TANNING EFFECTS OF ALUMINUM -GENIPIN OR -VEGETABLE TANNIN COMBINATIONS

by

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ABSTRACT

Genipin, a naturally occurring protein crosslinking agent, isolated from the fruit of *Gardenia jasminoides Ellis,* is beginning to replace glutaraldehyde as a fixative for biological tissues. Earlier research in this laboratory demonstrated that when hide powder was first tanned with 8% aluminum and retanned with (2% to 10%) genipin the thermal stability increased linearly with increasing concentrations of genipin, suggesting the possibility that a practical combination tannage based on genipin could be designed. When pieces of bated hide were pretanned with 6% aluminum, then split and tanned with 6% genipin based on the weight of the split wet-white pelt, the hydrothermal stability was about 89°C as determined from the onset of the melting curve in a differential scanning calorimetry (DSC) experiment, or T_s = 92°C by a traditional shrinkage temperature measurement. Values for the physical-mechanical properties were similar to those measured for aluminum-glutaraldehyde and mimosa-aluminum leathers prepared, as controls, under equivalent conditions. By subjective evaluation, the appearance of aluminum-genipin tanned leather was rated 4 on a scale of 1 (poor) to 5 (very good), and the leather was more stable to washing than were control leathers. These results suggest the potential for development of practical genipin-based tannages.

RESUMEN

Genipín, un agente reticulante de origen natural para proteínas, obtenible del fruto de la *Gardenia jasminoides Ellis,* está comenzando a reemplazar el glutaraldehído como un fijador de tejidos biológicos. Anteriores investigaciones en este laboratorio han demostrado que cuando piel en polvo precurtida con 8% de aluminio y recurtida con (2 a 10%) de genipin, la estabilidad térmica aumento proporcionalmente al aumento en la concentración de genipín, sugiriendo la posibilidad de un curtido práctico de combinación basado en genipín sería diseñable. Cuando trozos de piel rendida fueron precurtidos con 6% de aluminio, fueron luego divididas y recurtidas con un 6% de genipín basado en peso precurtido dividido, la estabilidad hidrotérmica fue alrededor de 89ºC tal como determinada al inicio de “derretido” en la curva determinada por observación calorimétrica por barrido diferencial (“DSC”), o T_s =92ºC por medición tradicional de la temperatura de contracción. Los valores de las propiedades físicas y mecánicas fueron similares a las observadas en cueros preparados por curtición de aluminio-glutardehído y mimosa-aluminio, como controles, bajo condiciones equivalentes. Bajo evaluación subjetiva, el aspecto del cuero curtido por aluminio- genipín fue evaluado como 4 en una escala de 1 (muy malo) a 5 (muy bueno), y el cuero resulto más estable al lavado que los cueros preparados como controles. Estos resultados sugieren la factibilidad del desarrollo de curticiones practicables basadas en genipín.

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INTRODUCTION

Quality, cost and yield have long been the main concerns of leather manufacturers, and were the driving force behind the development of chrome tanning. In recent years, environmental concerns, combined with consumer preference, particularly in the European market, for chromium-free leather have driven research into the development of reduced chrome and chrome-free tanning methods.

The stability of chrome-tanned leathers in the presence of heat and moisture makes them the standard to which leathers tanned by other means are compared. Considerable research has shown that the tanning effects of minerals other than chromium (Al, Zr, Ti, or Fe) are enhanced when they are used in combination with vegetable tannins, aldehydes, or other organic molecules.[1–5] Tannages comprised of vegetable tannin-aluminum,[2] vegetable tannin-aldehyde,[6,7] and aluminum-aldehyde[3] have been shown to be effective. Leathers tanned by these combinations have physical-mechanical properties adequate for a variety of applications and hydrothermal stability in the 85°C to 100°C range. Nevertheless, these combination tannages have not been widely adopted.

