthermore, a weak peak at 632 cm<sup>-1</sup> appeared, which might be caused by the generation of C-O-Al. In the spectrum of gallic acid-glycine compound, all of characteristic peaks of gallic acid remained but most of them underwent different levels of decrease in their strength. It could be speculated that there were no new chemical bonds generated between glycine and gallic acid but hydrogen bonds did exist.

Fig. 5b represents the characteristic absorption of glycine and glycine-aluminum complex, and bands assignment are given in Table III.<sup>21-22</sup> The stretching vibration of N-H appeared at 3170 cm<sup>-1</sup>. Because of the intramolecular hydrogen bond, it was much lower



**Figure 4.** Job's plots at 303 nm for mixtures of gallic acid and Al<sup>3+</sup> at different pH. Total concentration of the mixture was maintained at 0.2 mM. (a) pH 4.0, R<sup>2</sup>=0.9966 (b) pH 4.5, R<sup>2</sup>=0.9952.



**Scheme 1.** Speculation of the binding mode between gallic acid and Al<sup>3+</sup> under pH 4.0 and 4.5

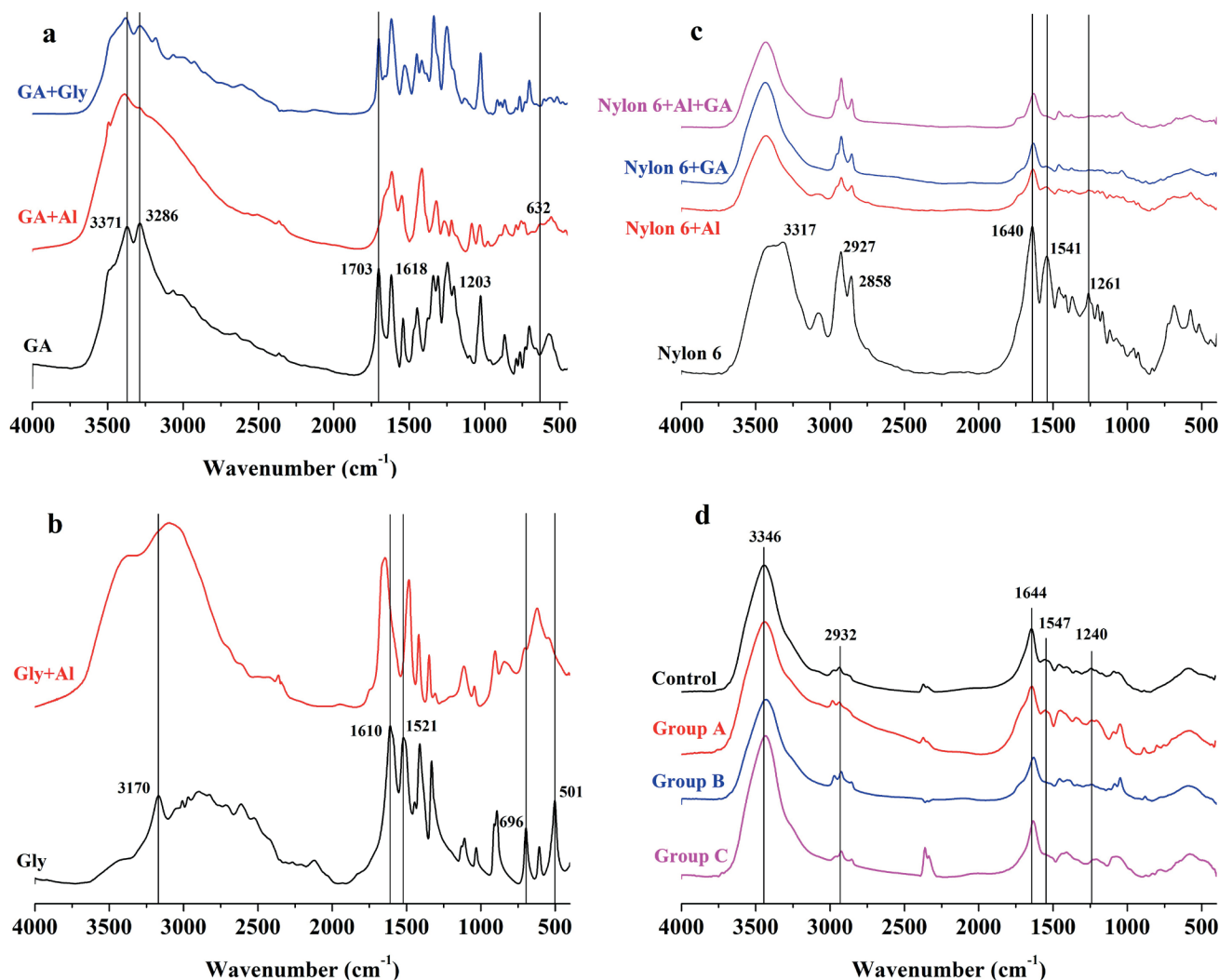


Figure 5. FTIR spectra of different kinds of the binary/ternary compounds and hide powder. (a) gallic acid and it mixed with aluminum chloride or glycine. (b) glycine and glycine-aluminum compounds. (c) polycaprolactam and it mixed with gallic acid and aluminum. (d) hide powder tanned with gallic acid and aluminum chloride (Control represents white hide powder).

Sample	GA	GA-Al	GA-Gly	Gly	Gly-Al
vO-H (Alcohol)	3371	3386	3385		3101
vO-H (Acid)	3268	3283	3283		
vC=O	1703	1670	1699	1610	1637
vPh-O	1203	1180	1131		
vC-O-Al		632			
$\delta$ N-H				3170	3101
$\delta$ C=O				690	705
$\rho$ C=O				501	535

**Table IV**  
FTIR major bands (in  $\text{cm}^{-1}$ ) assignment of polycaprolactam and hide powder

Sample	N6	N6-A1	N6-GA	N6-GA-A1	HP*	Group A**	Group B**	Group C**
Amide A					3446	3439	3430	3432
Amide B	2927	2927	2927	2927	2932	2936	2925	2923
