



Paper D4

Combination tanning properties with aluminum salts and amide derivatives prepared by gallic acid and melamine

Xi-huai Qiang, Yuan Feng, Hui Zhang

College of Resource & Environment, Shaanxi University of Science & Technology, Xi'an, China, Phone:
029-86168675 e-mail: qiangxihuai@163.com

Abstract

The amide derivatives were synthesized with gallic acid and melamine by protecting the phenolic group of gallic acid before preparation and unprotecting it after preparation. The result of Leather tanning application experiment showed that adding TBM into leather tanning process could improve the combination tanning property of leather collagen. When added 8% (based on the mass of pickled skin) of TBM, the shrinkage temperature of crust was 67.3°C and the mechanism of tanning was same as the vegetable tannin which has abundant of plant polyphenol. When the usage of TBM is 8% and the aluminum salts is 10% (consider the mass of Al_2O_3), the shrinkage temperature of crust can reach to 83.8°C. It can be concluded that it shows synergism when there are both TBM and aluminum salts in the process.

1. Introduction

The gallic acid (GA) is one of natural material which is extracted from the plant. GA esters, which can be synthesized with GA and alcohols, have been widely used in antioxidative activities of the fat or the oil base food, maintain the freshness of fruit and vegetables, also serve as the cosmetics, the feed and the chemical additive of photosensitive hot sensitive material^[1,2]. At the same time, it can enhance the fibrin, dissolve the thrombus and expansive blood vessel to increase the crown arteries blood stream, it is also an effective condensation inhibitor for blood platelet. The GA esters have the ability about postpone senility and can prevent cardiovascular disease because the GA esters have the intense scavenging action to free radical in human bodies^[3-5].

At present, the GA esters are the key point for research and application to GA and the derivative^[6-9], such as ethyl gallate, butyl gallate, iso-butyl gallate, octyl gallate and so on, the method to synthesize these esters has already been quite mature. The reports on the method and useful about small molecular and the GA synthesized the GA derivative periphery have many phenol hydroxyl groups are reported rarely. This kind of GA derivative structure includes many phenol hydroxyl groups, has effects to tanning the skin collagen, when tanning with the aluminum salt can also enhance the leather's Ts obviously^[10].

This article use GA as raw material, after phenol hydroxyl protection and cyclation to obtain 3,4,5-trimethoxybenzoyl chloride, responded it with the melamine after unprotection, obtain



N,N',N''-(1,3,5-triazine-2,4,6-triyl)tris(3,4,5-trihydroxybenzamide) (TBM).

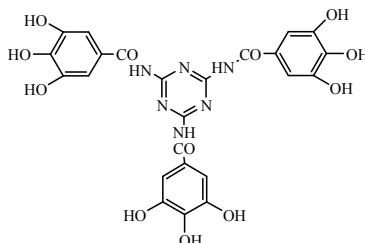


Fig.1 Structural formula of TBM

And research for the application in the leather tanning, discovered that the function to leather is similar with the vegetable tannin.

2. Materials and method

1 Reagents and instruments

GA; Acetic anhydride; Pyridine; Thionyl chloride; Melamine China; MJD-A 300 desktop plexiglass temperature control rotary drum, Xishan Xinda Leather Machinery Factory, China; MD-5 type leather shrinkage temperature detector, the Sunlight Electronics Research Institute of Shaanxi University of Science and Technology, China.

2 Procedures

2.1 Synthesis of 3,4,5-trimethoxybenzoyl

It is appropriate to add GA and acetic anhydride into a three-necked flask, after that, pyridine was added drop below 0°. After dropping, naturally warming it to room temperature, it is necessary to continue to react 12h. Then plunges the reaction fluid into the massive cold water to crystallize, add cold and diluted sulphuric acid. After the crystal was completely separated out, using a suction filter to collect the crystal, the filter cake was dissolved in saturated NaHCO₃ solution, and filter out the insoluble substance. Then add the diluted hydrochloric acid into the filtrate, several hours later, the crystal was completely separate out, use the filter eliminates the water, vacuum drying the filter cake, 3,4,5-trimethoxybenzoyl white crystal can be obtained.

2.2 Synthesis of 3,4,5-Trimethoxybenzoyl chloride

Add 3,4,5-Trimethoxybenzoyl chloride, SOCl₂ and few DMF into a three-necked flask, after heated to 65° reflux for 2h, the fluid was vacuum concentrated and washed with toluene, vacuum concentrated again, finally the mixture was extracted in CCl₄ to give a yellow acicular and penetrating odor crystal.

