THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

March 2021 **Vol. CXVI, No.3** ***JALCA* 116(3), 81–116, 2021**

Contents

ACLA News

116th Annual Convention

to be held at the
Eaglewood Resort & Spa
1401 Nordic Road
Itasca, IL 60143

DATE CHANGE:
COMING

For more information go to:
leatherchemists.org/
annual_convention.asp

Communications for Journal Publication

Manuscripts, Technical Notes and Trade News Releases should contact:
Mr. Steven D. Lange, Journal Editor, 1314 50th Street, Suite 103, Lubbock, TX 79412, USA
E-mail: jalcaeditor@gmail.com Mobile phone: (814) 414-5689

Contributors should consult the Journal Publication Policy at:
http://www.leatherchemists.org/journal_publication_policy.asp

Distributed by
University of CINCINNATI
LIBRARY PUBLISHING SERVICES

An imprint of the University of Cincinnati Press

ISSN: 0002-9726

JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

Proceedings, Reports, Notices, and News
of the
AMERICAN LEATHER CHEMISTS ASSOCIATION

OFFICERS

Mike Bley, *President*
Eagle Ottawa – Lear
2930 Auburn Road
Rochester Hills, MI 48309

Joseph Hoefler, *Vice-President*
The Dow Chemical Company
400 Arcola Rd.
Collegeville, PA 19426

COUNCILORS

Shawn Brown
Quaker Color
201 S. Hellertown Ave.
Quakertown, PA 18951

Jose Luis Gallegos
Elementis LTP
546 S. Water St.
Milwaukee, WI 53204

Steve Lange
Leather Research Laboratory
University of Cincinnati
5997 Center Hill Ave., Bldg. C
Cincinnati, OH 45224

LeRoy Lehman
LANXESS Corporation
9501 Tallwood Dr.
Indian Trail, NC 28079

John Rodden
Union Specialties, Inc.
3 Malcolm Hoyt Dr.
Newburyport, MA 01950

Marcelo Fraga de Sousa
Buckman North America
1256 N. McLean Blvd.
Memphis, TN 38108

EDITORIAL BOARD

Dr. Meral Birbir
Biology Department
Faculty of Arts and Sciences
Marmara University
Istanbul, Turkey

Chris Black
Consultant
St. Joseph, Missouri

Dr. Eleanor M. Brown
Eastern Regional
Research Center
U.S. Department of Agriculture
Wyndmoor, Pennsylvania

Kadir Donmez
Leather Research Laboratory
University of Cincinnati
Cincinnati, Ohio

Dr. Anton Ela'mma
Retired
Perkiomenville, Pennsylvania

Cietta Fambrough
Leather Research Laboratory
University of Cincinnati
Cincinnati, Ohio

Mainul Haque
ALCA Education
Committee Chairman
Rochester Hills, Michigan

Joseph Hoefler
Dow Chemical Company
Collegeville, Pennsylvania

Elton Hurlow
Buckman International
Memphis, Tennessee

Prasad V. Inaganti
Wickett and Craig of America
Curwensville, Pennsylvania

Dr. Tariq M. Khan
Research Fellow, Machine Learning
Faculty of Sci Eng & Built Env
School of Info Technology
Geelong Waurn Ponds Campus
Victoria, Australia

Nick Latona
Eastern Regional Research Center
U.S. Department of Agriculture
Wyndmoor, Pennsylvania

Dr. Xue-pin Liao
National Engineering Centre for Clean
Technology of Leather Manufacture
Sichuan University
Chengdu, China

Dr. Cheng-Kung Liu
Eastern Regional Research Center
U.S. Department of Agriculture
Wyndmoor, Pennsylvania

Dr. Rafea Naffa
New Zealand Leather & Shoe
Research Association Inc. (LASRA®)
Palmerston North, New Zealand

Edwin Nungesser
Dow Chemical Company
Collegeville, Pennsylvania

Dr. Benson Ongarora
Department of Chemistry
Dedan Kimathi University of Technology
Nyeri, Kenya

Lucas Paddock
Chemtan Company, Inc.
Exeter, New Hampshire

Dr. J. Raghava Rao
Central Leather
Research Institute
Chennai, India

Andreas W. Rhein
Tyson Foods, Inc.
Dakota Dunes, South Dakota

Dr. Majher Sarker
Eastern Regional
Research Center
U.S. Department of Agriculture
Wyndmoor, Pennsylvania

Dr. Bi Shi
National Engineering Laboratory
Sichuan University
Chengdu, China

Dr. Palanisamy Thanikaivelan
Central Leather
Research Institute
Chennai, India

Dr. Xiang Zhang
Genomics, Epigenomics and
Sequencing Core
University of Cincinnati
Cincinnati, Ohio

Dr. Luis A. Zugno
Buckman International
Memphis, Tennessee

PAST PRESIDENTS

G. A. Kerr, W. H. Teas, H. C. Reed, J. H. Yocum, F. H. Small, H. T. Wilson, J. H. Russell, F. P. Veitch, W. K. Alsop, L. E. Levi, C. R. Oberfell, R. W. Griffith, C. C. Smoot, III, J. S. Rogers, Lloyd Balderson, J. A. Wilson, R. W. Frey, G. D. McLaughlin, Fred O'Flaherty, A. C. Orthmann, H. B. Merrill, V. J. Mlejnek, J. H. Highberger, Dean Williams, T. F. Oberlander, A. H. Winheim, R. M. Koppenhoefer, H. G. Turley, E. S. Flinn, E. B. Thorstensen, M. Maeser, R. G. Henrich, R. Stubbings, D. Meo, Jr., R. M. Lollar, B. A. Grota, M. H. Battles, J. Naghski, T. C. Thorstensen, J. J. Tancous, W. E. Dooley, J. M. Constantin, L. K. Barber, J. J. Tancous, W. C. Prentiss, S. H. Feairheller, M. Siegler, F. H. Rutland, D.G. Bailey, R. A. Launder, B. D. Miller, G. W. Hanson, D. G. Morrison, R. F. White, E. L. Hurlow, M. M. Taylor, J. F. Levy, D. T. Didato, R. Hammond, D. G. Morrison, W. N. Mullinix, D. C. Shelly, W. N. Marmer, S. S. Yanek, D. LeBlanc, C.G. Keyser, A.W. Rhein, S. Gilberg, S. Lange, S. Drayna, D. Peters

---

THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION (USPS #019-334) is published monthly by The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412. Telephone (806)744-1798 Fax (806)744-1785. Single copy price: $8.50 members, $17.00 non-member. Subscriptions: $185 for hard copy plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers; $185 for ezine only; and $205 for hard copy and ezine plus postage and handling of $60 for domestic subscribers and $70 for foreign subscribers.

Periodical Postage paid at Lubbock, Texas and additional mailing offices. Postmaster send change of addresses to The American Leather Chemists Association, 1314 50th Street, Suite 103, Lubbock, Texas 79412.

Website: www.leatherchemists.org E-mail: carol.adcock@ttu.edu

COPYRIGHT 2020. THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Stahl's innovations driven by sustainability

With the rise of both electric and self-driving, cars are becoming quieter and anti-squeak and rattle materials are becoming increasingly important. At the same time, improved anti-stain performance is required, because of the current trend for pale-colored car seats. Therefore, we have developed Stay Clean. This low-VOC coating technology protects pale-colored leather and vinyl surfaces against common stains, such as dye from jeans, spilled coffee and dirt. Our solution also makes surfaces low-squeak, which is a great asset as global research has shown that a squeaking car interior is one of the biggest annoyances among car owners. Another trend in car interior is the popularity of matt surfaces. Therefore, we have developed PolyMatte®. This non-squeaking solution provides a luxurious feel to the finished article in combination with flexibility and scratch and abrasion resistance. Our portfolio contains many products, varying from beamhouse products, tanning systems to finishes, duller concentrates, crosslinkers and thickeners to leveling agents, defoamers, colorants and hand modifiers. Our most sustainable option is Green PolyMatte®, which is based on rapeseed oil (20%) instead of crude oil-derived intermediates. If you would like to know what our Stahl solutions for automotive can do for your business, please visit **www.stahl.com** or contact us at: **alexander.campbell@us.stahl.com**.

If it can be imagined, it can be created

Stay Clean

Low-VOC

PolyMatte®

www.stahl.com

Dual Functional Replacement Syntans for Leather

by
Jaya Prakash Alla,[a,b] Nishad Fathima Nishter [a] and Jonnalagadda Raghava Rao [a*]
[a]*Inorganic and Physical Chemistry Laboratory, CSIR-Central Leather Research Institute (CLRI),*
Adyar, Chennai, India. 600020
[b]*Regional Centre for Extension & Development (RCED), CSIR-Central Leather Research Institute (CLRI),*
Kanpur, Uttar Pradesh, India. 208010

Abstract

In the present study we have synthesised thermoresponsive syntan using phase changing material (PCM) encapsulated into a replacement syntan. Syntan was analysed for their particle size, thermal response was verified using Differential scanning calorimetry (DSC) and surface morphology was analysed using scanning electron microscopy (SEM). These syntans were applied to leathers for making leather thermoresponsive. The thermal comfort range achieved on leathers prepared using the experimental syntan was about 2.5°C, compared to control of about 0.5°C with an error of ±0.5°C. The physical and strength properties of experimental leathers were superior compared to control.

Introduction

Skin of a live animal is capable of adjusting towards heat/cold by the mechanism of thermoregulation. This property of skin is lost when the animal is flayed. Hence, to regain this unique functionality to certain extent, smart materials need to be added to skin while converting it to leather.[1] Skin/hides are termed as leather once the tanning material is treated to them. Tanning is basically conversion of putrescible (degrading) into non-putrescible material.[2]

Leather is a viscoelastic material, which has the unique property of breathability. Unlike other synthetic materials, leather and leather products are capable of absorbing and releasing air, heat and water vapour. These advantageous properties also come with a few drawbacks, such as leathers limited capability to adjust towards extreme climatic conditions such as heat/ cold.[3] In order to overcome these limitations leather needs to be treated with certain speciality chemicals which can impart those functionalities. Phase changing materials (PCM) are one such smart materials which can absorb and release heat over a particular temperature range.

The PCMs are the materials with high heat of fusion, which has the capability to transform its physical form from liquid to solid and vice versa upon absorbing and releasing heat. There are numerous phase changing materials available in the market, but our interest was with materials which can respond at human body comfort range of 28-34°C.[4] The PCM are hydrophobic in nature and leather processing is entirely carried out in aqueous medium. Hence, the compatibility issues are the major concern. In order to overcome this limitation, PCM are encapsulated into polymeric materials such as phenol or melamine-based condensate polymers.[5,6] These polymers are generally used as syntans in leather processing as filling agents, hence in this study we aim to prepare PCM encapsulated syntans. Thus, synthesised materials not only fill the leather matrix like conventional syntans but also impart the thermoregulation properties to leather.

In the present study we have synthesised PCM based thermoresponsive syntan which not only can fill the leather matrix like conventional syntan but also help in thermoregulation. The syntans were analysed using different techniques such as particle size measurement, scanning electron microscopy, differential scanning calorimetry and the syntan treated leathers were analysed for infrared thermal imaging, physical strength and organoleptic properties.

Materials and Methods

Materials

Phenol (>99% pure), formaldehyde (37%), n-Octadecane, from MERCK India, sodium hydroxide (NaOH, >99% pure), sodium lauryl sulphate (99% pure) from Himedia India.

Syntan Preparation

Phenol (0.2125mol) was stirred with equal molar sulphuric acid for 2h at 105°C. Followed by addition of 100g deionised water, formaldehyde (0.425mol) and stirred at 95°C for 2h (PF- at pH 3.5). PF solution pH was adjusted to 6 using 40% strength sodium hydroxide and stirring was continued for another 1h. Separate solution containing 1g of n-Octadecane (PCM), 0.5g anionic surfactant dissolved in 50ml deionised water and was homogenised for 15 min at 4000 rpm. To prepare the microcapsules, the emulsion containing PCM was gradually added to polymer solution and stirring was continued for 2h. The final solution pH was adjusted to 3.5. The small quantity of the resultant product obtained was dried in a hot air oven at 80°C for analysis. (PF-PCM)

---

*Corresponding Author E-mail: jrrao@clri.res.in, clrichem@mailcity.com
Manuscript received August 26, 2020, accepted for publication October 17, 2020.

Leather Application

Table I

Detail description of leather processing

Material: Goat wet blue leather
Number of pieces: 4 (2-control, 2- experiment)
Article: Softy upper
Total Weight: 3.6 kg

Process	Chemical	Percentage (%)	Time	Remarks
Neutralisation	Water	100		
	Sodium Formate	0.5	20	
	Sodium bicarbonate	0.5	10+ 30	10min run time, check pH-5.6 and additional 30min run time
				Drain/wash/drain
Post tanning	Water	100		
	Acrylic Syntan	2	30	In dilution with 10% water
	Syntan (C, E)	20	45+45	In two intervals of 45min each
	Synthetic Fatliquor	16	60	In dilution with 10% water
	Formic Acid	3	60	Dilution with 10% water. In 3 feeds of 10min and 30min additional run time

C-control (PF), E-Experiment syntan (PF-PCM)

Analysis of Syntan

The total solid content present in the liquid solution of the prepared polymeric syntan was estimated using APHA - 2540 B.[7] Particle size measurements were carried out using particle analyser (Zetasizer Nano series- ZS, Malvern) Scanning electron microscopy analysis was carried out using Hitachi S-3400 SEM microscope. The surfaces of the samples were studied with the microscope operating at 10-30 kV. The specimens were sputter coated with a thin layer of gold prior to examination. Differential Scanning Calorimeter (DSC)-Q200 TA Instruments was used for analysing the phase changes of the PCM. The samples were analysed at the heating rate of 5°C/min between 25°C to 200°C.

Analysis of Leather

Infra-red thermal imaging of leather surfaces was analysed using thermal imaging camera which has IR and visible systems (FLIR system E60). The leather analysis technique was developed in house using a double walled glass jacket with provision for circulating water. This jacket is connected to a temperature controller unit. The leathers were mounted onto the glass jacket and the temperature was increased. Leather surface images were taken by thermal imaging camera which has IR and visible systems (FLIR system E60) having a thermal sensitivity of < 0.05°C with a measurement range of -20°C to +650°C and images were taken with a resolution of 320 × 240 pixels. The samples were observed from a distance of 30 cm at room temperature of 25°C and 50% relative humidity.

Strength Property Analysis

Samples for physical testing were cut from control and experimental leathers. The samples were conditioned to the required relative humidity of 65±2% at 20±2°C for 48 h as per standard procedure.[8] The tensile,[9] tear strength[10] and grain crack index[11] were measured as per the standard procedures. Values reported were average of four samples.

Organoleptic Property Analysis

Crust leathers from the conventional as well as the experimental process were assessed for run, softness, fullness, grain smoothness and general appearance by standard hand evaluation technique. Four experienced leather technologists rated the leathers on a scale of 0-10 points for each functional property. Where higher points indicate better properties exhibited. An average of four samples were evaluated.

Results and Discussion

Solid Content and Particle Size Analysis

Solid content present in syntan gives information about the total solid matter present which actually binds/ fills the leather matrix. Solid content was measured for both control and experiment syntan, it was calculated to be 35 and 39%. The size of the particles was analysed using particle size analyser, the size distribution of the syntans were plotted in the Fig 1. It can be observed that the particle size of the PF syntan are in the range of 1700 to 3600 nm while the PF-PCM encapsulated syntan possessed larger diameter in the range of 1400-5600 nm. The bigger particle size of experimental syntan may be due to the encapsulation of PCM.