Genipin, an iridoid crosslinking-agent, of very low toxicity[8] which can be isolated from the fruits of *Gardenia jasminoides,*[9] has recently come to the attention of the biomaterials industry. The feasibility of using genipin as a fixative for biological tissues,[8] and a cross-linker of biopolymers, including gelatin, and chitosan[10–12] has been demonstrated. Recent research from this laboratory[13] has shown that treatment of hide powder with 5% genipin resulted in increased hydrothermal stability. When aluminum-genipin combinations were tested on hide powder, an aluminum pretreatment followed by a genipin treatment produced a higher hydrothermal stability than did the reverse.[14] This finding is in contrast with aluminum-vegetable tannin combinations where aluminum is typically applied after tanning with the vegetable tannin.[15,16] Thus for the present study, intact pieces of cattle hide were pretanned with aluminum, followed by a genipin or glutaraldehyde tannage, or pretanned with mimosa followed by an aluminum tannage.

EXPERIMENTAL

Materials

Genipin (MW= 226.23) with 98% purity as determined by HPLC was obtained from Challenge Bioproducts Co. LTD, Taiwan, China; vegetable tannins from the former Pilar River Plate, Inc. (Newark, NJ); Borron TS from Rohm Tech., Inc. (Malden, MA); Proxel from Chemtan Co. (Exeter, NH); Rohapon 6000 from TFL USA/Canada; Atlasol CSL and Eureka 400R were from Atlas Refinery, Inc. (Newark, NJ); aluminum sulfate hydrate, sodium citrate, glutaraldehyde (25% solution) and other common chemicals were from Sigma-Aldrich Chemical Company, USA. Hide pieces were from fresh hides collected at a local abattoir.

Preparative Procedures

Sample preparation. The hide pieces (~10 × 20 cm) were soaked, unhaired, relimed and delimed, and bated essentially as described by Cabeza et al.[17] In this study bating was performed at 25°C and 4 rpm, all other operations were performed at 20°C and 4 rpm. Experiments were carried out in 10 L experimental drums (Dose Systems AG, Lichtenau, Germany), the drums are jacketed and use circulating water for temperature control (± 1 °C). Samples for aluminum-genipin combination tanning were pickled in 150% water with 0.5% acetic acid, 1% sulfuric acid, 10% sodium chloride, and 10% sodium sulfate at 20°C for 90 min at 4 rpm to a final pH of 2.0–2.5. The pickling solution was specifically designed for this laboratory scale experiment. Weights of added chemicals were based on the weight of the delimed, bated hide. Sodium sulfate was included to improve the resistance to acid swelling. The 20% total for added salt was to provide a salt concentration in the float similar to tannery conditions where the ratio of liquid to solid is lower.

Aluminum pretanning. Aluminum pretanning was carried out in the pickling solution by the addition of $Al_2(SO_4)_3 \cdot 18\ H_2O$ to be the equivalent of 6.0 % Al_2O_3 with sodium citrate ($[Cit]/[Al^{3+}] = 1/4$) as a masking agent. The temperature was increased to 35°C and the process run for 12 h at 6 rpm. The pH was then adjusted first to 3.5–4.0 over 6 h and then to 4.5–5.0 over an additional 6 h by the addition of sodium bicarbonate. Samples were next drained, washed twice with 3000% water, drained and blotted with filter paper to a final moisture content of ~40%.

Genipin tanning. In preparation for genipin tanning, aluminum pretanned samples were split to 1.0–1.2 mm. Chemical offers for genipin tanning were based on the weight of the grain split. Initially, 6% genipin and 100% water were added to aluminum pretanned grain splits at pH 4.5–5.0 and the process run at 30°C ± 1 °C and 6 rpm for 6 h. The temperature was then increased to 35°C and the pH adjusted first to 6.0–6.5 over 6 h and then to 7.5–8.0 over an additional 12 h by the addition of sodium bicarbonate. After washing, draining, and fatliquoring as described by Cabeza et al.[17] samples were paste dried at ambient temperature (22 - 24 °C), followed by staking and milling.