Amide I	1640	1633	1629	1628	1644	1640	1631	1632
Amide II	1542	1541	1541	1541	1547	1550	-	-
Amide III	1261	1261	-	-	1240	1239	1236	1232

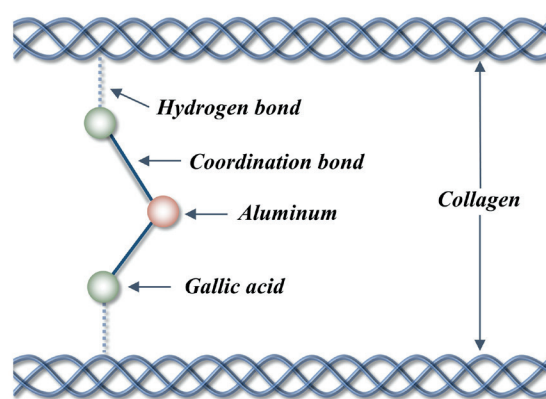
\*HP: hide powder; \*\*Group A/B/C: different groups of hide powder tanned by different methods.

than the normal vibration area of N-H ( $3500\text{--}3300\text{ cm}^{-1}$ ).<sup>21</sup> In the presence of aluminum, absorptions at  $3170\text{ cm}^{-1}$  and  $1610\text{ cm}^{-1}$  were blue-shifted relative to the spectrum of glycine due to the break of the intramolecular hydrogen bond by the formation of the complex. Meanwhile, bending vibration and rock vibration of C=O decreased dramatically and got blue-shifted, indicating that aluminum was coordinated with glycine by carboxyl.

Fig. 5c shows the FTIR spectra of polycaprolactam and its mixtures with gallic acid and aluminum chloride, and bands assignment are displayed in Table IV.<sup>23</sup> After introducing gallic acid or aluminum chloride, peaks of stretching vibration of C=O in amide bonds and N-H stretching vibration were blue-shifted and weakened, suggesting the occurrence of the reaction between polycaprolactam and gallic acid or aluminum chloride. Considering the characteristic peaks of gallic acid-polycaprolactam was similar to that of gallic acid-polycaprolactam-aluminum, it could be reasonable to get the inference that polycaprolactam would mainly react with gallic acid rather than aluminum chloride.

All of the characteristic peaks of collagen are exhibited in Fig. 5d, and bands assignment are shown in Table IV.<sup>24</sup> From the spectra, it could be concluded that the adding of gallic acid and aluminum chloride would yield a blue-shift on Amide II, but the presence of gallic acid would yield an additional decrease on the strength of Amide II, illustrating that gallic acid was the more active one to react with amide bonds of collagen than aluminum.