Scanning Electron Microscopy Analysis of Syntan

From Fig 2, scanning electron microscopy analysis of control (a) and experimental syntan (b) shows the surface morphology. It can be seen that the experimental syntan has formed microcapsules containing PCM material, while the control sample contain

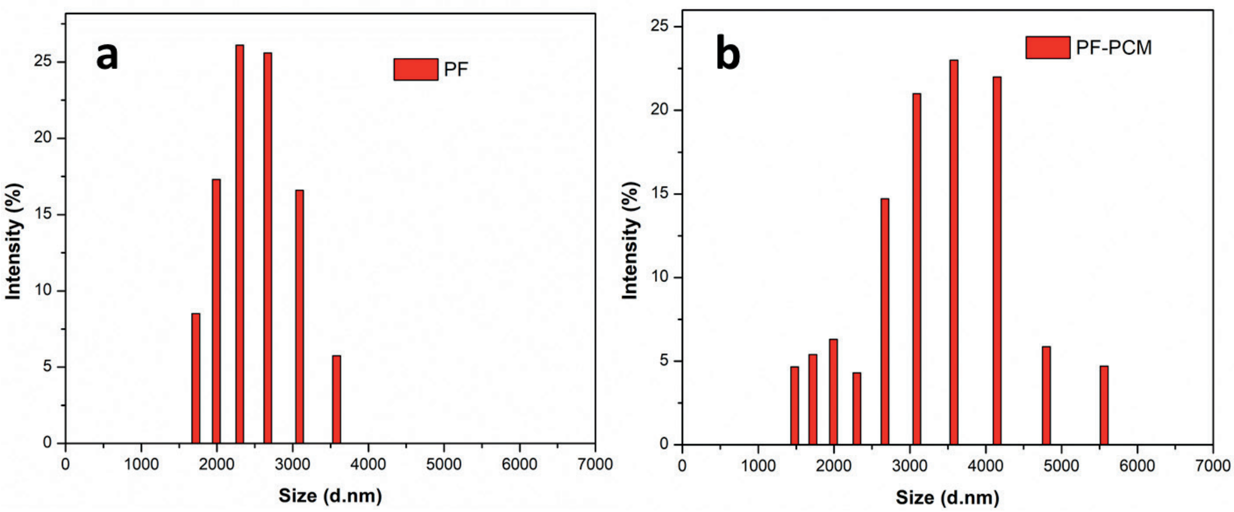


Figure 1. Particle size distribution of PF and PF-PCM syntan

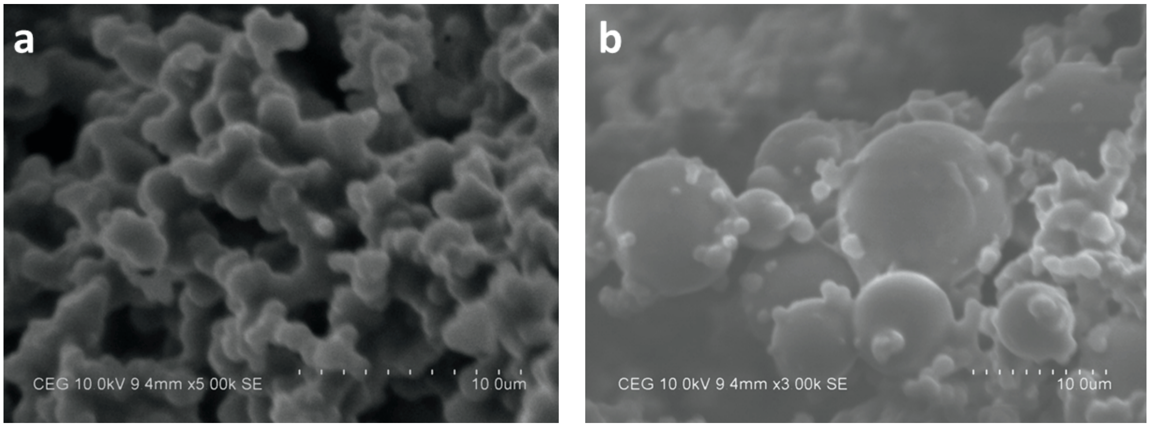


Figure 2. Surface morphology analysis of PF **(a)** and PF-PCM **(b)** syntan

clusters of syntan without PCM. The particle size data showing the variations can be validated from SEM, the size of the experimental syntan with microcapsules were larger in size compared to the control syntan.

Differential Scanning Calorimetry Analysis of Syntan

Differential scanning calorimetry analysis of syntan gives the information about the phase transformation of the material. From Fig 3, DSC thermographs of control (PF) and experimental (PF-PCM) syntan were plotted to understand the thermal changes exhibited by these syntans. It can be observed that the experimental syntan encapsulated using PCM (n-Octadecane) shows phase change at 27°C confirming the presence of PCM. The peaks above 100°C attributes to the polymers phase transformation.

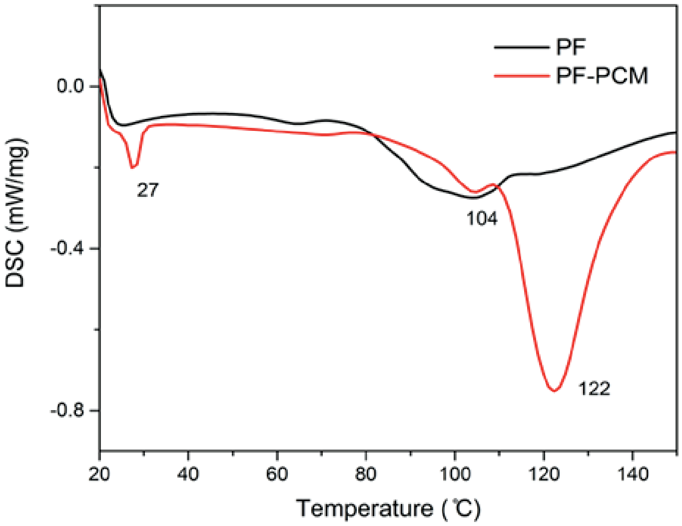


Figure 3. Differential scanning calorimetry analysis of PF and PF-PCM syntan

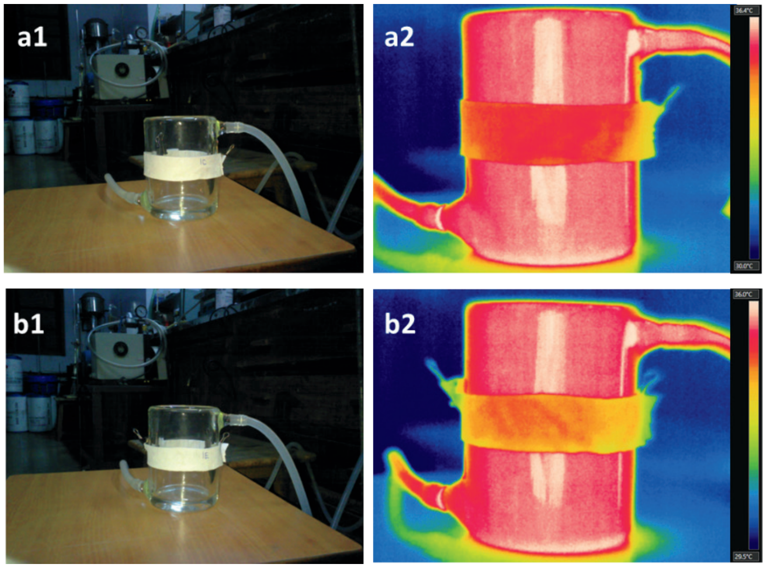


Figure 4. Digital and Infra-red thermal imaging of **(a1, a2)**PF and **(b1, b2)**PF-PCM syntan treated leathers

Infra-Red Thermal Imaging Leathers

Infra-red thermal imaging of leathers was performed to analyse the leathers ability for the absorption or release of heat. From Fig 4, digital image of control (a1), experiment (b1) and their corresponding thermal images (control-a2 and experiment-b2) are shown. The temperature of the glass jacket and the temperature on the leather surface were tabulated in table II. The flesh surface temperature values were noted after 60 sec exposure of heat on the grain surface. It can be observed that the experimental leathers absorbed more heat compared to control leathers. The thermal image of leather Fig 4: b2, the variation in color (yellow) compared to control (red) when exposed to similar conditions proves that the experimental leathers absorbed more heat compared to control. The difference in temperature can be compared with the temperature scale.

Scanning electron microscopy analysis of leather

In order to understand surface and cross-sectional morphology of leathers, scanning electron microscopy analysis was performed on the leathers. From Fig 5, surface and cross sections of leathers were imaged. Fig 5 (a,b) shows surface image of control and experimental leathers, it can be seen that both leathers show no surface deformities and cross sectional images of control and experimental leathers Fig 5 (c,d) shows the fiber structure, both leathers show compact fiber alignment.

Table II

Thermal analysis of control and experimental leathers

	Control		**Experiment**	
	Grain surface temperature °C	**Flesh surface temperature °C**	**Grain surface temperature °C**	**Flesh surface temperature °C**
	24.0	23.7	24.0	21.8
	25.1	24.5	25.0	22.7
	26.1	25.4	26.0	24.1
	27.2	26.2	27.1	24.8
	28.0	27.3	28.0	25.6
	29.1	28.7	29.1	26.4
	30.1	29.5	30.0	27.5
	31.0	30.4	31.1	29.0
	32.0	31.6	32.2	29.4
	33.1	32.4	33.1	31.1
	34.0	33.7	34.0	31.6
Average Change	**0.5±0.4**		**2.5±0.5**	

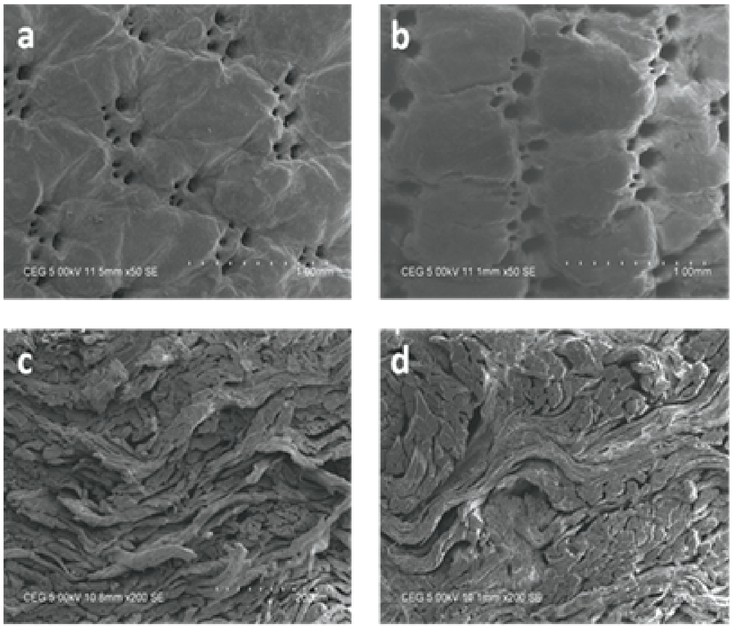


Figure 5. Scanning electron microscopy analysis of PF (**a**-surface, **c**- cross section) and PF-PCM (**b**-surface, **d**- cross section) syntan treated leathers

Physical Strength Analysis of Leathers

Strength properties such as tensile, tear and grain crack index were measured for control and experiment leathers. From table III, tensile strength and the percentage elongation values of experimental leathers were slightly increased compared to control leathers. Similarly, tear strength values of both the leathers were almost equal, while grain crack index value improved in case of experimental leathers. This shows that the experimental syntan improved grain tightness of the leather.

Organoleptic Property Analysis of Leathers

Organoleptic properties of leathers were assessed for softness, fullness, belly filling and grain tightness. From Fig 6, softness and fullness of both experimental and control leathers were similar, while experimental syntan treated leathers showed better belly filling and grain tightness compared to control leathers, the data is in agreement and can be confirmed from the grain crack index values.

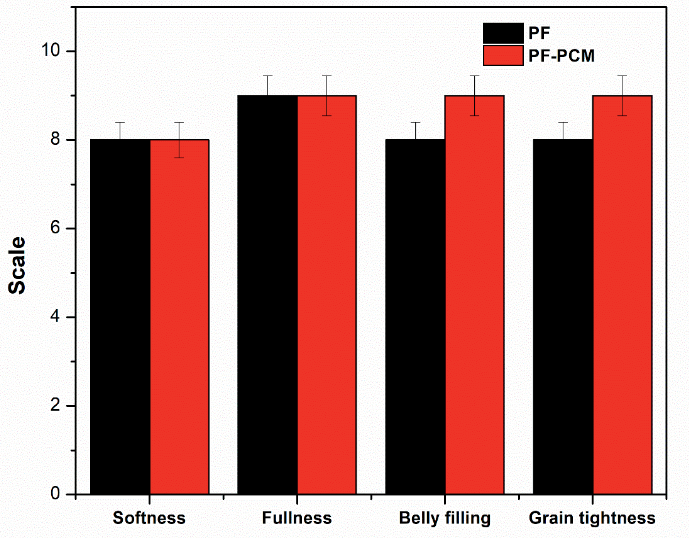


Figure 6. Organoleptic properties of PF and PF-PCM syntan treated leathers

Table III

Strength property analysis of control and experimental leathers

	Tensile Strength (N/mm²)	Percentage elongation (%)	Tear strength (N/mm)	Grain crack index	
				Load (N)	Distance(mm)
Control	24±0.5	63±4	55±3	25±1	11±0.5
Experiment	26±0.5	68±3	53±3	29±2	17±0.9

Conclusions

We have shown the synthesis, application and analysis of thermoresponsive syntan. Leathers made using the syntan exhibited thermoresponsive behaviour. From the SEM images, PF-PCM syntan showed perfect capsule formation. The differential scanning calorimetry analysis confirmed the presence of PCM inside the capsules. The thermal comfort range achieved on leathers prepared using the experimental syntan was about 2.5°C, compared to control of about 0.5°C. The physical and strength properties of experimental leathers were superior compared to control. From this study we have prepared syntan which not only helps in filling the leather matrix but also exhibits thermoresponsive character. Thus, these dual functional syntans find application in preparation of thermal comfort leathers. These leathers also find applications in preparation of shoes, garments and gloves which can be used at high altitudes and extreme climatic conditions.

Acknowledgements

JPA acknowledges CSIR for providing Senior Research Fellowship.

References

1. S. Sangeetha, N. N. Fathima, K. J. Sreeram, J. R. Rao, B.U. Nair; Stimuli Responsive Leathers using Smart Retanning Agents. *JALCA* **107**, 196, 2012.
2. P. Thanikaivelan, J. R. Rao, B. U. Nair, T. Ramasami; Recent Trends in Leather Making: Processes, Problems and Pathways. *Crit. Rev. Env. Sci. Technol.*, **35**, 37, 2005.
3. A. J. Prakash, M. Ragul, J. R. Rao, N. N. Fathima; Cool glove leathers made using thermoresponsive syntans. *JALCA* **109**, 411, 2014.
4. Fanger, P, O.; Assessment of man's thermal comfort in practice. *Br J Ind Med*, **30**, 313, 1973.
5. X. X. Zhang, X. M. Tao, K. L. Yick, Y. F. Fan; Expansion Space and Thermal Stability of Microencapsulated n-Octadecane. *J. Appl. Polym. Sci.,* **97**, 390, 2005.
6. Zhang, X, X., Fan, Y, F., Tao, X. M., Yick, K. L.; Crystallization and prevention of supercooling of microencapsulated n-alkanes. *J. Colloid Interface Sci.* **281**, 299, 2005.
7. Standard Methods for the Examination of Water and Wastewater, 17th edition, American Public Health, *APHA* 1989.
8. IUP 2, Sampling. *JSLTC*, **84**, 303, 2000.
9. IUP 6, Measurement of tensile strength and percentage elongation. *JSLTC*, **84**, 317, 2000.
10. IUP 8, Measurement of tear load-double edge tear. *JSLTC*, **84**, 327, 2000.
11. IUP 12, Determination of resistance to grain cracking and grain crack index, *JSLTC*, **84**, 347, 2000.