Preparation of controls. As controls, similar pieces of aluminum-glutaraldehyde (aluminum-pretanned, grain split, and tanned with 10% glutaraldehyde) and mimosa-aluminum (bated pelt pretanned with 25% mimosa, then tanned with 6% Al_2O_3) combinations were prepared.[14] Post-tanning processes for these control tannages were the same as for aluminum-genipin tanned leather.

Analytical Procedures

Thermal analysis. Hydrothermal stability of the test leathers both before and after fatliquoring was determined using a Multi-Cell Differential Scanning Calorimeter (model CSC-4100) from Calorimetry Sciences Corporation, Lindon, UT, as previously described.[13] A 6–8 mm sample was cut from tanned leather and soaked in distilled water overnight in order to be thoroughly wetted. The wet sample was removed from the soak, and excess surface water absorbed on filter paper. Moist, blotted samples (100–250 mg) were weighed into ampoules that were sealed and placed in the calorimeter. The temperature was programmed to record from 30°C to 130°C at 1.5°C/min with an equilibration period of 600 sec at the start. Samples were later dried, and the initial moisture content (usually 150%–250%) of each sample was calculated. DSC data was processed using CpCalc V2.2 software provided by the instrument manufacturer.

Shrinkage temperatures were determined for each tannage, before and after fatliquoring, as described by Fein et al.[18] Wet sample specimens, in the form of 5.6 × 57.2 mm strips, were inserted into appropriate holders, and placed into the water bath at room temperature. The water was heated at 3°C per min and the temperature at the first definite sign of shrinking was recorded.

Physical tests. Measurements of tensile strength, modulus and elongation were performed according to ASTM D 2209-00.[19] Tear strength was determined by ASTM D 4704-00.[20] Specimens of each tannage, after fatliquoring, were cut with a hydraulic pattern cutter (Clicker) (Sloan Machinery Co., Lynn, MA) and the thickness of each specimen was measured with a Randall-Stickney dead-weight (Waltham, MA) at three points. Samples were conditioned and measurements were made at 23°C and 50% RH with an INSTRON model 1122 (Canton, MA). Data were collected and processed by an Instron series IX automated materials testing system version 5.

Subjective Evaluation. Grain characteristics, fullness and handle were evaluated visually and by touch. Two professional tanners and three researchers graded the samples on a scale of 5 (very good) to 1 (poor).

Washability. To evaluate the stability of aluminum-genipin tanned leather when exposed to mild cleaning (washing) conditions, 6 × 6 cm pieces of tanned leather in 250 ml flasks with 1000% distilled water and 10% common non-ionic surfactant were placed in a shaking water bath at 30°C. A 1 × 1 cm piece of leather was cut from the test sample after shaking for 2 h, 4 h, 6 h, 8 h respectively and the hydrothermal stability was determined by DSC.

RESULTS AND DISCUSSION

Hydrothermal Stability

Hydrothermal stabilities of sample and control leathers were determined before and after fatliquoring both as apparent shrinkage temperatures by DSC, and as traditional shrinkage temperatures in a shrink-temperature apparatus as described by Fein et al.[18] The results are summarized in Table I, where the onset and peak temperatures determined by DSC are compared with traditional shrinkage temperatures (T_s). Although leather tanned with the mimosa-aluminum combination had the greatest hydrothermal stability and leather tanned with the aluminum-genipin combination tanned leather the least, the shrinkage temperatures (Ts) of these leathers are all greater than 90°C. As anticipated,[21] fatliquoring caused the thermal stability of all leathers tested to decrease. The largest effect of fatliquoring on the shrinkage temperature was observed for mimosa-aluminum tanned leather where the average decrease in T_s was nearly 15°C, possibly due to removal of mimosa by the fatliquoring agents. The smallest effect of fatliquoring on thermal stability was observed for the aluminum-genipin tanned leather where Ts was reduced by 2°C.

