THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

July 2021 **Vol. CXVI, No.7** ***JALCA* 116(7), 225–264, 2021**

116th Annual Convention

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

DATE CHANGE:
June 21-24, 2022

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

Contents

Distributed by
University of CINCINNATI
LIBRARY PUBLISHING SERVICES

An imprint of the University of Cincinnati Press

ISSN: 0002-9726

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

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.

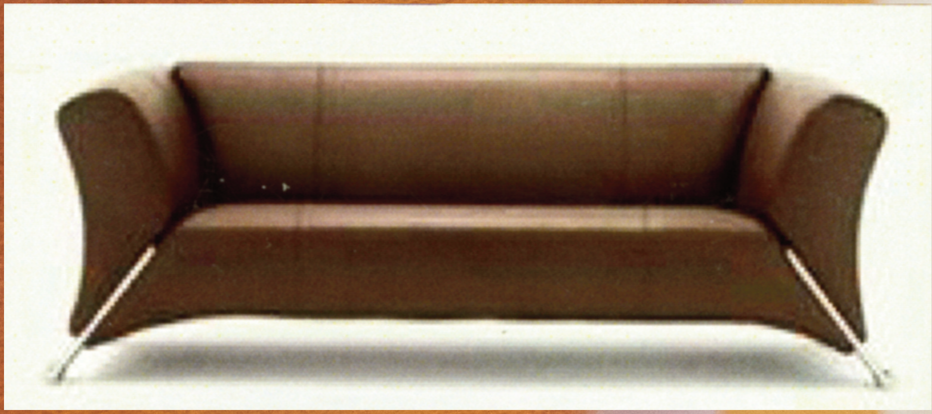
Website: www.leatherchemists.org E-mail: carol.adcock@ttu.edu

COPYRIGHT 2020. THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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

Studies on the Development of Benzoyl Peroxide Catalysed Rapid Oil Tanning using Linseed Oil

by

Bindia Sahu,[a*] Jaya Prakash Alla[b] and Gladstone Christopher Jayakumar[a]
[a]*Centre for Academic and Research Excellence,*
[b]*Regional Centre for Extension and Development,* Kanpur
Central Leather Research Institute, Council of Scientific and Research, Adyar, Chennai 600020, India.

Abstract

Leather tanning is a stabilisation process of collagen fibers. This is achieved by the interaction of collagen amino acids with tanning agents to stabilise skin from putrefaction. Tanning of collagen with oil is a special class of tanning known as chamois tanning. Chemically, the oil tanning involves oxidation of unsaturation present in the oil, which is generally achieved by exposing oil treated skins to air. In this study, Benzoyl peroxide has been used as an accelerating agent for oxidation of unsaturated bonds present in the linseed oil for oil tanning process. Results shows remarkable reduction in tanning duration from fifteen days to two days. The chamois leathers prepared using oxidation accelerant (Benzoyl peroxide) have been evaluated for physical properties such as water absorption (611%), tensile strength (18 N/mm^2) and percentage of elongation (66 %) which are found to be better than control leathers.

Introduction

Chamois leather finds application in various fields such as filtration of high-grade gasoline, cleaning and drying of optical instruments, manufacturing of gloves and garments, for lining trusses and prosthetics, and as sweat and water absorbent.[1] It is a mass market natural product having high demands for its utility and versatility in the application for satisfying the customer's needs. Yet, there are very few manufacturers of chamois leather that perpetuates to the ever-increasing demand for this product globally.[2,3]

In general, fish oil is known as the oil tanning agent for the manufacture of chamois leathers. Owing to unique fish oil smell in the final leather, research is being carried out to mitigate the effect.[4] Hence, alternate oils such as linseed oil,[5] jatropha oil,[6] rubber seed oil,[7] epoxidised oil,[8] have been utilised as an alternative source for fish oil for chamois tanning.