Alternative Tanning Agent for Leather Industry from a Sustainable Source: Dialdehyde Starch by Periodate Oxidation

by

Cigdem Kilicarislan Ozkan[1] and Hasan Ozgunay[1*]

[1]*Faculty of Engineering, Department of Leather Engineering, Ege University*, 35100 Bornova, Izmir, Turkey

Abstract

Dialdehyde starches with different aldehyde content from native corn starch were prepared by sodium periodate oxidation to be used as a tanning agent in leather making. For this purpose, native corn starch was oxidized with sodium metaperiodate in different molar ratios. After oxidation processes, the yields, solubility in water and aldehyde contents of the obtained dialdehyde starches were determined as well as structure characterizations by Proton Nuclear Magnetic Resonance Spectroscopy, Fourier Transform Infrared Spectroscopy and Gel Permeation Chromatography. Evaluating the gel permeation chromatography data, the dialdehyde starch samples which were thought to be in appropriate molecular weight/size to penetrate into skin fibers were selected to be used in the tanning process. Their tanning abilities were evaluated by investigating hydrothermal stabilities, filling and fiber isolation characteristics and physical properties determined by mechanical tests and organoleptically. From the evaluation of the results, it was revealed that sodium metaperiodate oxidized starches which have appropriate molecular weight and adequate aldehyde content has a remarkable tanning effect and can be utilized as a tanning agent with the advantages of not necessitating pickling process which means saving time and simplifying the production but more importantly offering an important advantage from an environmental point of view.

Introduction

Starch is an important raw material for producing sustainable green chemicals due to its features that it is an abundant, biodegradable, naturally renewable and inexpensive natural biopolymer. Considering the potential properties of starch, we had started to study how to modify it in order to generate an alternative tanning agent having no or less risk on health & environment. However, native starch cannot be used directly in leather industry due to its drawbacks. It has high molecular weight which does not allow it to penetrate within fiber structure. It is insoluble in water (a tanning material must be soluble or well dispersible in water to be transferred into fiber structure via water) and has no reactive groups that can establish stable bonds with the functional groups of collagen in order to achieve collagen stabilization and tanning effect. For these reasons, native starch must be properly modified and gain the desired properties before use in leather processing as a tanning material.

Hence, in the light of the above concerns in first part of our study,[1] oxidation of starch with H_2O_2 was successfully performed and although the first aim was controlled (gradual) degradation, selected oxidized starches were used in tanning and up to 61°C shrinkage temperatures were obtained. In the second part of our study, we decided to focus on introduction of reactive groups that can give reaction with the active groups of collagen and constitute quite enough stable bonds. From the literature review, it was seen that it is possible to introduce aldehyde groups by periodate ($NaIO_4$) oxidation.[2-5] Periodate is highly selective oxidant to cleave the C-2 and C-3 linkage of anhydroglucose units of native starch and include dialdehyde groups to starch structure. Dialdehyde starches bearing reactive aldehyde groups are used as crosslinking agents in many industrial applications such as paper, textile, pharmaceutical, gelatin and leather.[2,6]

Within the scope of this study, firstly native corn starch was oxidized with periodate to introduce dialdehyde groups into its structure and to reduce its molecular weight. Then, the obtained products (dialdehyde starches (DAS)) were characterized in detail. Furthermore, the selected dialdehyde starch samples' tanning performances were examined. Even though there are several studies in literature regarding utilization of modified starch in leather making as a tanning agent,[7-13] recently published studies show that natural biopolymers have become popular again.[14-18] However, compared to the former studies in which native starch was directly oxidized with periodate and used as a tanning agent,[7,10,19] the present study was thought to make an important contribution to the literature in terms of both applied tanning process parameters and the subject being investigated in detail.

Materials and Methods

Corn starch was selected to be used as raw material and purchased from Hasal Starch Company Izmir/Turkey. Sodium metaperiodate ($NaIO_4$, extra pure (Merck)), the solvents and the chemicals (Sigma

---

*Corresponding author email: hasan.ozgunay@ege.edu.tr

Manuscript received September 11, 2020, accepted for publication October 26, 2020.

Aldrich) used in oxidation processes and analysis were analytical grade. For tanning trials, pickled goat skins (pelts) were selected to be used.

Sodium metaperiodate oxidation of native corn starch: Before oxidation processes, the native corn starches were kept in an oven at 50°C for 48 hours in order to remove its moisture content and prevent weighing mistakes. The periodate oxidation was performed as described by Zhang et al.[4] with this minor change, 20g native corn starch was suspended in 120 mL pure water (rather than 80 ml) to avoid paste formation in the following stages. Then, different amounts of $NaIO_4$ were added into the suspensions. The starch:periodate molar ratios 1:0.3, 1:0.5, 1:0.7, 1:0.9, 1:1.1, 1:1.3 and the amounts of starch to be used, were calculated taking in account the anhydroglucose units of starch molecule. The pH was adjusted to 3.0 with 2% HCl solution. Then, the mixture was effectively shaken in a water bath at 35°C for 4 h in dark ambient conditions. After oxidation processes, the reaction mixtures were filtered. The filtered samples were washed firstly 10 times with distilled water (10x100 mL), then once with 50 mL acetone. The obtained products (oxidized/dialdehyde starches) were transferred into glass dishes and taken into a hot-air oven to be dried at 50°C for 48 h and weighed. Then, the dried products were ground to obtain the products in powder form. For determination of the yields of oxidized starches, the method described by Kilicarislan Ozkan et al.[1] was used. The experiments were carried out in three repetitions and the yields were calculated according to the formula 1 given below.

$$\text{Yield \%} = \frac{\text{Obtained oxidized starch (g)}}{\text{Amount of native starch used (g)}} \times 100 \qquad (1)$$

Determination of aldehyde group contents of oxidized starches*:* Rapid quantitative alkali consumption method described by Hofreiter et al.[20] and Zhang et al.[4] was used for determination of the aldehyde group contents of periodate oxidized starches. The experiments were done in three repetitions and the percentage of dialdehyde units (Da) was calculated by following formula 2:

$$\text{Da \%} = \frac{C_1.V_1 - 2.C_2.V_2}{\frac{W}{161} \times 1000} \times 100\% \qquad (2)$$

C_1 and C_2: Normality (mol/L) of NaOH and H_2SO_4, respectively.

V_1 and V_2: Total volume (mL) of NaOH and H_2SO_4, respectively.

W: Dry weight of DAS sample.

161: Average molecular weight of the repeat unit in DAS.

Determination of water solubility of dialdehyde starches: As described in our previous study,[1] in determination of water solubilities of native and dialdehyde starches the method given by Singh and Singh[21] was used with minor modifications. Native and dialdehyde starches' solubilities were calculated according to the formula 3 given below. The experiments were repeated three times and the results were given as mean values.

$$\text{Water solubility \%} = \frac{\text{Supernatant solid weight (g)} \times 2}{\text{Sample weight (g)}} \times 100 \qquad (3)$$

Fourier transform infrared (FT-IR) spectroscopy: Perkin Elmer Spectrum 100 FT-IR spectrometer was used to record FT-IR spectra of native and dialdehyde starches in the range of 4000-650 cm^{-1}. The starch samples were kept in an oven at 50°C for 24 h to remove absorbed moisture before analysis.

Gel permeation chromatography (GPC): Native and dialdehyde starches' molecular weight distributions and polydispersity indexes were analyzed by using Malvern Viscotek GPCMax GPC device (Bozok University Science and Technology Application and Research Center, Yozgat/Turkey) according to the method used in our previous study.[1]

Nuclear magnetic resonance (NMR) spectroscopy: The structures of native corn starch and selected dialdehyde starches with molecular weights/sizes thought to be fit for penetrating into the skin fibers were also identified by ^{1}H-NMR spectroscopy. 10 mg of sample (native and dialdehyde starches) was accurately weighed with analytical balance and dissolved in 500 µL DMSO-d6 (Dimethyl sulfoxide). Then, the spectra of the samples were recorded on a liquid MERCURY plus-AS 400 NMR spectrometer at Ege University Science Technology Research and Application Center, Nuclear Magnetic Resonance Satellite Laboratory, İzmir/Turkey.

Tanning trials with dialdehyde starches: In order to obtain homogenous tanning material, the croupon areas of the pelts (pickled goat skins) were used in trials. After removing the bellies, flanks, head and butt edges of the pelts, the croupon areas were divided into 20x20 cm pieces and used in tanning processes. The selected dialdehyde starches were used in tanning of the pelts according to the recipe given in Table I as preliminary tanning trials. From the evaluation of the preliminary tanning trials' results the dialdehyde starch sample having the best tanning effect was used for tanning a whole pelt according to a similar recipe with the changes: introduction of dialdehyde starch in 2 portions and running the drum for 120 minutes after each introduction, raising the pH up to 7.5-7.8 at the end of tanning process, introduction of a replacement syntan (3%) and an amphoteric polymer (4%) before fatliquoring process and application of a fatliquoring process consisting of natural+synthetic fatliquor combination (4%), synthetic fatliquor (3%), sulfone synthetic fatliquor (2%), polymeric fatliquor (2%) and phosphoester based fatliquor (1%).

Determination of tanning effects of dialdehyde starches: The shrinkage temperatures,[22] filling coefficients[1] and the cross section images of fibril bundles of tanned leather (by using Hitachi

Table I

Tanning recipe for the pelt pieces

Process	Amount (%)	Product	Temperature (°C)	Time (min.)	pH
Depickle	150	Water 7 °Be' NaCl	28-30	10	
	1	HCOONa		45	
	x	$NaHCO_3$		120	5.5
Draining					
Tanning	100	Water	30		
	20	Dialdehyde starch		180	
	0.25	$NaHCO_3$		30 (left in bath overnight statically)	
	0.25	$NaHCO_3$		30	
	0.25	$NaHCO_3$		30	
	x	$NaHCO_3$		60	7.0-7.5
Washing & Draining					
Fatliquoring	100	Water	45		
	5	Natural+synthetic fatliquor combination		60	
	3	Sulfone synthetic fatliquor			
	2	Phosphoester based fatliquor			
Fixation	x	HCOOH		60	3.8-4.0
Washing					

TM-1000 table top scanning electron microscope (SEM) at 400 magnifications) were examined for evaluating the tanning effects of selected dialdehyde starches. On the other hand, the tensile strength and percentage of elongation at break[23] and tear load[24] of leathers were also analyzed so as to determine physical performance of the leathers tanned by dialdehyde starches. However, the distension and strength of surface test[25] was also performed for whole leather tanned with dialdehyde starch having the best tanning effect. Shimadzu AG-IS Tensile Tester and Trapezium-2 software was used for all physical tests. Three horizontal and three vertical samples were taken from each leather sample according to related standards. After testing all samples, the results were given as mean values. Before the tests, all leather samples were conditioned[26] at 23±2°C and 50±5% relative humidity for 48 hours. SATRA thickness gauge was used to measure the thickness[27] of the conditioned leathers.

Results and Discussion

The yields of periodate oxidized starches: From the evaluation of the data regarding the yields of $NaIO_4$ oxidized starches which are shown in Figure 1, it was seen that the yields of oxidation processes with different molar ratios were very close to each other (the difference between the lowest and the highest yields is 4.3%) which means intensity of oxidation process did not make a significant effect on product yields. Considering very high yields, it was concluded that including aldehyde groups did not increase the water solubility noticeably.

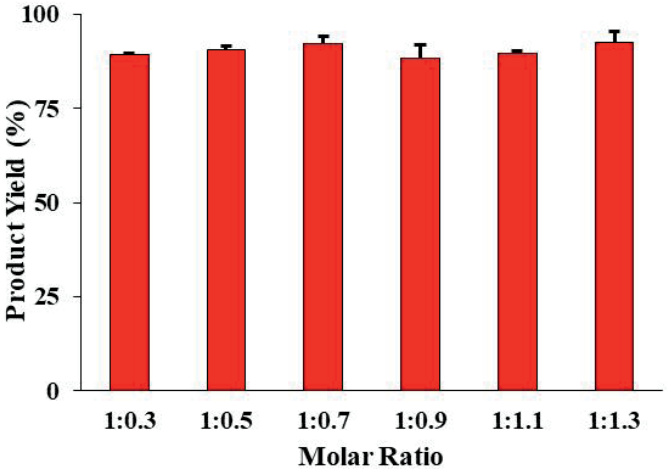


Figure 1. Yields of $NaIO_4$ oxidized starches

However, Zhang et al.[4] reported that the yields decreased in conjunction with increasing molar ratios (from 94.12% to 75.4%) by periodate oxidation of yam starch. The authors remarked that excessive amounts of periodate used in oxidation process may cause further degradation and thus increase starch molecule's solubility in water which results in a diminished yield of dialdehyde starch. However, it was noticed that there is no data on water solubility of obtained dialdehyde starches in mentioned study. On the other hand, it has been reported in many studies that the water solubility of dialdehyde starches obtained by periodate oxidation is low.[2,28-30]

Aldehyde group contents of starch samples oxidized by periodate: Dialdehyde starches (DAS) were obtained from periodate oxidation of native corn starch. Considering the results, it was clear that increasing the starch:periodate molar ratio provoked a significant increment in included aldehyde groups on starch molecule. Thus, it was confirmed that periodate is a selective oxidant and it can open C-2, C-3 bonds of anhydrous glucose units by formation of dialdehyde groups.

As can be clearly seen in Figure 2, the increase in aldehyde content was particularly pronounced from 1:0.3 to 1:0.9 molar ratios, and aldehyde content reached to 93.8% at 1:0.9 molar ratio. On the other hand, the increase in aldehyde content was only 5.3% between 1:0.9 and 1:1.3 molar ratios, while aldehyde content reached to 98.8% at 1:1.3 molar ratio. The similar results were also reported by Yu et al.[31] and Zhang et al..[32]

Water solubility of dialdehyde starches: Figure 3 shows the water solubility values of starches oxidized by periodate. From the obtained results, it was observed that the water solubilities of dialdehyde starches were very low, as expected. Comparing with the water solubility of native corn starch (0.9%), it was determined that water solubility did not increase noticeably by periodate oxidation, contrary to peroxide oxidation (51.7% to 86.9%).[1] The water solubilities of dialdehyde starches were found to be between 1.4% and 2.9%.

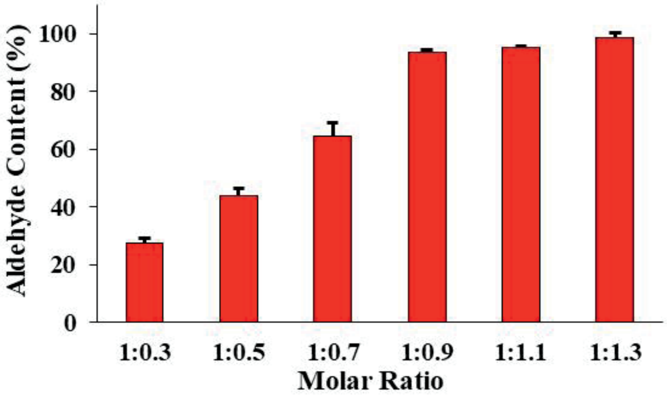


Figure 2. Aldehyde contents of oxidized starches prepared at different molar ratios by $NaIO_4$ oxidation

From the evaluation of solubility results shown in Figure 3, it was noticed that solubility in water decreased slightly by increasing molar ratio. At this juncture, water solubility may be decreased due to the difficulty of entering water into the molecule depending on the number of aldehyde groups included to structure of native starch by increasing amount of periodate, on account of possible crosslinking between aldehyde groups. A similar approach was expressed by Veelaert et al..[28] The authors remarked that aldehyde groups in C-2 and C-3 tend to form inter- and intra-molecular hemiacetal and acetal cross-links, and the low solubility of dialdehyde starch in water may be due to these bonds. Similarly, Yi et al.[30] reported that native starch and dialdehyde starch do not dissolve in cold water due to their crystal structure and acetal groups, respectively.