2.3 Synthesis of TBM

3,4,5-Trimethoxybenzoyl chloride and melamine dissolved in 1,4-dioxane and pyridine was added drop. After that warming up to 85° and reflux for 8h. After filtration, the fluid was spin-evaporated. The production was added into 70% acetic acid sodium solution to unprotect, add diluted NaOH solution to keep weakly alkaline, After vacuum concentration, dissolved the



system product in absolute ethyl alcohol, lay aside 2h above in the low temperature ($5^{\circ}\sim 10^{\circ}$), after air pump filtration, vacuum concentration the filtrates, then vacuum drying and obtain the yellow powder

2.4 Tanning technology

Carries on the sheep pickled skin for the experiment, splits along the back crestline, and cut along the back crestline to get the $4\times 1\text{cm}$ specification small piece of skins. Put into the conical flask and shake in the water-bath. Before the experiment, the pickled skins' Ts was determined.. Tanning technology was as follows.

(1) TBM tanning

Weighing: Increase the weight of acid skin by 100% and use it as the benchmark of the following Process materials.

Repickling: Water 150%, regulate the bath pH value between 4 to 5 with formic acid, salt 8%.

Tanning: Add TBM (0%, 2%, 4%, 6%, 8%, 10% of the tare) to the repickling liquor, oscillate 6h, and regulate the bath pH value between 3.0 to 3.5 slowly in two hours. Standing overnight, oscillate 30min the next day, and then flowing. the pickled skins' Ts was determined.

(2) TBM-Al tanning

Weighing: Increase the weight of acid skin by 100% and use it as the benchmark of the following Process materials.

Repickling: Water 150%, regulate the bath pH value between 4 to 5 with formic acid, salt 8%.

Tanning: Add TBM (2%, 4%, 6%, 8%, and 10% of the tare) to the repickling liquor, oscillate 6h, and regulate the bath pH value between 3.0~3.5 slowly in 2h. Standing overnight, oscillate 30min the next day, and then flowing.

Aluminium tanning: water 100%, regulate the pH value between 2 to 3 with formic acid. Salt 8%, anhydrous aluminium sulfate 10%; after 4 to 5 hours' oscillation at 25° , regulate the pH value to 4 slowly in two hours with baking soda solution (mass fraction 5%), standing overnight, oscillate 30min the next day, and then flowing, wash out the skin, to sample and test the crust leather Ts.

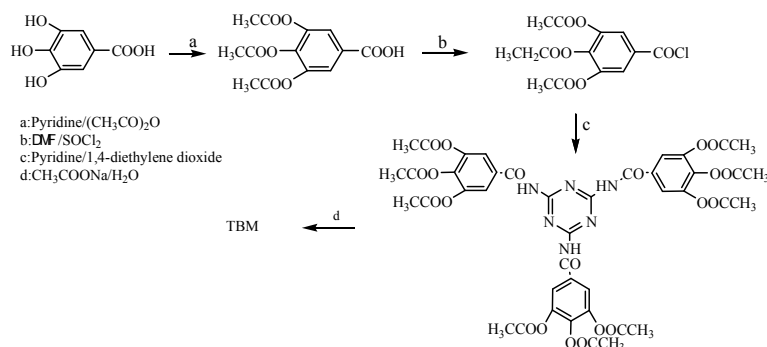
2.5 The test of resistance to damp and hot stability changes of TBM tanning crust leather deal with different solution.

Put the TBM tanning sample into water, formic acid liquor (pH about 2.5), soda solution (pH about 9.5), salt solution (10%), urea solution (10%) and acetone aqueous (Vacetone : $V_{\text{water}}=1:1$) in the tapered bottle, oscillate 12h and then standing overnight. The next day wash the crust leather and test the Ts.



3. Results and discussion

1. Synthetic procedures of TBM



2. The structure characterization of TBM

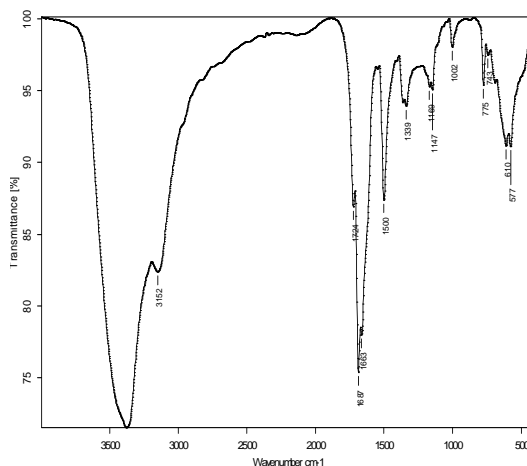


Fig. 2 IR spectrum of TBM

IR $\nu_{\text{max}}/\text{cm}^{-1}$: a large blunt peak appears at the position of 3426, indicating that the synthetic product contains a large amount of phenolic hydroxyl groups.