Linseed oil is known for its high unsaturation which makes it susceptible for oxidation. The presence of high unsaturation in linseed oil also has significant industrial applications in coatings such as floor covering and film formation[9] in order to protect it from oxidation a suitable antioxidant is required to enhance its shelf life.[10] The high linolenic acid content (>50%) makes it vulnerable to chemical reactions associated with double bonds, especially addition reaction.[11] Oxidation of oil is one of the most studied reactions where double bonds play important role. The two methods associated with oxidation of oils, are autoxidation and photo-oxidation of fatty acids present in the linseed oil. This can be catalysed by metals, oxidising agents and enzymes.[12]

The chamois process is a time-consuming operation which takes 10-15 days to complete the tanning process. To accelerate the chamois process, various oxidising agents have been used, such as, hydrogen peroxide,[13] sodium percarbonate,[14] ozone,[15] benzoyl peroxide,[16] benzenecarboperoxoic acid.[17] The use of these oxidation agents reduces the process time drastically compared to air oxidation process. Apart from the longer time duration required for making chamois leather, odor from the fish oil treated chamois is of concern.

In order to eliminate odor and reduce process time for preparation of chamois leathers, there is need for process modifications in chamois making. Use of natural oils may be a step forward towards an eco-friendly approach in chamois making. Also, the present study extensively deals with the effect of different percentage of benzoyl peroxide (BPO) on the rate of oxidation of linseed oil and the benefits imparted by the current process. The prepared chamois leathers were analysed for water absorption, tensile strength and organoleptic properties.

Materials and Methods

Materials

Linseed oil was purchased from local supplier, Chennai. Benzoyl peroxide was procured from Sigma-Aldrich, Chennai. All the other chemicals obtained were of commercial grade. Sheep skins were used as raw material for the chamois process.

Processing of chamois leather

Wet salted sheep skins were processed conventionally up to pickling process and then de-pickled and tanned using glutaraldehyde tanning agent (2%). The detail process is provided in Table I. The glutaraldehyde treated skins were piled overnight. The leathers were then sammyed and the grain was completely shaved off followed by oil tanning.

---

*Corresponding author email: bindiya1480@gmail.com

Manuscript received December 18, 2020, accepted for publication March 1, 2021.

Table I

Detail description of process for making chamois leather

Process	Chemical	Percentage (%)	Time (min)	Remarks
Washing	Water	100	10	Wash and drain
Deliming	Water	100		
	Ammonium chloride	2	40	
				Check de-liming using phenolphthalein
	Alkaline bate	0.5	30	Drain
	De-greasing agent	1	90	Drain
	Wetting agent	0.5		
Washing	Water	200	10	Wash and drain
Partial pickling	Water	80		
	Salt	8	30	
	Formic Acid	0.5	30	In 1:10 dilution with water
	Sulphuric Acid	0.2		In three feeds with 1:10 dilution with water, adjust pH to 4
	Glutaraldehyde	1	60	Drain, pile for overnight
Next day				
	Linseed oil	25		
	Benzoyl peroxide (experiment)	X1/X2/X3/X4		
	Sodium carbonate	0.5		Mix using stirrer, make paste. add to drum along with skin

X1 to X4= 0.25, 0.5, 0.75 and 1% of BPO

For the control process (X), glutaraldehyde tanned sheep skins were treated with 25% of linseed oil along with 0.25% of Soda ash. The oil tanning process was carried out in the drum for 2 h. The skins were hung up in the oxidation chamber having good air circulation for 15 days. The completion of oil tanning was ascertained by the golden yellow color on the surface of leather. Finally, the leather was washed with water (100%), soda ash (1%) and wetting agent (1%) for the removal of unfixed oil.

The resultant leathers were squeezed and hung up for drying. After drying the leathers were staked and buffed on both sides to get a uniform nap on both the sides. Finally, the leathers were dry milled for a period of 2 h to open up the fibers and the rigid fibers and increase softness.

Effect of Benzoyl peroxide

The linseed oil (L) was mixed with 0.25, 0.50, 0.75 and 1% (based on oil weight) of the benzoyl peroxide to obtain oil catalyst mixtures; X1, X2, X3 and X4 respectively. The oil and catalyst ratio was mixed thoroughly until a turbid mixture formed. This mixture was employed for oil tanning. The glutaraldehyde tanned sheep skins were treated with 25% of the linseed oil mixture and 0.25% of soda ash and drummed for 2 h followed by above said process.

Scanning electron microscope analysis

Scanning electron microscopy technique was employed to understand the morphology of leather fibers. The cross sections of chamois leathers were examined field-emission scanning electron microscopy (FE-SEM) (TESCAN MIRA3 LMU) at CSIR-CECRI. The instrument is equipped with light and electron optical modes operating at 5 kV acceleration voltage.

Porometry analysis of chamois leathers

PMI capillary flow porometer was used to measure the air permeability. The pressure varied from 0-20 psi.