Wongsagon et al.[2] examined the water solubility at 60°-90°C of dialdehyde starches obtained by periodate oxidation from tapioca starch. They reported that the highest solubility values (between 30-48%) were achieved at 90°C and the solubility at 60°C were between 1-4%. In another study, Para[29] remarked that the water solubility at 25°C of dialdehyde starch obtained from potato starch by periodate oxidation was 1.8%.

Characterizations

The FT-IR spectra of native starch and dialdehyde starches are shown in Figure 4. As previously mentioned, OH groups in C-2, C-3 of anhydrous glucose units replaces with the aldehyde group by periodate oxidation. From the spectra, it was seen that the most characteristic absorption peak of C=O vibrations of aldehyde groups occurred at 1726.94 cm^{-1}, distinct from native starch spectrum. The intensity of this peak is very weak due to the hemiacetal bonds that occur between oxidized and non-oxidized starch residues during preparation.[33] However, the intensity of this peak has become more

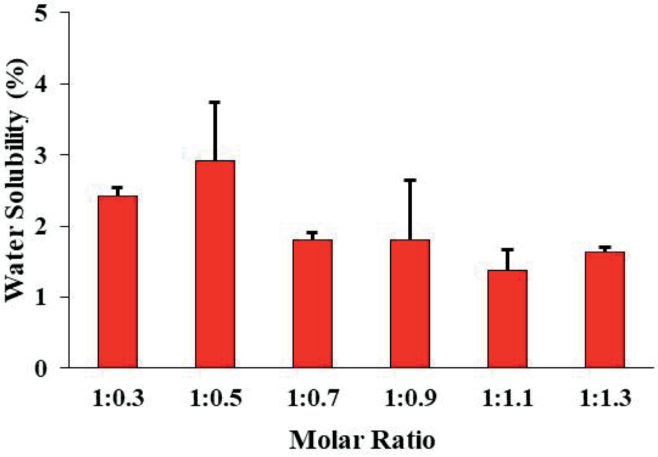


Figure 3. Water solubilities (%) of oxidized starches at room temperature

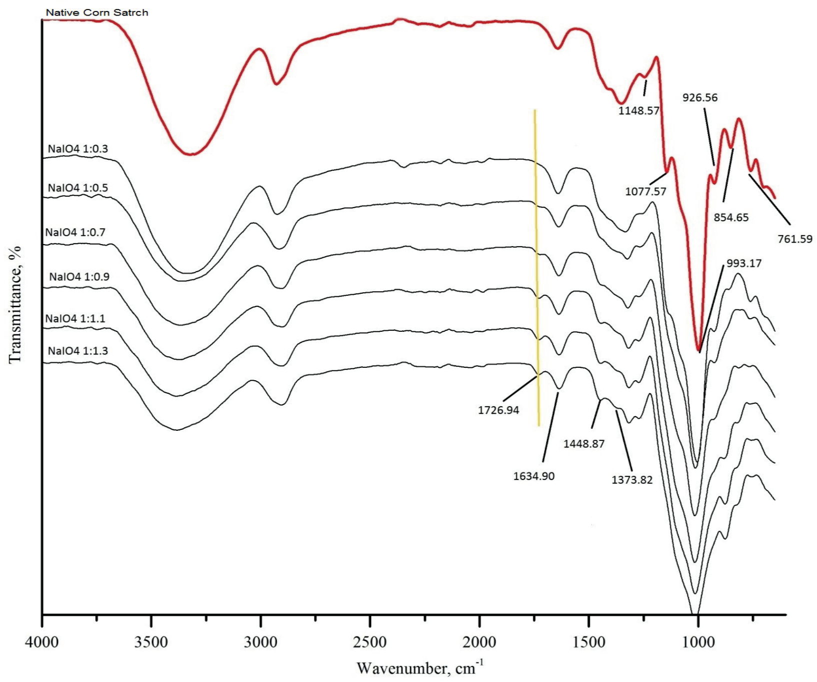


Figure 4. FT-IR spectra of native and dialdehyde starches

apparent by increasing amount of periodate used in oxidation. Because, by increasing intensity of oxidation the amount of non-oxidized starch residues remain less with higher aldehyde content. The peaks at 1148.57, 1077.57, 993.17 and 926.56 cm^{-1} are attributed to C-O bond stretching. The peaks at 1634.90 and 1448.87cm^{-1} are attributed to scissoring vibrations of two O–H bonds of water and CH_2, respectively. The bands at 854.65 and 761.59 cm^{-1} are due to skeletal stretching vibrations of starch. It was observed that the intensity of these peaks decreased in conjunction with increasing oxidation degree. While the characteristic peak for C=O groups (C-C in C-CHO) at 1373.82 cm^{-1} increased with increasing aldehyde group content, the peaks at 1148.57 and 1077,57 cm^{-1} which are attributed to C-O bond stretching of C-OH group weakened in spectra of oxidized samples. Zhang et al.[4] reported that the reason might be that the periodate oxidation mainly results in a cleavage at C-2 and C-3 bonds of anhydroglucose units of starch molecule and occurred aldehyde groups replace with the C–OH groups at C-2 and C-3.

Native corn starch and dialdehyde starches were also characterized by gel permeation chromatography (GPC) and the results were given in Table II. From the measurements, it was observed that Mw, Mn and Mw/Mn values decreased for all starch samples oxidized with periodate compared to native corn starch. This is attributed to cleavage of C-2 and C-3 bonds in glucose units of native starch.

From examining the data, it was noticed that the molecular weight of dialdehyde starches decreased gradually up to 1:0.7 molar ratio, however the molecular weight of dialdehyde starches increased with increasing molar ratios. At this point increasing aldehyde groups in starch molecule are led to formation of intermolecular cross-links, thereby causing an increase in molecular weight of

Table II

Molecular weight distribution of native and oxidized starches

Sample	Oxidation Method/ Molar Ratio	M_w(Da)	M_n(Da)	M_w/M_n
Native corn starch	—	2.23Kx10^3	271K	8.22
Oxidized Starch	$NaIO_4$ Oxidation/1:0.3	6.16K	2.76K	2.23
Oxidized Starch	$NaIO_4$ Oxidation/1:0.5	3.68K	1.92K	1.92
Oxidized Starch	$NaIO_4$ Oxidation/1:0.7	2.35K	1.70K	1.38
Oxidized Starch	$NaIO_4$ Oxidation/1:0.9	18.86K	5.33K	3.55
Oxidized Starch	$NaIO_4$ Oxidation/1:1.1	11.03K	4.20K	2.63
Oxidized Starch	$NaIO_4$ Oxidation/1:1.3	13.09K	6.28K	2.08

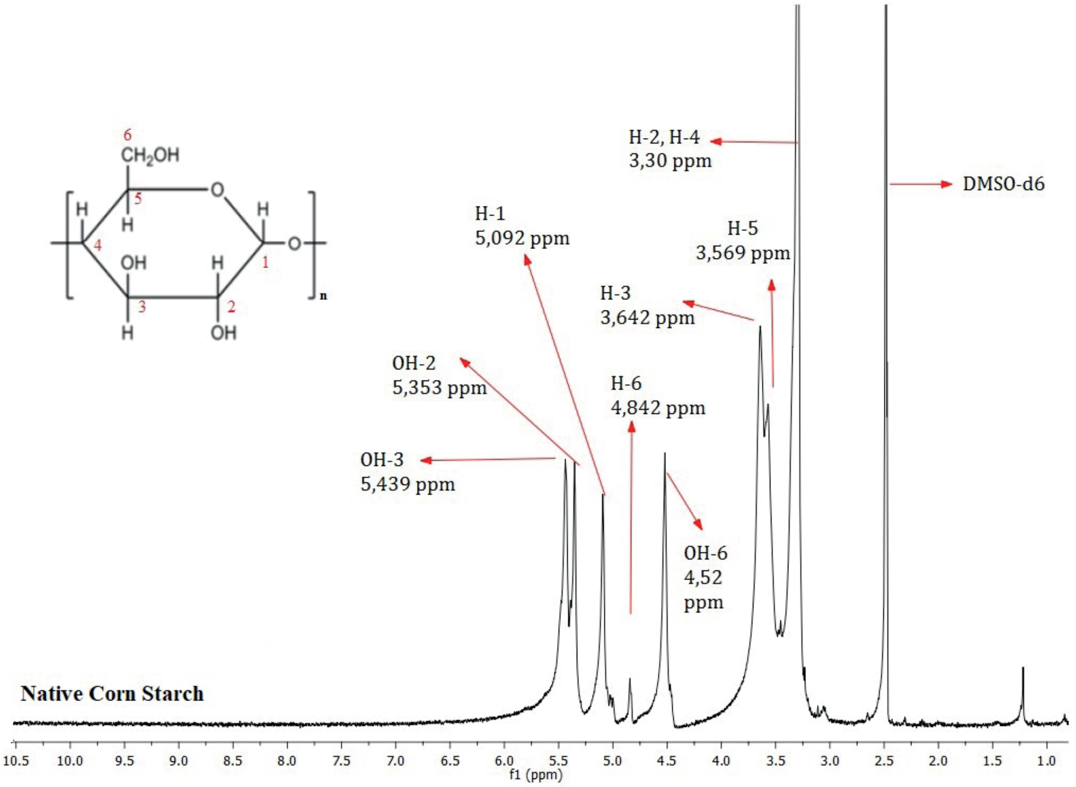


Figure 5. NMR spectrum of native corn starch

dialdehyde starches. Comparing with native and dialdehyde starches regarding polydispersity index (Mw/Mn), it was determined that polydispersity indexes of oxidized starches significantly decreased. Especially, the polydispersity index was quite low at 1:0.7 molar ratio (Mw/Mn=1.38) which means that the oxidized starch has a high homogeneity. Considering the necessity of a tanning material's molecular size should allow it to penetrate into the collagen fiber structure; it was decided that the molecular weights/sizes of dialdehyde starch samples obtained by 1:0.3, 1:0.5 and 1:0.7 molar ratios of $NaIO_4$ oxidation are more appropriate for penetrating into the collagen fiber structure and picked to be used in tanning trials.

The ^{1}H-NMR spectrum of native corn starch was shown in Figure 5. Some characteristic peaks at 4.520-5.439 ppm are attributed to proton signals of hydroxyl groups at C-2, C-3 and C-6. The signal at 5.092 ppm and the small peak at 4.842 ppm are attributed to anomeric H-1 proton at α-1,4 linkage and protons at α-1,6 branching point, respectively. The proton signals of CH and CH_2 groups of starch unit were determined between 3.30 and 3.642 ppm. On the other hand, the signal of H-3, overlapping signal of H-3 and H-5, combined signal of H-2 and H-4 were observed at 3.642, 3.569, 3.30 ppm, respectively.[34,35]

The ^{1}H-NMR spectra of dialdehyde starches (1:0.3, 1:0.5 and 1:0.7) which were selected to be used in tanning trials are shown in Figure 6. Comparing with the spectra of native corn starch, the small peaks occurred between 9.095-9.585 ppm (aldehydic proton) in ^{1}H-NMR spectrum of dialdehyde starches confirmed that periodate oxidation performed successfully. However, since the aldehyde groups are in balance with the hemiacetal formations, the intensity of signals in this range is very weak. Also, additional peaks in dialdehyde starches are attributed to the protons of –OH and –CH groups in hemiacetal structures.[36,37] Furthermore, while the peak related to aldehyde protons was seen at 9.292 ppm in 1:0.3 molar ratio oxidized starch sample, as well as this peak, new peaks were occurred at 9.095 and 9.585 ppm in 1:0.5 and 1:0.7 molar ratio oxidized starches respectively which proves that more aldehyde groups were introduced into the structure by increasing oxidation degrees.

Tanning properties of dialdehyde starch samples

The results of hydrothermal stability and filling coefficient of pelt pieces tanned with dialdehyde starches were given in Table III. Comparing with intact pelt, it was determined that tanning with dialdehyde starches resulted a remarkable increase in shrinkage temperature (25.5° - 29.5°C) as well as filling coefficient (25.7-34.6 %). From the evaluation of filling effect gained to the pelts, it was determined that the thickness of leathers increased in conjunction

Table III

Tanning properties of oxidized starches

Sample	Filling coefficient (%)	Shrinkage temperature (°C)
Intact Pelt	—	43.5(±0.9)
$NaIO_4$ 1:0.3	25.7(±0.3)	69.0(±0.6)
$NaIO_4$ 1:0.5	30.6(±0.5)	70.0(±0.3)
$NaIO_4$ 1:0.7	34.6(±0.6)	73.0(±0.5)
Tanned Whole Pelt	—	74.5(±0.4)

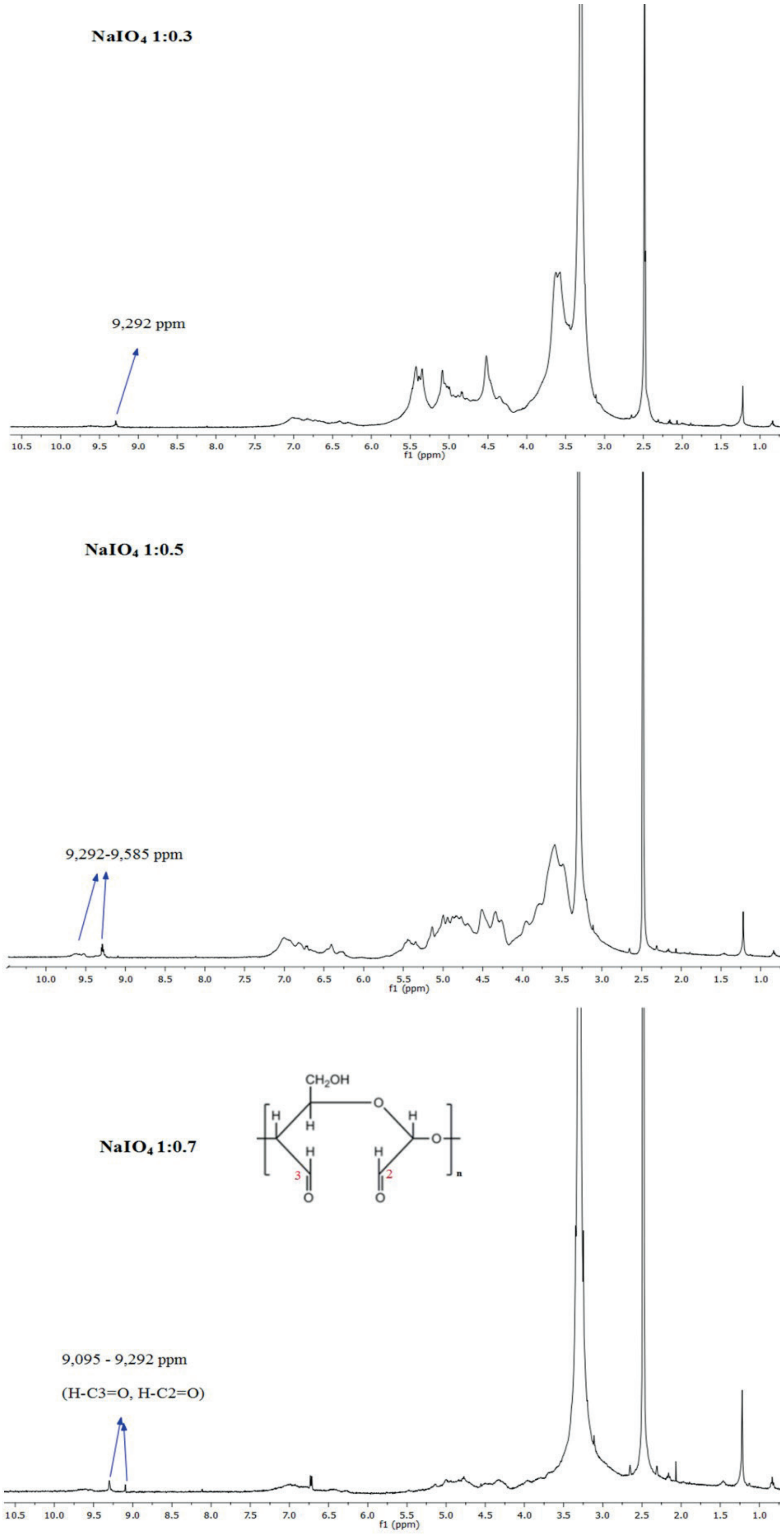


Figure 6. NMR spectrums of dialdehyde starches

with increasing molar ratio. As mentioned earlier, the molecular weight distributions decreased with increasing oxidation degree. So, it is commented that oxidized starches having smaller molecular weight could penetrate into the fiber structure of the pelts quite easily and result in a higher filling effect.