According to these consequences, the mechanism of the tanning with aluminum-gallic acid complex is speculated as scheme 2. Gallic acid would attach to peptide bonds in main chain or carboxyl groups and amino groups inside chains of collagen by hydrogen

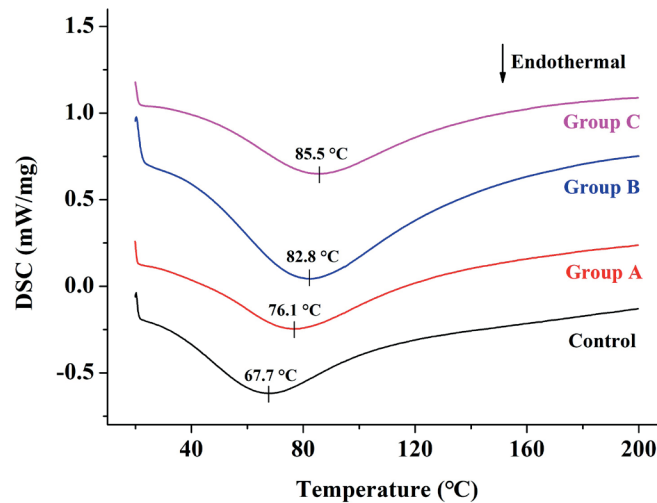


**Scheme 2.** Speculated mechanism of aluminum-gallic acid complex tanning

bonds, while aluminum would bind carboxyl or hydroxyl groups by coordination bonds between gallic acid molecules. The complex of gallic acid-aluminum played the role of links that connected collagen molecules, rather than individual bridges of aluminum or gallic acid.

#### Thermal Stabilities of Hide Powder

To ensure the effect of the tanning with gallic acid and aluminum chloride on hide powder, thermal denaturation and decomposition properties were examined by DSC and TG measurements, respectively. Fig. 6 shows the denaturation temperatures ( $T_d$ ) of different groups of hide powder. Tanning with aluminum chloride would increase  $T_d$  of hide powder from  $67.7$  to  $76.1^\circ\text{C}$ . While with gallic acid, it could get another raise of  $7.6^\circ\text{C}$  (Group B) or  $9.4^\circ\text{C}$  (Group C) comparing to  $T_d$  of hide powder in Group A. Results

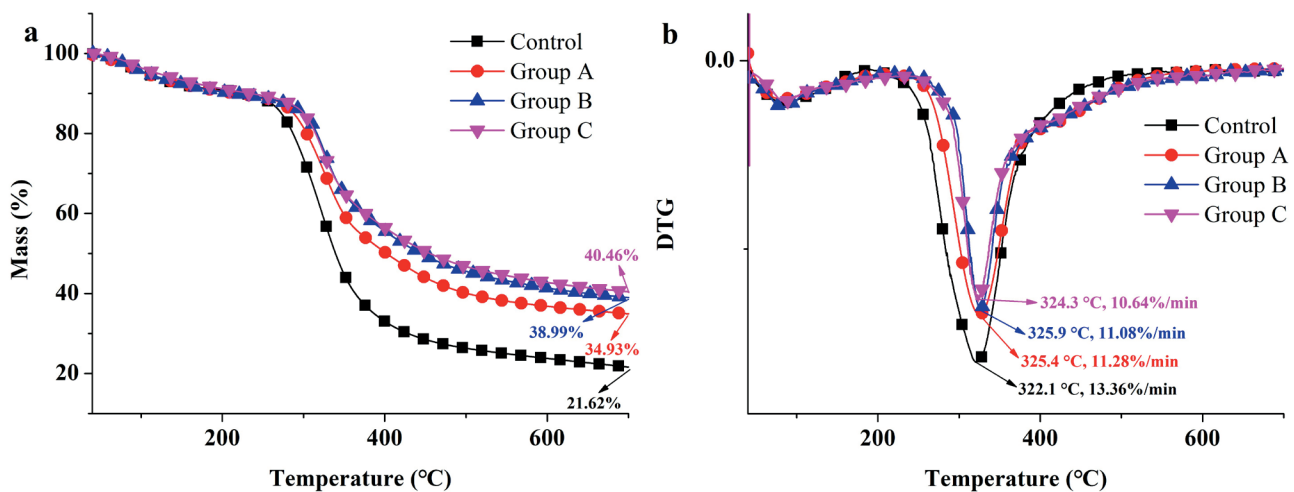


**Figure 6.** DSC curves of white hide powder (Control) and tanned hide powder. (Group A: aluminum tannage, Group B: gallic acid-aluminum combination tannage, Group C: aluminum-gallic acid complex tannage)