Water absorption

Water absorption is the ability of leather to absorb water per unit weight of leather and expressed in percentage. Water absorption is an important parameter in determining the quality of chamois leather, as the main use of the leather is for filtering, cleaning and drying this requires high water absorption capability. The higher the water absorption capacity of the chamois leather, the better is its quality. Measurement of water absorption was carried out as per the standard procedure.[18]

Shrinkage temperature measurement

Shrinkage temperatures of the experimental and control leathers were measured according to standard procedure.[19] Hydrothermal shrinkage of chamois leathers was measured to understand the leathers behavior towards hydrothermal heat.

Physical, chemical and organoleptic characterization of the chamois leather

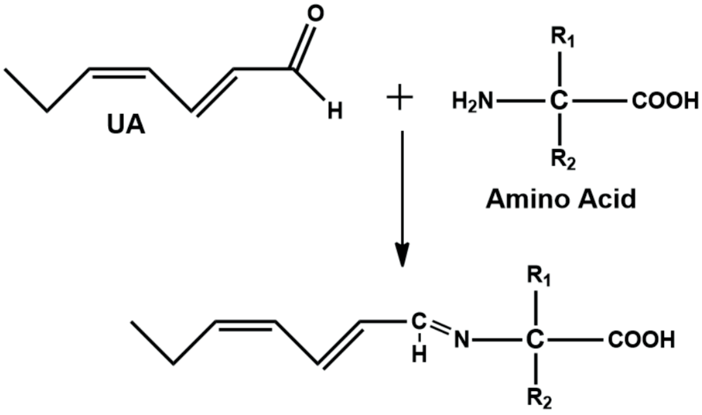
The leathers were subjected to physical characterization in order to ascertain whether they can withstand the standard requirements of chamois leather. The leathers were sampled from the official sampling location.[20] The leathers were characterized for tensile strength and percentage of elongation.[21] Organoleptic properties were assessed by four experienced leather technologists, four samples of chamois leathers were assessed for softness, fullness, odor and visual appearance.

Results and Discussion

Plausible chemistry

The autoxidation of monounsaturated acid (oleic acid) can be achieved at high temperatures while polyunsaturated acids such as linolenic and linoleic acids undergo rapid oxidation even at room temperature.[22] The reactivity of bis allylic methylene group is mainly because of its resonating stabilised structure after the removal of active hydrogen atom along with less bond dissociation energy between carbon and methylene hydrogen.[12] This activity is taken into consideration for initiation of the oxidation of Polyunsaturated Fatty Acids (PUFAs) of the linseed oil. Linseed oil contains active methylene groups, therefore experience more exposure towards oxidation. These PUFA radicals quickly get attached with oxygen to form peroxyl radicals which again can undergo resonance stabilisation. The peroxyl radical can attract a hydrogen atom from another fatty acid chain of linseed oil to form the primary oxidation product, a Lipid Hydroperoxide (LOOH) leaving behind another reactive PUFA radical which can again start the process and the propagation will continue. The lipid hydroperoxides (ROOH) are unstable and rapidly decompose into alkoxyl radical which further decompose to form several secondary oxidised products such as saturated aldehydes, unsaturated aldehydes, short-chain ketones, alcohols, acids, esters, ethers and hydrocarbons.[23-26] The rate of oxidation of oil found to be increased by the use of oxidising agents which act as an accelerator for the chemical process.[27,28]

The aldehydes being highly diffusible compound interact with amino acids of skin and form stabilised cross-linked protein (Scheme 1). The chemistry behind the stabilisation of protein during oil tanning is of great interest if the oxidation can be accelerated by the presence of oxidising agents such as BPO which can enhance the rate of abstraction of bis allylic methylene hydrogen atom in the initiation step.[16]



Scheme 1. Interaction of Unsaturated Aldehydes (UA) generated from series of oxidation of linseed oil with amino acids of protein collagen

Leather Processing

Conventionally, the oxidation of oil tanned leathers requires 10-15 days. In order to minimize the duration of oxidation process, benzoyl peroxide has been used as a catalyst to enhance the oxidation of oil. Adoption of the new process technique has reduced the oxidation duration to two days.

Characterization of chamois leather

The chamois leathers made using linseed oil have comparable properties to that of the fish oil treated chamois.[16] The chamois leather was characterized for various physical and organoleptic properties and the results are discussed below.