Considering the shrinkage temperatures, it was seen that a significant increase occurred in shrinkage temperature, expectedly due to the introduction of increasing number of aldehyde groups which can bond with reactive sites of collagen (-NH_2), with increasing oxidation degrees (Figure 7). From the tanning trials with pieces of pelts, the

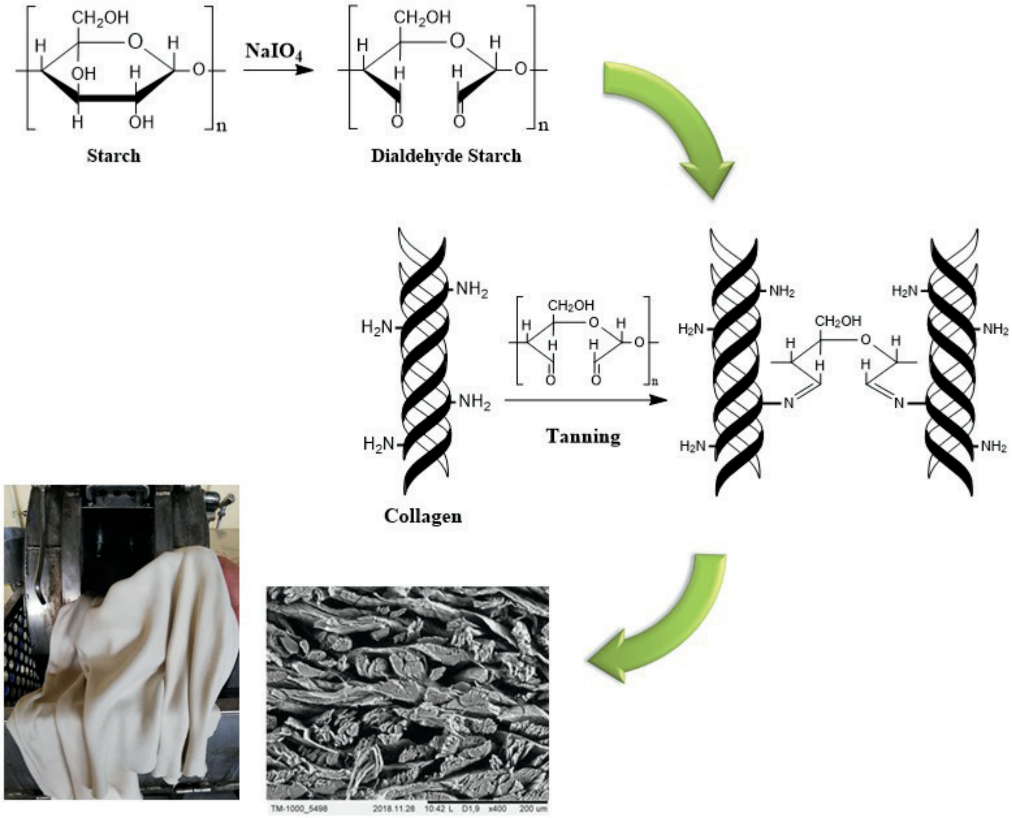


Figure 7. Dialdehyde starch production from native corn starch by NaIO$_4$ oxidation and dialdehyde & collagen reaction mechanism in tanning

highest shrinkage temperature (73°C) and filling coefficient (34.6%) were obtained with 1:0.7 molar ratio oxidized starch sample. However, since it had a quite high astringency and resulted rough handle and loss of area, 1:0.5 molar ratio oxidized starch sample, having more gentle tanning effect, was chosen among dialdehyde starches as having the best tanning effect and decided to be used in tanning of a whole pelt.

From the tanning of the whole pelt with 1:0.5 molar ratio oxidized starch sample, 74.5°C of shrinkage temperature was obtained which means 31°C of increase was achieved comparing with shrinkage temperature of intact pelt. From the comparison of the shrinkage temperature increases with limited studies in literature,[7,10,19] it was seen that they were also achieved approximately same ranges of increases (26°-32°C) in shrinkage temperatures.

At this point another issue which is needed to be discussed in detail is that from the literature review of many research studies[7,10,19] the introduction pH to the tanning process was rather high (pH:10). In spite of expecting a very rapid reaction considering reaction parameters and behavior of aldehyde groups at this pH, accordingly with previous studies in our preliminary tanning trials we also used pH:10 for introduction to tanning process. However, suddenly swelling and correspondingly loss of area occurred over pH:8 as foreseen. For this reason, lower introduction pH (pH:5.5) was decided to be tried. However, at pH:5.5 the oxidized starch samples showed poor solubility which was not surprising recalling their solubility results. So, after starting the tanning process, the pH was decided to be increased. After the first partial additions of alkali, it was observed that the solubility of the dialdehyde starches in tanning bath increased along with increasing pH and thus their penetration into the pelts was also started to increase. The final pH was raised up to 7.0-7.5 (just below the swelling pH of collagen, taking in account of a possible swelling) by gradual addition of alkali and frequently checking. Thus, a safer and complete tanning was achieved without any drawback such as swelling, excessive astringency, coarse or pebbled grain or loss of area etc.

The scanning electron micrographs (SEM) of intact pelt and the leathers tanned with dialdehyde starch samples are shown in Figure 8. From the comparison of the cross-section images of pickled goat skin with tanned leathers it was clear that the fibril bundles of the tanned leathers were isolated indicating that dialdehyde starch samples performed a tanning effect. However, it was also clear that isolation of fibril bundles was increased especially in leathers tanned with higher degree oxidized starch samples (1:0.5, 1:0.7).

As already mentioned, preliminary tanning trials were carried out with pieces. Then, a whole pickled goat skin was tanned with selected modified starch (1:0.5 molar ratio) having the best tanning effect. For this reason, physical test results for both pieces and whole

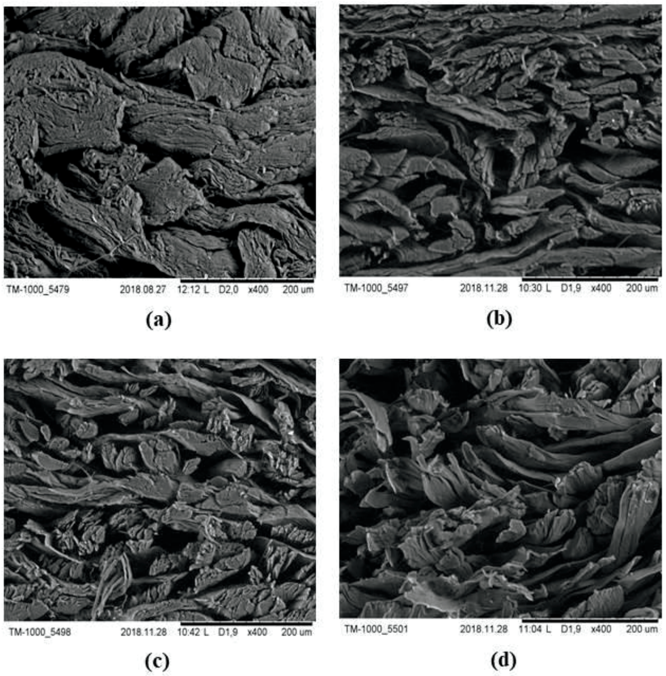


Figure 8. SEM images of **a)** pickled goat skin, **b)** 1:0.3, **c)** 1:0.5, **d)** 1:0.7 oxidized starch tanned leathers

leathers were given in Table IV. Comparing with the tensile strength and tear strength results of the leathers tanned with dialdehyde starch samples with recommended value for goat leathers (20 N/mm^2 for tensile strength and 40 N/mm for tear strength) by UNIDO,[38] excluding the tensile strength value (17.4 N/mm^2) of the leather which was tanned with 1:0.7 periodate oxidized starch, all leather samples meet the recommended values.

Additionally, the whole leather which was tanned with 1:0.5 molar ratio oxidized starch was also tested in terms of distension and strength of surface and the cracking and bursting values were found to be 32±1.2 kgf, 41±1.4 kgf and 16.2±1.6 mm respectively which meets the recommended value (min. 7mm) for shoe upper leathers by UNIDO[38].

On the other hand, after drying, the leather samples were mechanically softened and evaluated organoleptically (Table V) and from the evaluation, it was seen that the dialdehyde starch tanned leathers were bone colored, firm and had a compact structure similar with vegetable tanned leathers.

Conclusion

Native corn starch was oxidized with different molar ratios of $NaIO_4$ to obtain dialdehyde starches bearing different amounts of aldehyde groups to be used as a tanning agent in leather making. Modified starch samples were characterized by FT-IR, NMR, GPC and aldehyde contents revealed that periodate oxidation of native corn starch was carried out successfully. Afterwards, the selected modified starch samples were used in tanning and tanning abilities of oxidized starches were evaluated in terms of shrinkage temperature, filling coefficient, isolation of fibril bundles. Also, physical performances of the leathers tanned by modified starch samples were determined and the leathers were evaluated organoleptically. From the evaluation of all results, it was concluded that $NaIO_4$ oxidation product of corn starch (dialdehyde starch) has a remarkable tanning effect and can be utilized as a tanning agent in leather making. Thus, besides

Table IV

Physical properties of tanned leathers with oxidized starches.

				Tear Strength	
	Oxidized Starch	**Tensile Strength (N/mm^2)**	**Elongation (%)**	**Max. Force (N)**	**Thickness (mm)**
Tanning with pelt pieces	1:0.3	35.9(±6.6)	55.6(±4.5)	106.0(±10.5)	0.6(±0.03)
	1:0.5	26.8(±5.0)	57.6(±8.1)	103.3(±2.8)	0.8(±0.02)
	1:0.7	17.4(±5.2)	55.2(±11.8)	86.0(±12.1)	1.1(±0.10)
Tanning with whole pelt	1:0.5	28.2(±2.9)	72.9(±10.1)	97.4(±1.2)	0.84(±0.02)

Table V

Organoleptical properties of tanned leathers with oxidized starches.

	Oxidized Starch	**Color**	**Handle**	**Grain smoothness**
Tanning with pelt pieces	1:0.3	Bone c.	Firm	Slightly rough
	1:0.5	Bone c.	Firm	Slightly rough
	1:0.7	Bone c.	Very firm	Rough
Tanning with whole pelt	1:0.5	Bone c.	Firm	Slightly rough

detailed investigation and characterization of dialdehyde starch, a safer way of tanning without any drawback such as swelling, excessive astringency, coarse or pebbled grain or loss of area etc., was developed by optimizing tanning process conditions different from the existing studies in literature. Since the new tanning process does not necessitate a pickling process, it brings the advantages of saving time and simplifying the production but more importantly by avoiding use of acids and salts it offers an important advantage from an environmental point of view.

The results obtained from our first and the present studies strongly encourage us regarding utilization of starch as a source for a natural based tanning agent and we think that further studies should be carried on alternative modifications within this scope considering its advantages of being generated from renewable natural sources with biodegradable property which has big importance in terms of sustainability, human & environmental health.

Acknowledgement

The authors would like to thank the Ege University Faculty of Engineering Scientific Research Projects Commission, which supported this study financially (Project No: 14MUH029).

References

1. Kilicarislan Ozkan, C., Ozgunay, H. and Akat, H.; Possible se of corn starch as tanning agent in leather industry: Controlled (gradual) degradation by H_2O_2. *Int J Biol Macromol* **122**, 610-618, 2019. https://doi.org/10.1016/j.ijbiomac.2018.10.217
2. Wongsagon, R., Shobsngob, S and Varavinit, S.; Preparation and physicochemical properties of dialdehyde tapioca starch. *Starch-Starke* **57**, 166-172, 2005. https://doi.org/10.1002/star.200400299
3. Zhang, S.D, Zhang, Y.R, Zhu, J., et al.; Modified corn starches with improved comprehensive properties for preparing thermoplastics. *Starch/Stärke* **59**, 258-268, 2007. https://doi.org/10.1002/star.200600598
4. Zhang, L., Liu, P., Wang, Y., et al.; Study on physico-chemical properties of dialdehyde yam starch with different aldehyde group contents. *Thermochim Acta* **512**, 196-201, 2011. https://doi.org/10.1016/j.tca.2010.10.006
5. Lee, J., Park, S., Roh, H., et al.; Preparation and characterization of superabsorbent polymers based on starch aldehydes and carboxymethyl cellulose. *Polymers* **10(6)**, 605, 2018. https://doi.org/10.3390/polym10060605
6. Fiedorowicz, M. and Para. A.; Structural and molecular properties of dialdehydestarch. *Carbohydr Polym* **63(3)**, 360-366, 2006. https://doi.org/10.1016/j.carbpol.2005.08.054
7. Filachione, E.M., Clarke, J.D., Harris, E.H., et al.; Tanning studies with dialdehyde starch preliminary evaluation of the leather. *JALCA* (ISSN: 0002-9726) **56**, 200, 1961.
8. Celades, R., Duque, J. and Palma, J.J.; Titanium tannage. *AQEIC Boletin Tecnico* **41(3)**, 190-196, 1990.
9. Zhen, J. and Ma, J.; Modification of starch and its application in leather making. *J Soc Leather Technol Chem* (ISSN: 0144-0322), **86**, 93-95, 2002.
10. Kanth, S.V., Madhan, B., Rao, J.R., et al.; Studies on the stabilization of collagen using dialdehyde starch: Part I. Effect of autoclaving on dialdehyde starch. *JALCA* **101(12)**, 444-453, 2006.
11. Lv, S., Gong, R. and Hu, J.; Study on modified starch by glutaraldehyde and its properties and application. *Adv Mater Res* **455(456)**, 575-581, 2012. https://doi.org/10.4028/www.scientific.net/AMR.455-456.575
12. Lv, S., Gong, R. and Ma, Y.; Structure and properties of the graft copolymer of starch and p-hydroxybenzoic acid using horseradish peroxidase. *Polym Advan Technol* **23**, 1343-1349, 2012. https://doi.org/10.1002/pat.2052
13. Yu, Y., Wang, Y., Ding, W., et al.; Preparation of highly-oxidized starch using hydrogen peroxide and its application as a novel ligand for zirconium tanning of leather. *Carbohydr Polym* **174**, 823-829, 2017. https://doi.org/10.1016/j.carbpol.2017.06.114
14. Ding, W., Yi, Y., Wang, Y., et al.; Preparation of a highly effective organic tanning agent with wide molecular weight distribution from bio-renewable sodium alginate. *Chemistry Select* **3**, 12330-12335, 2018. https://doi.org/10.1002/slct.201802540
15. Ding, W., Yi, Y., Wang, Y., et al.; Peroxide-periodate co-modification of carboxymethylcellulose to prepare polysaccharide-based tanning agent with high solid content. *Carbohydr Polym* **224**, 115169, 2019. https://doi.org/10.1016/j.carbpol.2019.115169
16. Chen, H., Hu, Y., Li, S.Q., et al.; The tanning performance of dialdehyde cellulose prepared by electrochemical oxidation system. *J Soc Leather Technol Chem* **103(6)**, 305-310, 2019.
17. Ariram, N. and Madhan, B.; Development of bio-acceptable leather using bagasse. *J Clean Prod* **250**, 119441, 2020. https://doi.org/10.1016/j.jclepro.2019.119441
18. Yi, Y., Jiang, Z.C., Yang, S.J., et al.; Formaldehyde formation during the preparation of dialdehyde carboxymethyl cellulose tanning agent. *Carbohydr Polym* **239**, 116217, 2020. https://doi.org/10.1016/j.carbpol.2020.116217
19. Nirenjana, M., Archana, T.N., Kanth, S.V., et al.; Stabilization of collagen using dialdehyde alginic acid-an ecofriendly tanning system, 2006. https://pdfs.semanticscholar.org/876d/0e7344f3c0fd4e9b2f19c80f0f255fc6c0eb.pdf (accessed 26 June 2020).
20. Hofreiter, B.T., Alexander, B.H. and Wolff, I.A.; Rapid estimation of dialdehyde content of periodate oxystarch through quantitative alkali consumption. *Anal Chem* **27**, 1930-1931, 1955. https://doi.org/10.1021/ac60108a023
21. Singh, J. and Singh, N.; Studies on the morphological and rheological properties of granular cold water soluble corn and potato starches. *Food Hydrocoll* **17(1)**, 63-72, 2003. https://doi.org/10.1016/S0268-005X(02)00036-X
22. IUP 16, Official Methods and Analysis, Measurement of Shrinkage Temperature up to 100 °C, 2002.
23. TS EN ISO 3376, Leather - Physical and Mechanical Tests - Determination of Tensile Strength and Percentage Extension, 2012.