The hydrothermal stability of leather is a primary characteristic of the effectiveness of a tannage. The standard shrinkage temperature (T_s) measurement of the hydrothermal stability of leather (ASTM D 6076-03)[22] uses the Theis shrinkage meter, an instrument that is no longer obtainable. The Fein[18] method, which like the Theis method uses strips of leather as the samples, but with equipment that can be assembled from items commonly found in the laboratory, is also suitable for measurements in the tannery. In research centers, where calorimeters, particularly DSC's, are more likely to be available, they are generally used for studies of hydrothermal stability. At least three general types of DSC instruments are available, and although each type measures the same thermal transition, the design of the calorimeter affects the apparent result. The DSC method used in this research differs from the most common DSC methods in the following three ways: (1) the sample holder has a volume of about 1 mL as opposed to <100 µL and making it feasible to increase the magnitude of the signal by using a 200 mg sample as opposed to the usual 5–10 mg sample; (2) the instrument is designed for measurements on solutions or mixtures of solid with liquid, thus a moisture level greater than 150% of dry sample weight can be maintained and accurately measured; (3) with this instrument, a heating rate of 1.5°C/min was used in contrast with the usual 10°C/min, a particularly important factor because of the slow rate of collagen denaturation.[23] These differences combine to make the conditions of the measurement of thermal stability by this method more similar to the conditions for measurement of a shrinkage temperature (T_s). DSC data in the form of a plot of heat flow vs. temperature gives both an onset and a peak temperature for each thermal transition. In the Fein measurement of T_s, only the temperature at the first definite sign of shrinking is recorded. Using the data in Table I, T_s

TABLE I
Hydrothermal Stability of Leather from Combination Tannages

	Before fatliquoring			After fatliquoring		
Tannage[a]	**Al-GP**	**Al-GLUT**	**Mimosa-Al**	**Al-GP**	**Al-GLUT**	**Mimosa-Al**
T_o[b]	89.1 ± 1.2	92.4 ± 1.4	110.6 ± 2.2	88.2 ± 1.7	88.6 ± 1.9	94.3 ± 2.6
T_p	112.2 ± 0.5	114.8 ± 0.6	127.2 ± 1.2	104.3 ± 0.7	106.8 ± 0.6	104.7 ± 1.5
T_s	92.3 ± 1.8	94.6 ± 1.6	111.5 ± 1.7	90.2 ± 1.9	90.7 ± 1.5	96.6 ± 1.6

[a] Tannages are aluminum-genipin (Al-GP), aluminum-glutaraldehyde (Al-GLUT), and mimosa-aluminum (Mimosa-Al)
[b] T_o and T_p are the onset and peak temperatures from DSC, T_s is the shrinkage temperature. Temperatures in °C are the average of three separate determinations

TABLE II
Properties of Leather from Different Tannages

	Al-GP	**Al-GLUT**	**Mimosa-Al**
Tensile strength (MPa)	16.8 ± 1.2[a]	20.2 ± 1.2	17.2 ± 0.8
Elongation (%)	82.1 ± 9.1	60.1 ± 3.2	59.3 ± 4.7
Modulus (1–10%) (MPa)	8.4 ± 0.2	13.4 ± 3.7	11.5 ± 2.0
Toughness (J/cm^3)	6.4 ± 1.3	5.2 ± 0.3	4.6 ± 0.5
Tear strength (N/mm)	40.2	57.6	51.8
Handle	4.4	3.4	2.2
Fullness	4.2	3.5	3.2
Grain characteristics	4.3	2.7	2.1
Color	Dark blue	Pale yellow	Light brown

[a] Values for tensile strength, elongation, modulus, and toughness are the averages and standard deviations based on three separate determinations. A single measurement of tear strength was made for each tannage. Values for subjective properties are the average of five separate assessments.

measured by the Fein method is an average of 2.1 ± 0.7°C higher than the onset temperature and 15.7 ± 4.4°C lower than the peak temperature measured by DSC. Thus the onset temperature, by a DSC method that uses experimental parameters similar to those of the traditional shrinkage temperature measurement, can be correlated with T_s in meaningful fashion.