Water absorption

Chamois leather is known for high water absorption.[29] The water absorption results for chamois leathers obtained from different benzoyl peroxide ratios with linseed oil are shown in Table II. It has been observed that the percentage of water absorption gradually increasing from 0.25 to 0.75% (from 463.35 to 611.11) and again slightly decreasing to 555.35%.

By this observation it can be concluded that the addition of 0.75% of BPO (X3) can produce chamois leather with greater water absorption capacity (611.11%) than the control leathers tanned using linseed oil alone (441.17%). The slight decrease in water absorption with the addition of 1% BPO indicates that the better

Table II

Water absorption capability of chamois leathers

S No.	Sample	Water Absorption (%)
1	X	441±20
2	X1	463±20
3	X2	511±25
4	X3	611±30
5	X4	555±27

Table III

Shrinkage temperature analysis of chamois leathers

S No.	Sample	Shrinkage temperature
1	X	78 ± 2 °C
2	X1	77 ± 2 °C
3	X2	78 ± 2 °C
4	X3	78 ± 2 °C
5	X4	77 ± 2 °C

Table IV

Physical strength properties of chamois leathers

S No.	Sample	Tensile Strength (N/mm^2)	Percentage elongation (%)
1	X	12±2	52±5
2	X1	12±2	58±6
3	X2	14±2	57±6
4	X3	18±2	66±7
5	X4	17±2	54±5

performance can be achieved by the use of appropriate percentage of BPO (0.75%) which may have high impact on the rate of oxidation of linseed oil. It is also observed that the experimental leathers are showing better water absorption than that of leathers exhibited better water absorption (611.11%) than the control leathers and leather tanned with fish oil and benzoyl peroxide.[16]

Shrinkage temperature analysis of chamois leather

Shrinkage temperature of chamois leathers was analysed to understand the stability of the leathers towards heat. In general oil tanned leathers exhibit hydrothermal stability of up to 78±2^{0}C. The experimental leathers in this study resisted temperature of up to 77-78°C compared to control of 78°C, the results are mentioned in Table III. The data also gives information about the hydrothermal stability of leathers, which is not impacted by the addition of oxidising agent in the leather processing.

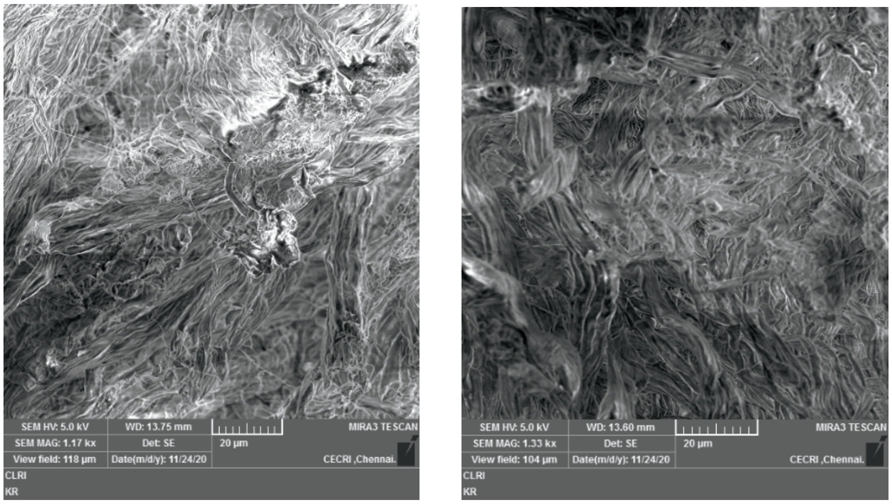
Scanning electron microscopy analysis of chamois leathers

Scanning electron microscopy imaging shows the fiber alignment of the chamois leathers. This gives information about compactness of the leathers. It can be seen from Figure 1 (a) and (b), that the fiber alignments of control leathers and experimental leathers (X3) show the compact fiber structure, which also influences the porosity of the oil tanned leathers. With the increase in percentage of the oxidizing agent in chamois processing there was an increase in pore size which is an expected quality of high performance chamois leathers.[16]

Physical strength and organoleptic properties of the chamois leather

The chamois leather made using linseed oil has been evaluated for physical strength parameters. Tensile strength and percentage elongation parameters of leathers have been analysed to understand the leathers' ability to withstand force. The results are tabulated in Table IV.