24. TS EN ISO 3377-2, Leather - Physical and Mechanical Tests - Determination of Tear Load Part 2: Double Edge Tear, 2016.
25. TS EN ISO 3379, Leather - Determination of distension and strength of surface (Ball burst method), 2016.
26. TS EN ISO 2419, Leather - Physical and Mechanical Tests - Sample Preparation and Conditioning, 2012.
27. TS EN ISO 2589, Leather - Physical and Mechanical Tests - Determination of Thickness, 2016.
28. Veelaert, S., Wit, D., Gotlieb, K.F, et al.; The gelation of dialdehyde starch. *Carbohydr Polym* **32**, 131-139, 1997. https://doi.org/10.1016/S0144-8617(96)00160-9
29. Para, A.; Complexation of metal ions with dioxime of dialdehyde starch. *Carbohydr Polym* **57(3)**, 277-283, 2004. https://doi.org/10.1016/j.carbpol.2004.05.005
30. Yi, X., Zhang, S. and Ju, B.; Preparation of water-soluble oxidized starch with high carbonyl content by sodium hypochlorite. *Starch/Stärke* **65**, 1-9, 2013. https://doi.org/10.1002/star.201300037
31. Yu, J., Chang, P.R. and Ma, X.; The preparation and properties of dialdehyde starch and thermoplastic dialdehyde starch. *Carbohydr Polym* **79**, 296-300, 2010. https://doi.org/10.1016/j.carbpol.2009.08.005
32. Zhang, L., Zhang, S., Dong, F., et al.; Antioxidant activity and in vitro digestibility of dialdehyde starches as influenced by their physical and structural properties. *Food Chem* **149**, 296-301, 2014. https://doi.org/10.1016/j.foodchem.2013.10.126
33. Veelaert, S., Wit, D., Gotlieb, K.F., et al.; Chemical and physical transitions of periodate oxidized potato starch in water. *Carbohydr Polym* **33**, 153-162, 1997. https://doi.org/10.1016/S0144-8617(97)00046-5
34. Wang, Q., Hu, Y., Zhu, J., et al.; Convenient synthetic method of starch/lactic acid graft copolymer catalyzed with sodium hydroxide. *Bull Mater Sci* **35(3)**, 415–418, 2012. https://doi.org/10.1007/s12034-012-0295-5
35. Kemas, C.U., Ngwuluka, N.C., Ochekpe, N.A., et al.; Starch-based xerogels: effect of acetylation on physicochemical andrheological properties. *Int J Biol Macromol* **98**, 94-102, 2017. https://doi.org/10.1016/j.ijbiomac.2017.01.101
36. Heidelberg, T. and Thiem, J.; Structure and reactions of glycopyranoside derived dialdehydes. *J Prakt Chem/Chem-Ztg* **340(3)**, 223-232, 1998. https://doi.org/10.1002/prac.19983400305
37. Chauhan, K., Kaur, J., Kumari, A., et al.; Efficient method of starch functionalization to bis-quaternary structure unit. *Int J Biol Macromol* **80**, 498-505, 2015. https://doi.org/10.1016/j.ijbiomac.2015.07.011
38. United Nations Industrial Development Organization (UNIDO). Constraints affecting the leather and leather products industry and measures required, 1994. https://open.unido.org/api/documents/4805022/download/CONSTRAINTS%20AFFECTING%20THE%20LEATHER%20AND%20LEATHER%20PRODUCTS%20INDUSTRY%20AND%20MEASURES%20REQUIRED%20(20423.en. (accessed 26 June 2020)

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

by
Hanyu Su[1] and Guoying, Li[1,2]*
[1]*National Engineering Research Center of Clean Technology in Leather Industry, Sichuan University,*
Chengdu 610065, China
[2]*Key Laboratory of Leather Chemistry and Engineering (Ministry of Education), Sichuan University,*
Chengdu 610065, China

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,[1] transforms pickled pelt into white, soft, fine and tight, bright and stretchable leather whose grain surface is as fine as woolen cloth.[2] However, a moderate shrinkage temperature (about 75°C) of tanned leather and the weak link between aluminum and collagen molecule[3] 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[4] as well as aluminum used in conjunction with other compounds, like glutaraldehyde,[5] genipin,[6] some polymers[2] and syntans[7] 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,[5, 8] increasing shrinkage temperature of hides and skins to near 100°C.[6, 9-11] Note that vegetable tanning also limits the denaturation temperature to 85°C,[12] 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.*[13] 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.*,[14] 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[15] 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,

---

*Corresponding author e-mail: liguoyings@163.com
Manuscript received October 12, 2020, accepted for publication November 18, 2020.

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.*[8] 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.[16] 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 ($[\text{-NH(CH}_2)_5\text{CO-}]_n$, 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°~25°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. Alkalescent 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°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[16] 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

	Binary System										Ternary System		
Group	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 $NaHCO_3$ 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^{-1} and 400 cm^{-1} and a resolution of 2 cm^{-1} 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_2O_3/%	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.

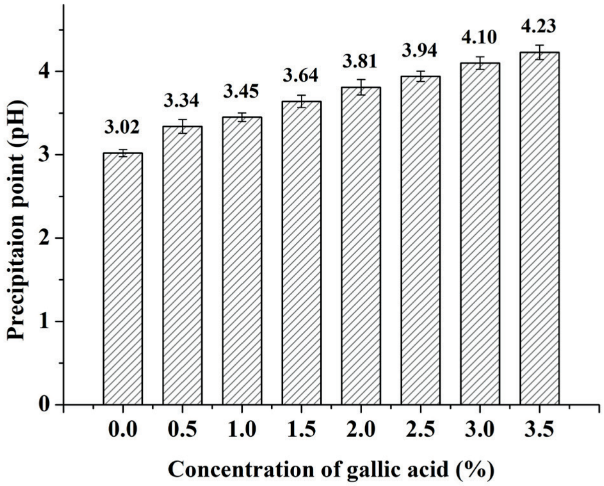


Figure 1. Precipitation points of different concentrations of aluminum and gallic acid mixed solutions. Concentrations of Al_2O_3 in initial mixed solutions was 1.5% (w/w)

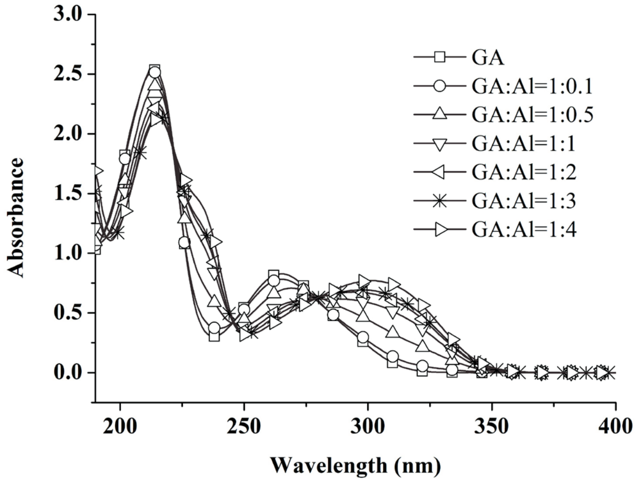


Figure 2. Spectra of gallic acid reacted with different concentrations of aluminum chloride at pH 4.0. Concentrations of Al^{3+} were 0.01, 0.05, 0.1, 0.2, 0.3 and 0.4 mM, respectively, and concentration of gallic acid was 0.1 mM.

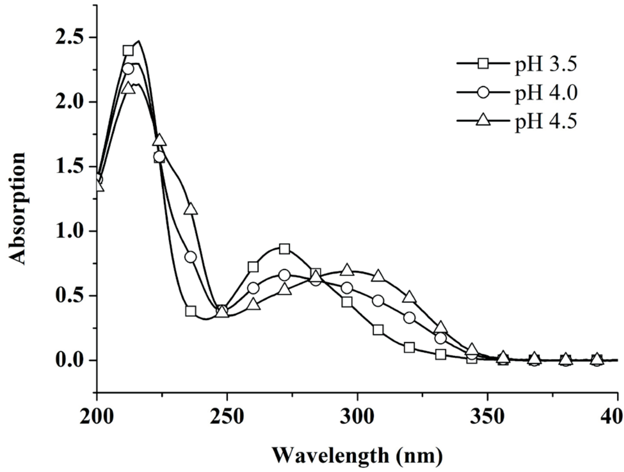


Figure 3. Impact of pH value on complexation of aluminum and gallic acid. Concentrations of gallic acid and Al^{3+} were both 0.1 mM.

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, Al^{3+} would form precipitation with OH^- at pH 3.02. As the concentration of gallic acid increased, the alkali resistance of Al^{3+} was also improved. When the concentration of gallic acid reached 3.5% in mixed solution, the precipitation point of Al^{3+} could be increased to 4.23, which may be resulted by the carboxyl or hydroxyl groups occupying the empty orbital of Al^{3+} so that the combination of OH^- and Al^{3+} was inhibited. Therefore, it could be indicated that complexation took place. Because gallic acid was dissolved in the equimolar $NaHCO_3$ 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 tannage 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 265nm. With the increase of the concentration of Al^{3+}, the spectra red-shifted incrementally relative to gallic acid and the peak at 265nm weakened, almost disappeared when the molar ratio of gallic acid and Al^{3+} was 1:4. When the molar ratio of gallic acid and Al^{3+} was 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 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 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)[17] was used to calculate the number of gallic acid molecules that attached to each Al^{3+}.

$$n = \frac{x_{max}}{1 - x_{max}} \tag{1}$$

where n is the number of gallic acid each Al^{3+} 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^{3+} 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^{3+} 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.[18-20] After reacting with aluminum chloride, absorbance at 3371 cm^{-1} shifted to 3386 cm^{-1} and peaks at 3286 cm^{-1} together with 1703 cm^{-1} weakened obviously, demonstrating that both hydroxyl and carboxyl would participate in the complexation with aluminum. Furthermore, a weak peak at 632 cm^{-1} 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.[21-22] The stretching vibration of N-H appeared at 3170 cm^{-1}. Because of the intramolecular hydrogen bond, it was much lower

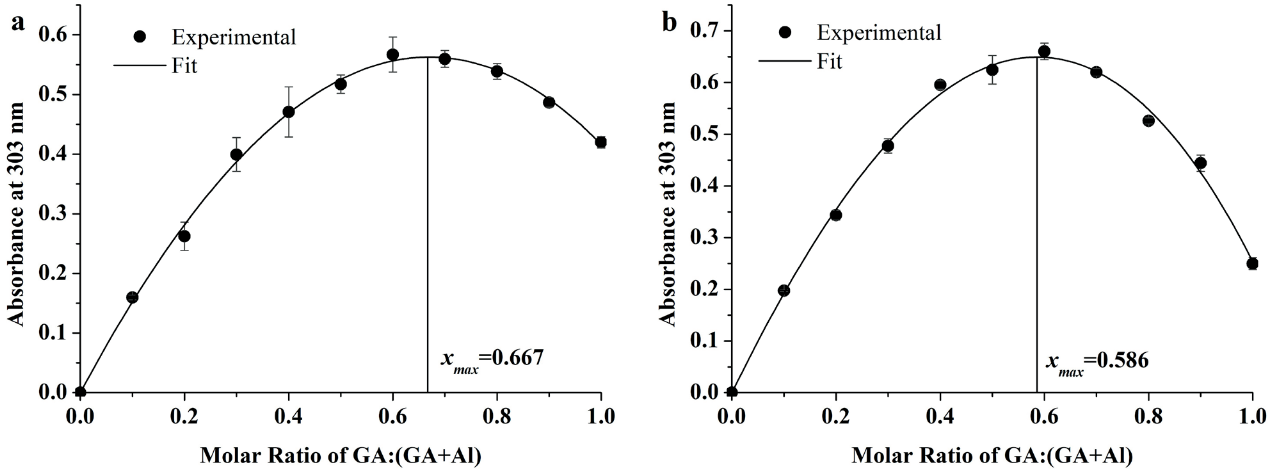
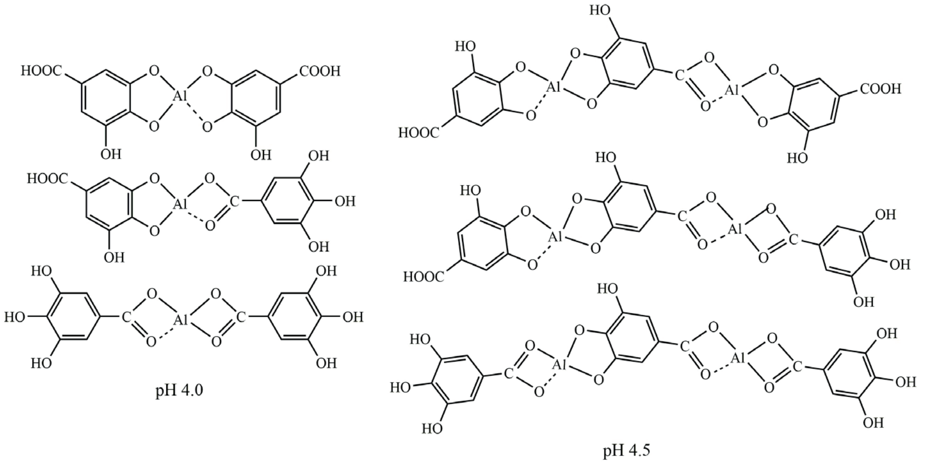


Figure 4. Job's plots at 303 nm for mixtures of gallic acid and Al^{3+} at different pH. Total concentration of the mixture was maintained at 0.2 mM. **(a)** pH 4.0, R^2=0.9966 **(b)** pH 4.5, R^2=0.9952.



pH 4.0

pH 4.5

Scheme 1. Speculation of the binding mode between gallic acid and Al^{3+} under pH 4.0 and 4.5