3. TBM tanning properties

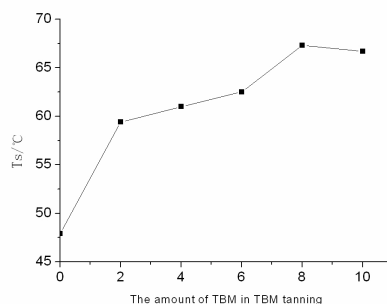


Fig. 3 The shrinkage temperature of TBM tanning leather (°C)



According to the 2.4 tanning process, tan with TBM separately and the experiment results can be seen in Fig.3. It showed that with the increase of TBM, Ts of leather rises gradually. When the dosage of TBM has reached 8%, Ts of leather can get 67.3°. But if continuing increasing the dosage of TBM, there will be no effect on the Ts of crust leather.

Sample the crust leather tanned by 8% TBM and test the resistance to damp and hot stability changes of the sample after dealing with acid liquor, alkali liquor, salt, urea and acetone. The results are shown in the Fig. 3.

Table 1 The change of TBM tanning leathers' Ts dealing with six eluants

Eluants	Water	Formic acid	Soda	Salt	Urea	acetone
Ts (°C)	65.2	62.3	52.1	59.1	55.7	61.7
ΔTs (°C)	2.1	5	15.2	8.2	11.6	5.6

It can be seen that alkaline and urea medium have more positive effect on detanning than salt and acetone. So it figures out that the same as vegetable tanning, the tanning between TBM and collagen is mainly based on the hydrogen and electrovalent bond between phenolic hydroxyl group and the amino of collagen.

4. TBM-Al tanning

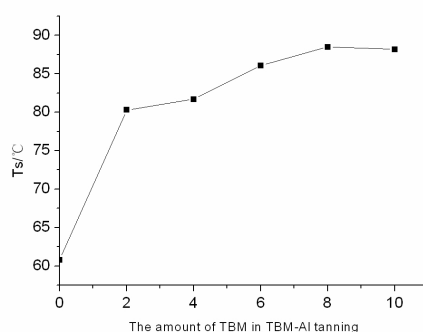


Fig.4 The shrinkage temperature of TBM-Al tanning leather (°C)

Fig. 4 shows that without TBM, the Ts of pickled skin tanned by aluminium can only get 60.8°, using 2% (based on the mass of pickled skin) of TBM tanned with aluminium, the Ts can rise from 47.9° to 80.3°, the effect of aluminium auxiliary tanning is obviously. The Ts is gradually rising along with the increase of TBM. When the dosage of TBM is 8%, the Ts can reach to 88.5°. And if the dosage of TBM is higher than that, there is little effect to the Ts.

For TBM has many phenolic hydroxyls, two adjacent phenolic hydroxyls could make complexing with Al^{3+} to form stable five ring structure, to increase the junctures of tanning



agent and collagen fiber. The Al^{3+} of five ring structure can make complexing with carboxyl of adjacent collagen peptide pendant group, while the phenolic hydroxyl make hydrogen bond with collagen fiber to form cross-linked structure between collagen fibers. The Ts will increase obviously because of the collaborative tanning effect as a result.

4. Conclusions

1. The amide derivatives (TBM) were synthesized with gallic acid and melamine by protecting the phenolic group of gallic acid before preparation and unprotecting it after preparation. Because of the many phenolic hydroxyls of the TBM, add TBM into leather tanning process can improve the combination tanning property of leather collagen. When we add 8% (based on the mass of pickled skin) of TBM, the shrinkage temperature of crust can improve 20%.
2. Alkaline and urea medium have more positive effect on detanning of crust tanned by TBM than salt and acetone. So it figures out that the same as vegetable tanning, the tanning between TBM and collagen is mainly based on the hydrogen and electrovalent bond between phenolic hydroxyl group and the amino of collagen as vegetable tanning.
3. When the usage of TBM is 8% and the aluminum salts is 2.5% (consider the mass of Al_2O_3), the shrinkage temperature of crust can reach to 83.4% and it is 23% more than aluminium tanning. It can be concluded that it shows synergism when there are both TBM and aluminum salts in the process.

5. References

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