suggested that aluminum-gallic acid complex tannage would give a higher  $T_d$  than gallic acid-aluminum combination tannage, confirming pre-synthesis of the complex in tanning was favorable for promotion on thermal stability of hide powder.

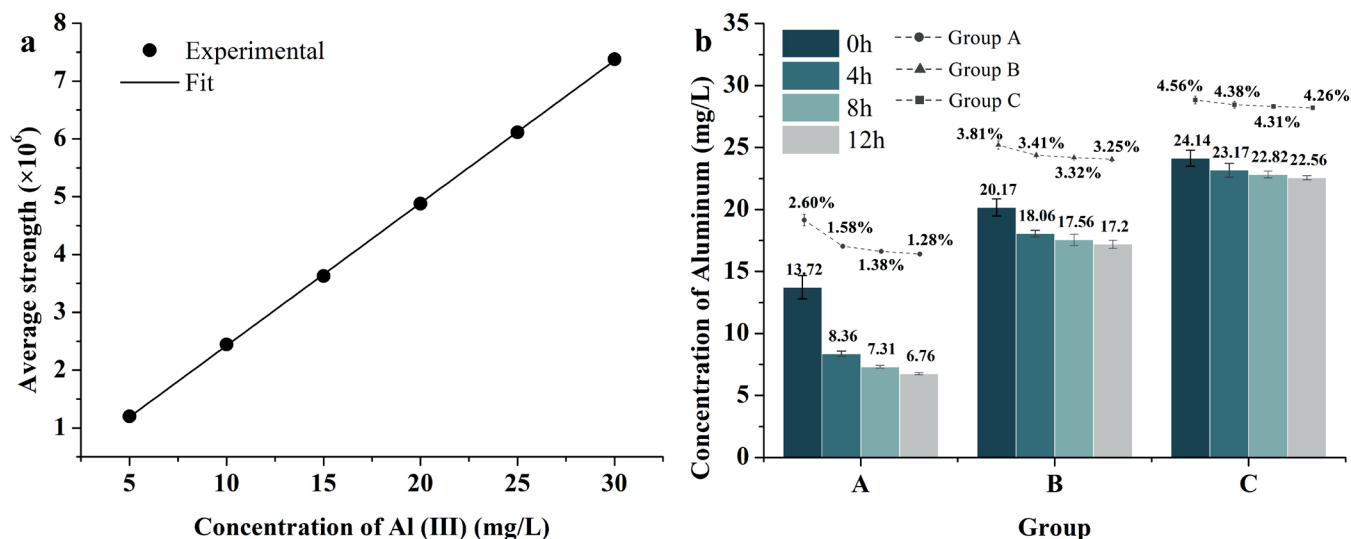
Fig. 7a and 7b exhibit the thermal gravity and differential thermal gravity curves of different groups of hide powder, respectively. There were two stages in the weight loss process of hide powder. The first stage from 50° to 150°C was on behalf of the evaporation of the water in hide powder. The second stage between 200° and 500°C was designated to the decomposition of the collagen molecules.<sup>25,26</sup> After tanning, initial decomposition temperature of hide powder was raised from 271.1°C (Control) to 292.8°C (Group A), 299.2°C

(Group B) and 300.7°C (Group C), respectively. Moreover, residual mass of hide powder was promoted from 21.62% (Control) to 34.93% (Group A), 38.99% (Group B) and 40.46% (Group C), respectively. From Fig. 7b, it could be concluded that under different tanning methods, temperature of the maximum weight loss rate increased from 322.1°C (Control) to 325.4°C (Group A), 325.9°C (Group B) and 324.3°C (Group C), respectively. And the maximum weight loss rate decreased from 13.36%/min (Control) to 11.28%/min (Group A), 11.08%/min (Group B) and 10.64%/min (Group C), respectively. Hide powder in Group C showed better thermal stability than hide powder in Group B, which was similar to the results of DSC measurements.