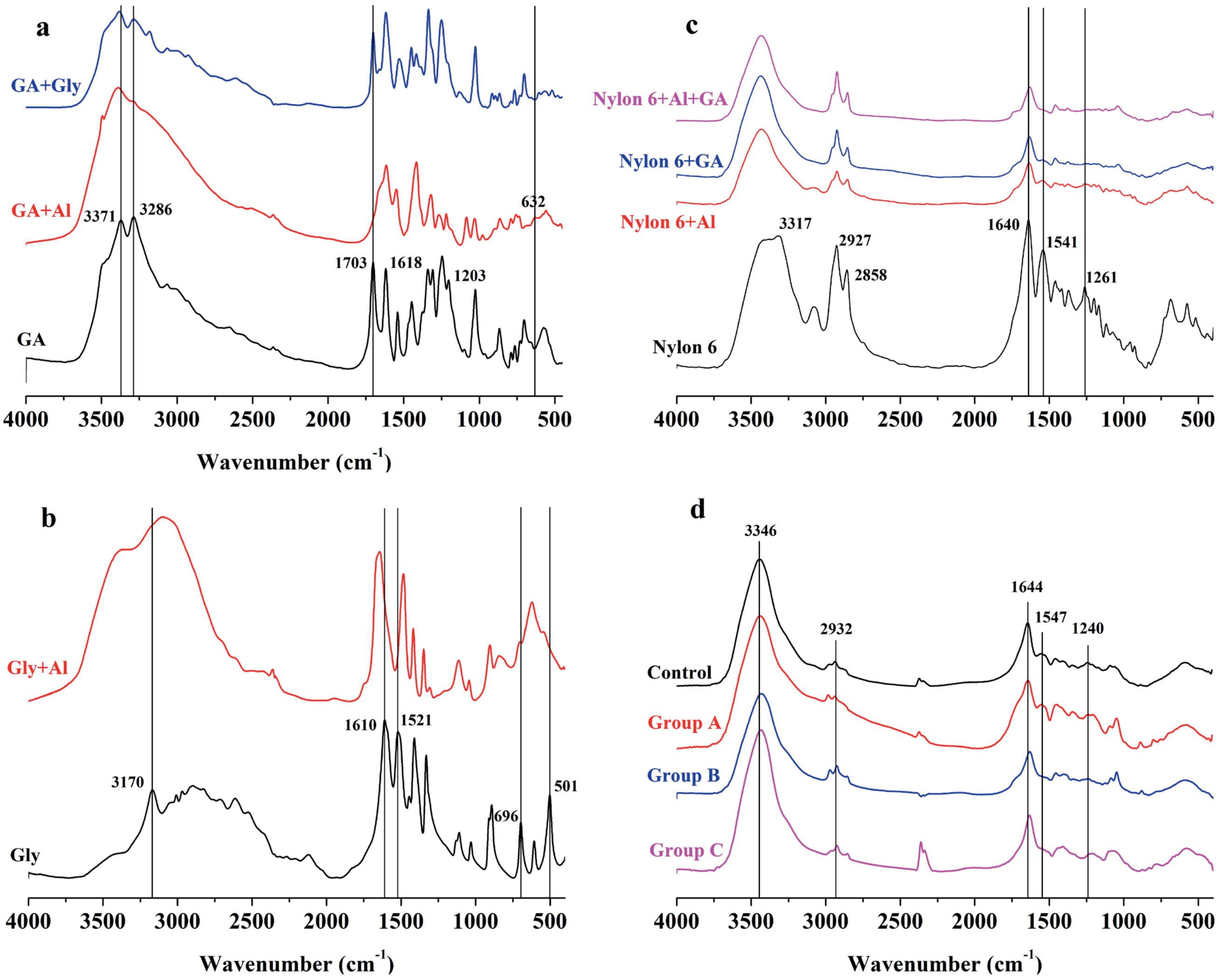


Figure 5. FTIR spectra of different kinds of the binary/ternary compounds and hide powder. **(a)** gallic acid and it mixed with aluminum chloride or glycine. **(b)** glycine and glycine-aluminum compounds. **(c)** polycaprolactam and it mixed with gallic acid and aluminum. **(d)** hide powder tanned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

Table III

FTIR major bands (in cm^{-1}) assignment of gallic acid, glycine and their compounds

Sample	GA	GA-Al	GA-Gly	Gly	Gly-Al
νO-H (Alcohol)	3371	3386	3385		3101
νO-H (Acid)	3268	3283	3283		
νC=O	1703	1670	1699	1610	1637
νPh-O	1203	1180	1131		
νC-O-Al		632			
δN-H				3170	3101
δC=O				690	705
ρC=O				501	535

Table IV

FTIR major bands (in cm^{-1}) assignment of polycaprolactam and hide powder

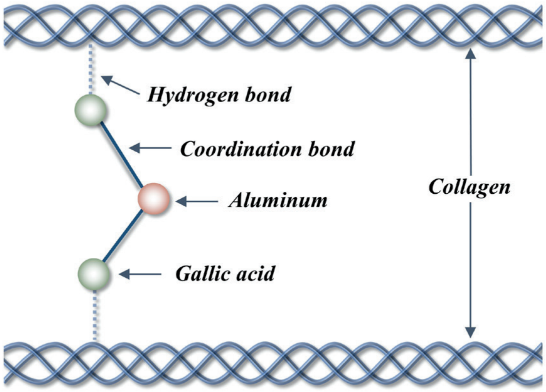
Sample	N6	N6-Al	N6-GA	N6-GA-Al	HP*	Group A**	Group B**	Group C**
Amide A					3446	3439	3430	3432
Amide B	2927	2927	2927	2927	2932	2936	2925	2923
Amide I	1640	1633	1629	1628	1644	1640	1631	1632
Amide II	1542	1541	1541	1541	1547	1550	-	-
Amide III	1261	1261	-	-	1240	1239	1236	1232

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

than the normal vibration area of N-H (3500-3300 cm^{-1}).[21] In the presence of aluminum, absorptions at 3170 cm^{-1} and 1610 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.[23] 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.[24] 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 Amie II, illustrating that gallic acid was the more active one to react with amide bonds of collagen than aluminum.



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

According to these consequences, the mechanism of the tannage 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 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°C. While with gallic acid, it could get another raise of 7.6°C (Group B) or 9.4°C (Group C) comparing to T_d of hide powder in Group A. Results

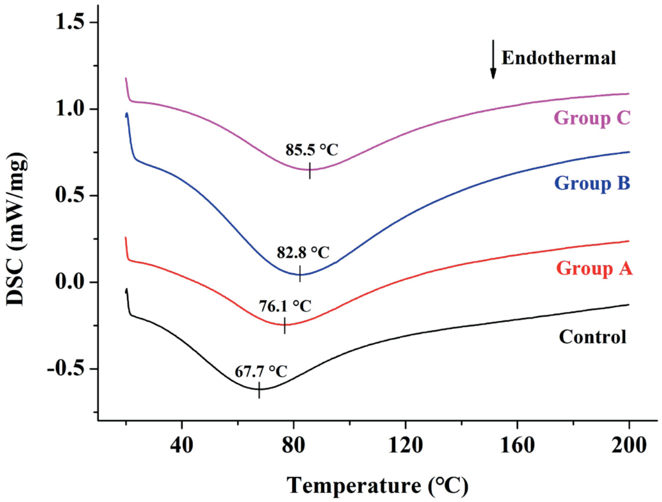


Figure 6. DSC curves of white hide powder (Control) and tanned hide powder. (Group A: aluminum tannage, Group B: gallic acid-aluminum combination tannage, Group C: aluminum-gallic acid complex tannage)

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.[25,26] 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.

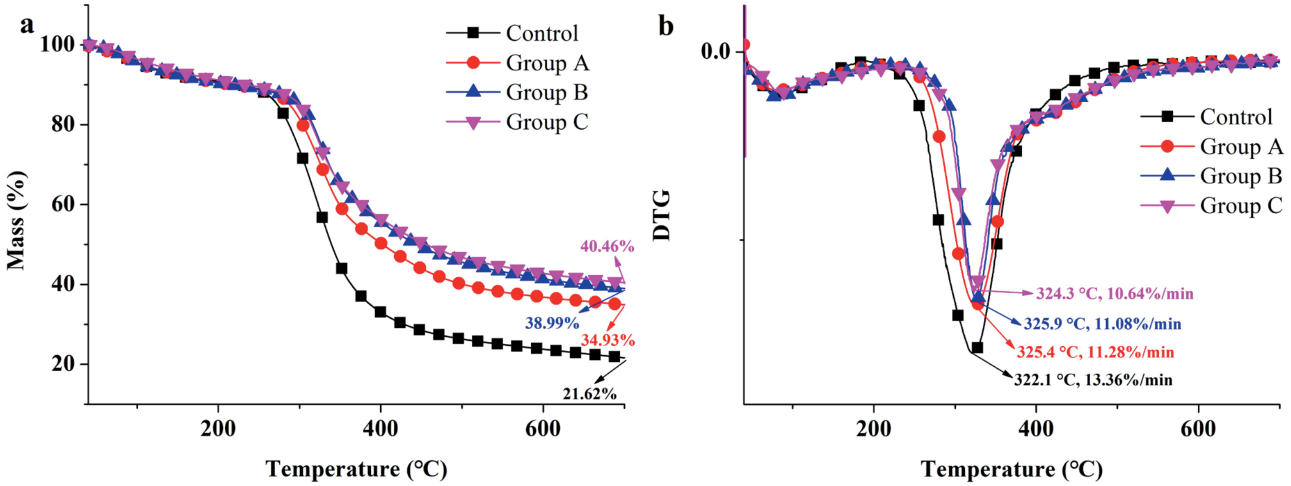


Figure 7. Thermal gravity **(a)** and differential thermal gravity **(b)** of different groups of hide powder. (Group A: aluminum tannage, Group B: gallic acid-aluminum combination tannage, Group C: aluminum-gallic acid complex tannage)

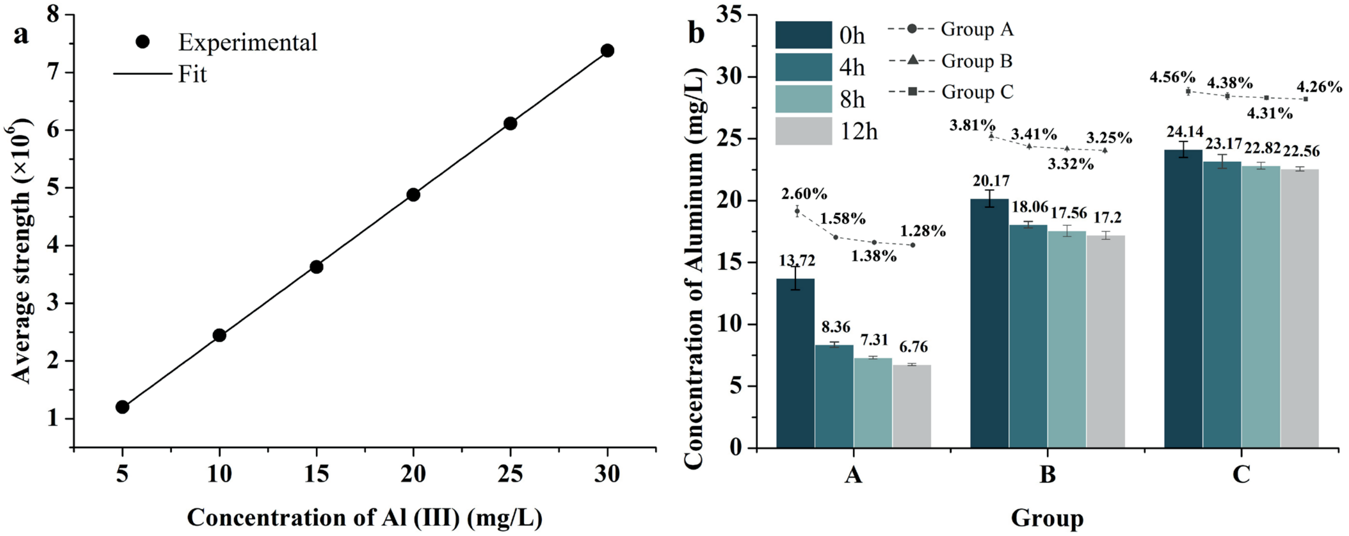


Figure 8. Standard curve of aluminum (**a**, $R^2 = 0.9999$), tested concentrations of the aluminum in diluted digestion solutions (**b**, bar chart) and binding capacity of Al_2O_3 in hide powder (b, line chart). (Group A: aluminum tannage, Group B: gallic acid-aluminum combination tannage, Group C: 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),

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

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.*,[27] 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.[28] 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.[29] The complex tannage and gallic acid-aluminum combination tannage shared the similar mechanism with what was reported.[15] 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.

References

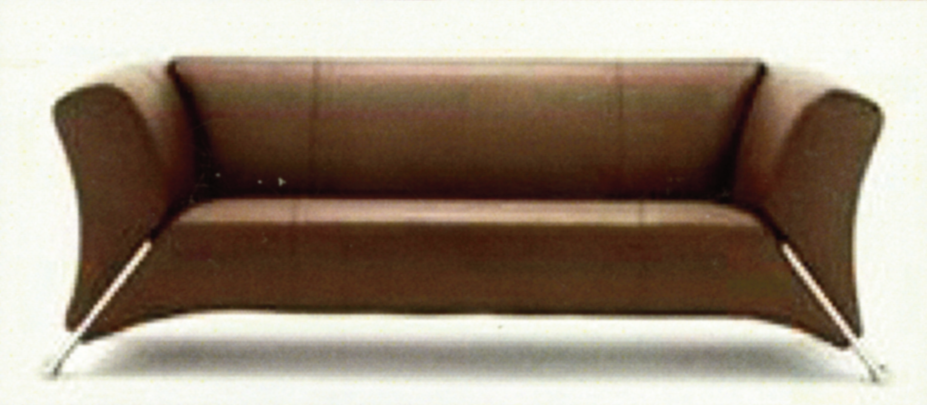
1. Covington, A. D.; The 1998 John Arthur Wilson Memorial Lecture: New tannages for the new millennium. *JALCA* **93**, 168-182, 1998.
2. Gao, D. G., Cheng, Y. M., Wang, P. P., Li, F., Wu, Y. K., Lye, B., Ma, J. Z., Qin J. B.; An eco-friendly approach for leather manufacture based on P(POSSMAA)-aluminum tanning agent combination tannage. *J. Clean Prod.* **257**, 120546, 2020.
3. China, C. R., Halona, A., Maguta, M. M., Nyandoro, S. S., Kanth, S. V., Jayakumar, G. C., Njau, K. N.; Preparation of aluminum sulphate from kaolin and its performance in combination tanning. *Carbohydr. Polym.* **215**, 179-188, 2019.
4. Liu, Y., Zhang, J. W., Chen, W. Y., Astruc, D., Gu, H. B.; Microwave-irradiated tanning reaction of aluminum with collagen. *J. Appl. Polym. Sci.* **137**, 48682, 2020.
5. Vitolo, S., Seggiani, M., D'Aquino, A. et al.; Tara-aluminum tanning as an alternative to traditional chrome tanning: Development of a pilot -scale process for high-quality bovine upper leather. *JALCA* **98**, 123-131, 2003.
6. Ding, K., Taylor, M. M., Brown, E. M.; Tanning effects of aluminum-genipin or -vegetable tannin combinations. *JALCA* **103**, 377-382, 2008.
7. Zhang, L., Zhao, X. Y., Wang, C. H., Lin, W.; A novel approach for lightfast wet-white leather manufacture based on sulfone syntan-aluminum tanning agent combination tannage. *JALCA* **113**, 192-197, 2018.
8. Madhan, B., Aravindhan, R., Siva, M. S., Sadulla, S., Rao, J. R., Nair, B. U.; Interaction of aluminum and hydrolysable tannin polyphenols: An approach to understanding the mechanism of aluminum vegetable combination tannage. *JALCA* **101**, 317-323, 2006.
9. Marsal, A., Manich, A., Gratacos, E.; Optimization methods in leather research-vegetable extract-aluminum salt combination tannage. *JALCA* **89**, 105-116, 1994.
10. Musa, A. E., Aravindhan, R., Madhan, B., Rao, J. R., Chandrasekaran, B.; Henna-Aluminum combination tannage: A greener alternative tanning system. *JALCA* **106**, 190-199, 2011.
11. Dsagupta, S.; Chrome free tannages: Part 1 Preliminary studies. *J. Soc. Leather Technol Chem.* **86**, 188-194, 2002.
12. China, C. R., Hilonga A., Nyandoro, S. S., Schroepfer, M., Kanth, S. V., Meyer, M., Njau, K. N.; Suitability of selected vegetable tannins traditionally used in leather making in Tanzania. *J. Clean Prod.* **251**, 119687, 2020.
13. Sykes, L. R., Cater, W. C.; Tannage with aluminum salts. Part I: reacting involving simple polyphonic compounds. *J. Soc. Leather Technol. Chem.* **64**, 29-31, 1980.
14. Sykes, L. R., Hancock, A. R., Orszulik, T. S.; Tannage with aluminum salts. Part II: Chemical basis of the reactions with polyphenols. *J. Soc. Leather Technol. Chem.* **64**, 31-32, 1980.
15. Hernandez, M., Juan F.; Combination tannages with vegetable tannins, aluminum, and other substances (leather, polyphenolics). Ph. D. Thesis, University of Cincinnati. Cincinnati, Ohio. 119-121, 1983.
16. Renny, J. S., Tomasevich, L. L., Tallmadge, E. H., et al.; Method of continuous variations: Applications of Job plots to the study of molecular associations in organometallic chemistry. *Angew. Chem., Int. Ed.* **52**, 11998–12013, 2003.
17. Li, J. L., Kim, S. Y., Chen, X. G., Park, H. J.; Calcium-alginate beads loaded with gallic acid: Preparation and characterization. Food Sci. *Technol. -Lebensm. -Wiss. Technol.* **68**, 667-673, 2016.
18. Likussar, W., Boltz, D. F.; Theory of continuous variations plots and a new method for spectrophotometric determination of extraction and formation constants. *Anal. Chem.* **43**, 1265-1272, 1972.
19. Jyothi, K. L., Kumara, K., Hema, M. K., Mahesha, Gautam, R., Row, T. N. G., Lokanath, N. K.; Structural elucidation, theoretical insights and thermal properties of three novel multicomponent molecular forms of gallic acid with hydroxypyridines. *J. Mol. Struct.* **1207**, 127828, 2020.
20. Araujo, P. Z., Morando, P. J., Blesa, M. A.; Interaction of catechol and gallic acid with titanium dioxide in aqueous suspensions. 1. Equilibrium studies. *Langmuir.* **21**, 3470-3474, 2005.
21. Zheng, X. L., Zhang, H. H., Wei, K. M.; Synthesis and spectroscopic characterization of lanthanum and glycine amino acid with 1,10-phenanthroline. *Spectrosc. Spectr. Anal.* **20**, 852-854, 2000.
22. Al-Fifi, Z., Eid, M., Ibrahim, M.; On the spectroscopic analyses of protein. *J. Comput. Theor. Nanos.* **10**, 2375-2379, 2013.
23. Li, N. Y., Xu, J. Q., Shan, D., Zhang, D., Xue, H. G.; Eiectrochemical synthesis of conducting copolymer of pyrrole and capprolactam. *Acta Polym. Sin.* **5**, 441-445, 2011.