It is worth noting that the tensile strength of the chamois leather made out of linseed oil and oxidising agent shows better results as compared to control. The graphical representation of organoleptic properties of leathers are shown in Figure 2. It can be observed that control and experimental leathers are comparable for softness, fullness, odor and visual appearance values. The performance of X3 leather treated with 0.75% of oxidizing agent performed better compared to other experimental leathers, which can be confirmed



(a) (b)

Figure 1. **(a)** Scanning electron microscopy analysis of control chamois leathers; **(b)** Scanning electron microscopy analysis of experimental chamois leathers

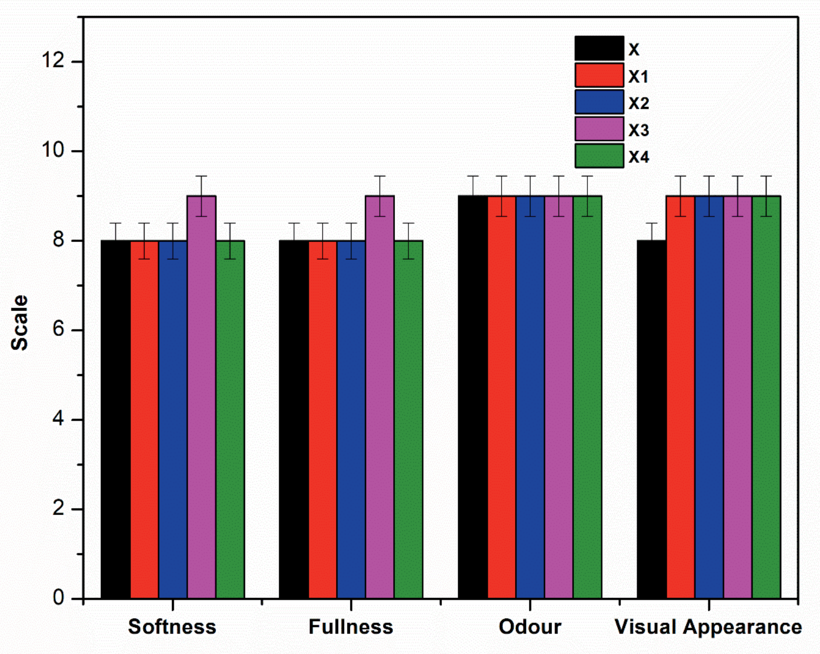


Figure 2. Organoleptic properties of chamois leathers

from the SEM analysis. Similarly, experimental leathers show better organoleptic properties when compared to the earlier study,[16] where the preparation of chamois leathers were carried out using fish oil with benzoyl peroxide. The odor from the chamois leathers was avoided in this study by the use of vegetable oil instead of fish oil. Also, the color and visual appearance of the experimental leathers (X1 to X4) improved by the use of linseed oil with benzoyl peroxide. The intensity of yellowing on the experimental leathers was observed to be lighter compared to leathers prepared using linseed oil (using goat skin) and fish oil with benzoyl peroxide.[5,16]

Porometry analysis of chamois leathers

Porometry analysis of chamois leathers gives information about the pore structure of the leather matrix. Porosity of the experimental leathers increased with increase in BPO content, it can be inferred from the Figure 3, that leathers made up of 0.25% BPO (X1) show porosity similar to control leathers. With increase in concentration of BPO, leathers exhibited improved porosity values. The chamois containing 0.50 % of BPO (X2) along with linseed oil exhibited better flow rate values compared to X4 (1% BPO) with fish oil.[16] The experimental leathers X3 and X4 (0.75 % and 1 % of BPO) prepared using linseed oil shows excellent flow rate compared to the leathers treated with BPO and fish oil.[16]