**Figure 7.** Thermal gravity (a) and differential thermal gravity (b) of different groups of hide powder. (Group A: aluminum tannage, Group B: gallic acid-aluminum combination tannage, Group C: aluminum-gallic acid complex tannage)





**Figure 8.** Standard curve of aluminum (a,  $R^2 = 0.9999$ ), tested concentrations of the aluminum in diluted digestion solutions (b, bar chart) and binding capacity of  $Al_2O_3$  in hide powder (b, line chart).

(Group A: aluminum tannage, Group B: gallic acid-aluminum combination tannage, Group C: aluminum-gallic acid complex tannage)

### Washability of Tanned Hide Powder

The standard curve of aluminum is shown in Fig 8a, and the tested contents of aluminum in diluted digestion solutions (bar chart) and the binding capacity of  $Al_2O_3$  in hide powder (line chart) are shown in Fig 8b, respectively. The binding capacity was calculated using Equation (2),

$$\text{binding capacity (\%)} = \frac{c \times V \times 102}{27 \times 2 \times m} \times 100\% \quad (2)$$

where  $c$  was the tested content of aluminum in the diluted digestion solution (mg/L),  $V$  was the volume of the diluted digestion solutions (L),  $m$  was the mass of hide powder used to digest (mg), 27 and 102 was the relative molecular mass of Al and  $Al_2O_3$  (g/mol), respectively.

The binding capacity of  $Al_2O_3$  of hide powder in Group A was 2.60%, while the participation of gallic acid would improve  $Al_2O_3$  content to 3.81% (Group B) and 4.56% (Group C), respectively. After washing for 4 h, the  $Al_2O_3$  content in hide powder became 60.77% (Group A), 89.50% (Group B) and 96.05% (Group C) of that in unwashed samples, while after washing for 12 h, the values decreased to 49.23% (Group A), 85.30% (Group B), 93.42% (Group C), respectively, which demonstrated that gallic acid would contribute to the fixation of aluminum in hide powder by its complexation capacity and the tanning with aluminum-gallic acid complex showed the best binding ability as well as the best binding stability with hide powder. The results illuminated the fact that the complex could form a stable

structure with hide powder thus hide powder in Group C got a fairly good washability.

### Analysis on the Tanning Effect of Aluminum-Gallic Acid Complex

According to the research of Covington *et al.*,<sup>27</sup> there was no change in the nuclear magnetic resonance (NMR) spectrum of 27-Al before and after the shrinkage of aluminum tanned leather, demonstrating that the shrinkage of leather wasn't caused by the break of the coordination bond between collagen and aluminum. Therefore, it could be inferred that the shrinkage reaction did not depend on the nature of the tanning bonding but a rigid matrix among collagen fiber formed by collagen and tanning agents, and this rigid matrix could restrain the conformation transition of collagen at the temperature where native collagen would get denatured.<sup>28</sup> In this study, the aluminum-gallic acid complex entered the void of collagen fiber and connected neighboring collagen molecules to form a rigid matrix. Thus, the stability of this whole rigid matrix containing collagen and complex was improved due to the reduction of configurational entropy of the structure.<sup>29</sup> The complex tannage and gallic acid-aluminum combination tannage shared the similar mechanism with what was reported.<sup>15</sup> However, due to the experimental results of DSC, TG and ICP measurements of hide powder, the complex seemed to generate a stabler structure with collagen. Therefore, aluminum-gallic acid complex tannage would confer a higher thermal stability and washability on hide powder.

## Conclusion

The complexation between gallic acid and aluminum was pH reliable. Higher pH value would facilitate the complexation reaction and result in the formation of the polynuclear complex. In the interaction of gallic acid, aluminum chloride and hide powder, it was gallic acid that directly attached to carboxyl or peptide bonds of hide powder and  $Al^{3+}$  was the one to connect gallic acid molecules. In the presence of gallic acid, tanning effect of aluminum was improved. In addition, due to the stabler rigid matrix formed in aluminum-gallic acid complex tannage, a higher thermal stability and washability of hide powder among three tanning methods was obtained. The complex tannage can be an effective way to improve aluminum tannage and provide an alternative to the modification of collagen-based materials.

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