Physical-Mechanical Properties

The physical-mechanical properties of these leathers are summarized in Table II. At 16.8 MPa, the tensile strength of the aluminum-genipin tanned leather is essentially the same as the tensile strength of the mimosa-aluminum tanned leather. It is marginally lower than the tensile strength of aluminum-glutaraldehyde tanned leather (20.2 ± 1.2 MPa) prepared in this study or the glutaraldehyde-tara-aluminum tanned bovine upper shoe leather (21 MPa) of Vitolo et al.,[19] but is within the 15–37 MPa range of acceptable values for shoe leathers.[24] Modulus (1–10%) and tear strength of aluminum-genipin combination tanned leather are lower than those of aluminum-glutaraldehyde and mimosa-aluminum combination tanned leathers; however, elongation and toughness are greater. Toughness is closely correlated with leather handle, a high toughness parameter typically indicates a good handle, this correlation is reflected clearly in Table II, where the visual and touch assessment of aluminum-genipin combination tanned leather were superior to those of aluminum-glutaraldehyde and mimosa-aluminum combination tanned leather. An additional observation is that this aluminum-genipin combination tannage produced an attractive dark blue, almost black, leather without the need of a dyeing step. If a truly black leather were desired, a dyeing protocol could undoubtedly be developed.

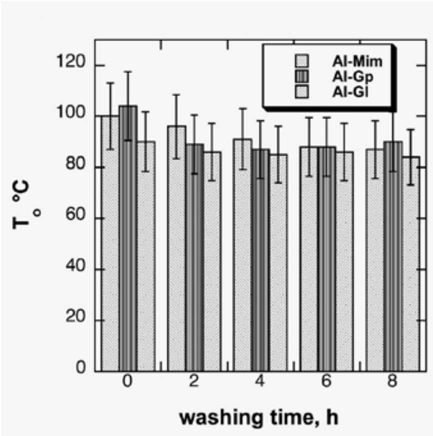

Figure 1: To, represents the onset temperature in the DSC melting plot for samples of aluminum-mimosa (Al-Mim), aluminum-genipin (Al-Gp) or aluminum-glutaraldehyde (Al-Gl) tanned leather after washing for up to eight hours with water and a nonionic surfactant.

Washability

Aluminum is a desirable component of combination tannages with chromium, other metals, aldehydes and vegetable tannins. Its use as a solo tannage is limited by the ease with which it is removed from the hide, either by soaking in water or by washing with a detergent. The removal of aluminum from the hide is associated with a decrease in hydrothermal stability. The hydrothermal stability as measured by DSC was determined after washing of these samples from 2 h to 8 h (Figure 1). After 8 h of washing, the onset temperature of aluminum-genipin tanned leather decreased from 89°C to 84°C, while the onset temperatures of the two reference samples, aluminum-glutaraldehyde and mimosa-aluminum tanned leather decreased from 92°C to 85°C and from 110°C to 93°C respectively. Although the hydrothermal stabilities of the control leathers were higher than that of the aluminum-genipin leather, the aluminum-genipin combination was more stable to the washing protocol.

CONCLUSIONS

The results reported here suggest that development of a chrome-free tanning process using citrate-masked aluminum sulfate and genipin in a combination tannage may be possible. Pretanning full thickness hide with $Al_2(SO_4)_3$, followed by splitting, and tanning the grain layer with genipin produced a leather with a shrinkage temperature (T_s) of 92°C before fatliquoring and 90°C after fatliquoring. This research examined two of the basic steps, tanning and fatliquoring, in the processing of a hide into leather. The hydrothermal stability, mechanical properties and subjective evaluation of the leather are marginally adequate for garment, upholstery or shoe-upper leather. Further improvements in these properties might be expected to result if the full range of leather processing steps including retanning and filling were undertaken. In addition, this research provides a way to correlate hydrothermal stability as determined by a DSC method with the traditional shrinkage temperature.

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