24. Liu, S. C., Liu, W. T., Li, G. Y.; Effect of ionic liquids pretreatment on the extraction of collagen from calf skin. *JALCA* **114**, 391-399, 2019.
25. Teng, S. H., Lee, E. J., Wang, P., Kim, H. E.; Collagen/hydroxyapatite composite nanofibers by electrospinning. *Mater. Lett.* **62**, 3055-3058, 2008.
26. Li, Q. P., Xu, B., Wang, Y., Zhuang, L. H., Wang, Q., Lie, C., Xu, X. Q., Wang, G. W.; Effect of cationic structure of ionic liquids on dissolution and regeneration of white hide powder. *Fiber. Polym.* **18**, 1512-1522, 2017.
27. Covington, A. D., Hancock, R. A., Ioannidis, I. A.; Mechanistic studies of mineral tanning. 1. Solid-state Al-27 NMR-studies and the thermodynamics of shrinking. *J. Soc. Leather Technol Chem.* **93**, 1-8, 1989.
28. Covington, A. D.; Theory and mechanism of tanning: presenting thinking and future implications for industry. *J. Soc. Leather Technol Chem.* **85**, 24-34, 2000.
29. Miles, C. A., Ghelashvili, M.; Polymer-in-a-box mechanism for the thermal stabilization of collagen molecules in fibers. *Biophys. J.* **76**, 3243-3252, 1999.

LEATHER

AVELLISYNCO

Selected Dyestuffs



CHEMTAN

17 Noble Farm Drive • Lee, NH 03861 (Office)
57 Hampton Road • Exeter, NH 03833 (Manufacturing)
Tel: (603) 772-3741 • Fax: (603) 772-0796
www.CHEMTAN.com

COLD Milling

Smooth Leather Milling

Erretre
Tannery Innovations

Erretre s.p.a. | Via Ferraretta,1 | Arzignano (VI) 36071 | tel. +39 0444 478312 | info@erretre.com

Lifelines

Jaya Prakash Alla is currently pursuing his Ph.D studies in leather technology, he has bachelors and master's degree in leather technology. His research interests include development of smart materials for leather processing.

N. Nishad Fathima is a Sr. Principal Scientist, working for Central Leather Research Institute, India. Her research interests include study of ionic liquids for collagen stabilization and leather processing, extraction-structure- property relationship of keratin peptides, collagen – small molecule interactions: Directed ordering of collagen assembly, value added materials from tannery solid waste and smart chemicals for smart leathers.

J. Raghava Rao is a Chief Scientist, working for Central Leather Research Institute, India. His research interests include study of chromium management in leather processing, cleaner leather processing, secured utilization of solids waste, zero discharge concepts, development of eco-benign leather chemicals, green chemistry approach for leather processing, waterless leather processing, smart chemicals for intelligent leathers.

Cigdem Kilicarislan Ozkan graduated from Ege University Department of Leather Engineering in 2008. The same year she started to M.Sc. She studied on extraction of vegetable tanning materials. She joined the staff of Leather Engineering Department as research assistant in 2010 and completed her PhD in 2018. Her research activities and fields of interests are tanning materials, extraction techniques, modification of biopolymers and leather technologies.

Hasan Ozgunay studied Leather Technology at the University of Ege (Turkey). After working in Leather Industry for one year, he joined the staff of Leather Engineering Department as research assistant in 1996. He obtained his M.Sc. in the same department. He studied on vegetable tanning materials and obtained his PhD in Leather Engineering. He is currently working as researcher / lecturer in the Leather Engineering Department. His research activities and fields of interests are tanning materials, leather processing technologies and cleaner leather processing methodologies.

Hanyu Su obtained her Bachelor's Degree in Light Chemical Engineering from Sichuan University of China in 2018. Now she is studying as a master candidate in Leather Chemistry and Engineering at Sichuan University of China. Research interest: The applications of aluminum complexes in tanning and collagen-based materials.

Guoying Li, see *JALCA* **112**, 436, 2017.

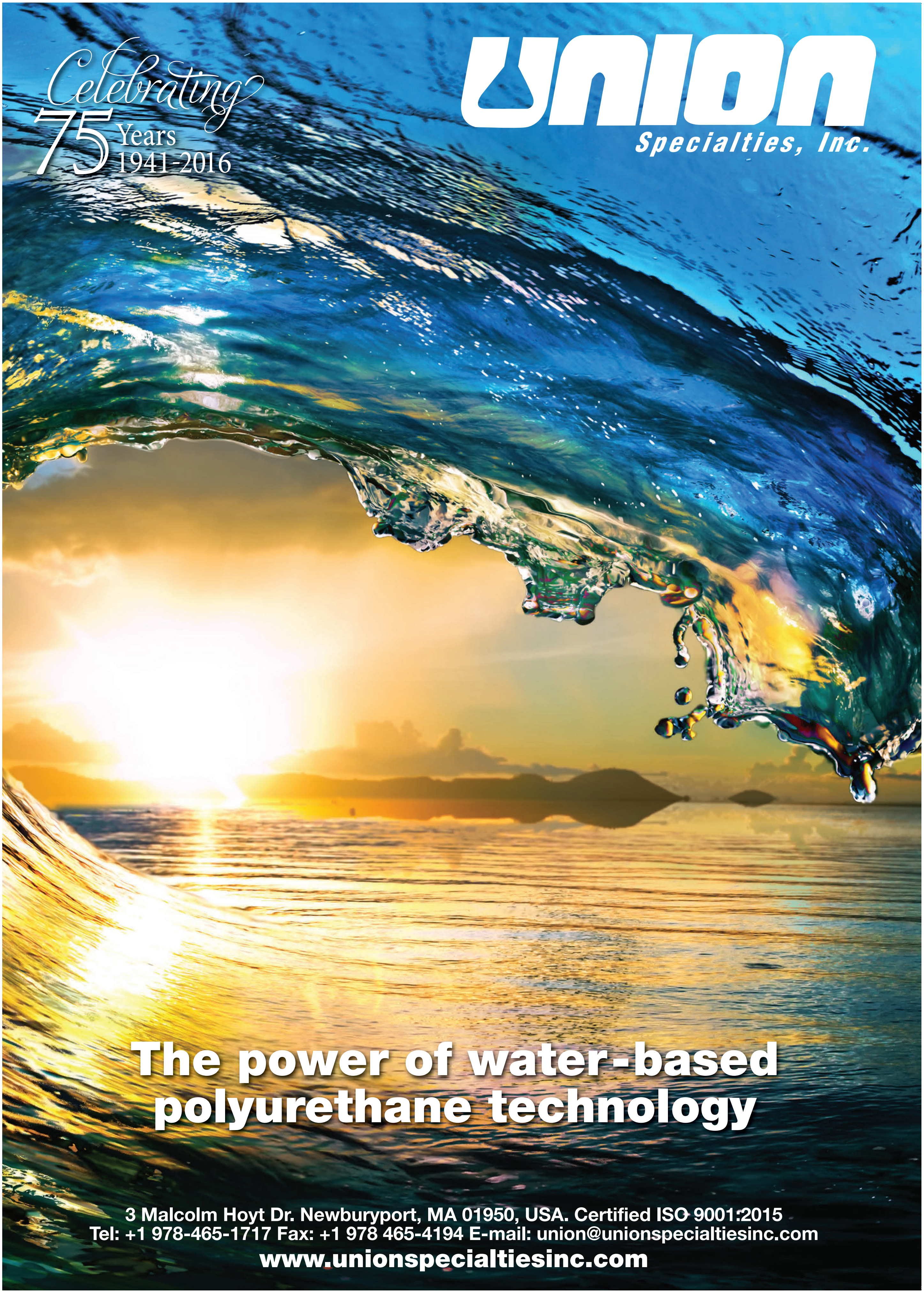
Obituary

Heinrich "Henry" Walter Koelblinger, 79 of Hernando, went to his heavenly home on December 10th 2020. Henry was one of a kind and always had a joke or a funny story. Henry was born in Salzburg, Austria on August 23, 1941, the son of the late Kamillo and Aenne Koelblinger. He grew up in Vocklamarkt, Austria home of his family's 400 year old leather business with his sisters Annemarie and Gretel and brother Kamillo He could recount stories of the end of WWII when American GI's came through town and passed out gum and Hershey bars. Growing up he loved spending time at the family cottage on Wallersee Lake. He received a master's degree in leather chemistry at the West German Tanners school in Germany. He met the love of his life, Mary (Hunt) when he moved to Beacon, New York to work for BASF Leather Chemical division. They were married then soon moved back to Austria to help with the family business. While in Austria they had their first daughter, Andrea (Steve Kroll). They decided to move back to the USA and moved to Milwaukee, Wisconsin where their second daughter, Margaret "Peg"(Ted Christian) was born and Henry proudly became a US citizen. He managed several leather tanneries that prompted moves to West Virginia and then Mercersburg, PA. While in Pennsylvania, two more children were added to their family: Michelle (Joe Kozlowski) born in Mercersburg, PA and Christopher Koelblinger (Lori) born in Hagerstown, MD. They then moved to Luray, VA for another management position. BASF called again and they moved back to Wisconsin. Henry worked as a sales manager for leather chemicals and was considered a legend in the industry due to his knowledge, commitment and friendship with his clients. The family enjoyed many great adventures together travelling back to Europe and visiting with their Austrian family. Henry and Mary loved to travel and visited over 30 countries including China, Hong Kong, Italy, Thailand, and every state in the USA.

Henry loved to talk to strangers and share jokes. He was an avid reader and very knowledgeable including knowing 4 languages: German, English, French and Italian. He loved to play cards with his close friends and family. Mary and he were the ultimate hosts and known for their wonderful parties. Henry was an accomplished cook and people rarely declined an invitation. He especially loved to make Austrian dishes like goulash and Rahm Schnitzel. Henry and Mary were featured in an article in the Milwaukee Journal's Best Cook on the Block and their recipes are in the Milwaukee Journal's cookbook. Henry and Mary were Citrus Hills Women's Club Mardi Gras King and Queen. They have many close friends that they have made and kept through the years and loved sharing their home and travels with them. Henry loved his daily walks with his dog, Yanni and stopping to visit with neighbors.

Henry was adored as "OPA" to his 11 grandchildren: Kati, Chad, Hallie, Max, Abbie, Rachel, Nik, Kyle, Karstan, Megan, and Ryan and 3 great-grandchildren: Kashton, Carson and Melody who loved listening to him tell stories about their family history.

A private celebration of life was held due to COVID. Donations can be made to the Lupus Foundation. He will be sorely missed-Auf Wiedersehen Henry!


Celebrating
75 Years
1941-2016
UNION
Specialties, Inc.
The power of water-based polyurethane technology

THE AMERICAN LEATHER CHEMISTS ASSOCIATION
1314 50th Street, Suite 103, Lubbock, Texas 79412-2940
Ph: 806-744-1798 **Fax:** 806-744-1785 **Web:** www.leatherchemists.org
Email: carol.adcock@ttu.edu

Past Issues of *Journal* Needed

If you or someone you know wants to donate past issues of the *Journal* to the Association, please contact us.

Below is a list of issues needed.

Missing Issues:

1906–1909; 1911; 1913; 1915; 1921
1937 – January and December
1939 – January, March and April
1940 – January

Extremely Low Supply:

1931 – February
1936 – January and February
1944 – Jan., Oct., Nov. and Dec.
1945 – June
1946 – January – April
1947 – January, April and August
1948 – January – March
1949 – January – June
1955 – January
1969 – March
1970 – February
1979 – July
1983 – March
1984 – July
1999 – June and July
2000 – January and February
2001 – May and June
2002 – January and March

INDEX TO ADVERTISERS

116th ALCA
ANNUAL CONVENTION
Change of Date:
Coming Soon
Eaglewood Resort & Spa
Itasca, IL

Featuring the 61st John Arthur Wilson Memorial Lecture
By Randy Johnson, President and CEO
of GST AutoLeather
Title: Road Ahead

Tentative Schedule

Tuesday

Golf Tournament, Opening Reception and Dinner

Wednesday

John Arthur Wilson Memorial Lecture
All Day Technical Sessions, Fun Run
Reception and Dinner, Activities - Bowling, Pool,
Darts and an Open Bar

Thursday

All Day Technical Sessions, Annual Business Meeting
Activities Awards Luncheon
Social Hour, ALCA Awards Banquet

Visit us at www.leatherchemists.org for full details
under Annual Convention as they become available

Tel: (603) 772-3741 • Fax: (603) 772-0796 • www.CHEMTAN.com