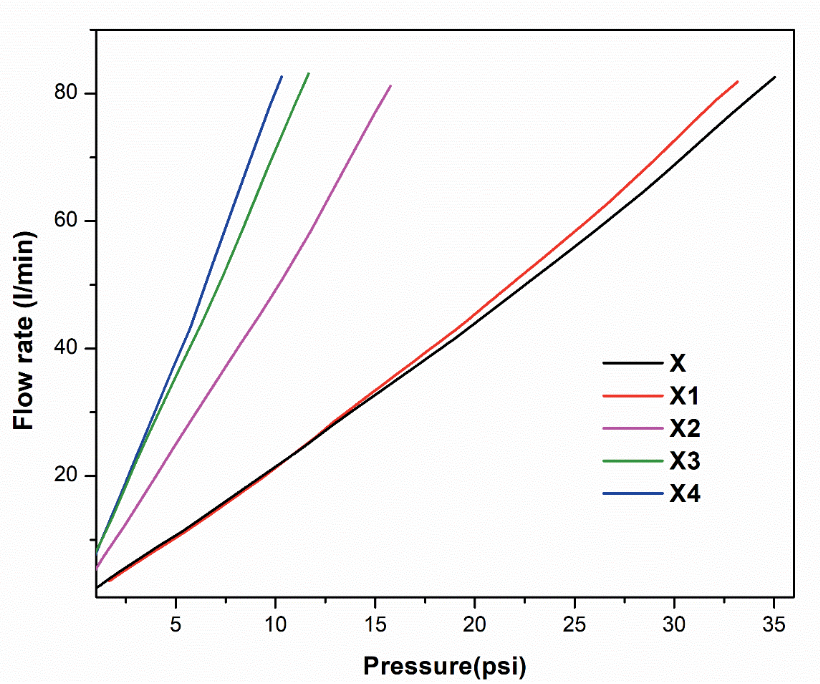


Figure 3. Porometry analysis of chamois leathers

Conclusion

The oil tanning, using linseed oil with 0.75% of benzoyl peroxide as a catalyst, shows better quality chamois leather through rapid oxidation of oil as compared to leather which is tanned with linseed oil alone (control). The study concentrated on the complete elimination of characteristic odor of fish oil associated with conventional fish oil tanned chamois leather and reduction in process time over conventional chamois making. The water absorption property of the experimental leather increased greatly compared to control. Physical strength and organoleptic properties of experimental leathers are comparable with the control.

Acknowledgements

Authors acknowledge financial support from CSIR-CLRI. The authors thank CSIR-CECRI for SEM Analysis. The authors thank Dr. J. Raghava Rao, Chief Scientist, IPC lab, CSIR-CLRI and Dr. B. Madhan, Senior Principal scientist, CARE, CSIR-CLRI for their encouragement. The authors thank Director, CSIR-CLRI for his support. Authors acknowledge Department of Leather Technology, Anna University, Chennai. CSIR-CLRI communication number is -A/2020/CRE/CLRI/1490.

References

1. Alla, J. P., Aravindhan, R., Fathima, N. N., Rao, J. R.; Dyeing of chamois leather using water soluble sulphur dyes, *JALCA* **111**, 383-388, 2016.
2. Giallourakis, N. M.; Scrubber washer apparatus US Patent No US5361445A, 1994.
3. Barnett, G. A., James, P., Shealy, Jr.; Synthetic chamois wiping cloths, US Patent No US4341832A, 1982.
4. Vedaraman, N., Vijayan, S., Sundar, V.J., Velappan, K.C.; Studies on use of fish oil methyl ester for chamois leather manufacture *JALCA*, **107(12),** 422-428, 2012.
5. Sandhya, K., Vedaraman, N., Sundar, V., Mohan, R., Velappan. K. and Muralidharan, C.; Suitability of Different Oils for Chamois Leather Manufacture. *JALCA* **110(7)**, 221-226, 2015.
6. Vedaraman, N., Muralidharan, R. Sundar, V. J., Velappan, K.C., Muralidharan, C.; Modified jatropha oil for making chamois leather. *BTAIJ* **9**, 203-205, 2014.
7. Suparno, O., Kartika, I. K., Muslich; Chamois leather tanning using rubber seed oil *JSLT*, **93(4),**158-161, 2009.
8. Weihua, D., Years, B., Rui, Z.; Method for producing chamois leather using epoxidized oil. *China Patent No* CN101550459A, 2013.
9. Shim, Y.Y., Gui, B., Arnison P. G., Wang, Y. Reaney, Martin J.T.; Flaxseed (Linum usitatissimum L.) bioactive compounds and peptide nomenclature: A review, *Trends in Food Science & Technology* **38 (1)**, 5-20, 2014.
10. Rudnik, E., Szczucinska,A., Gwardiak,H., Szulc, A.; Comparative studies of oxidative stability of linseed oil, *Thermochimica Acta* **370 (1)**, 135-140, 2016.
11. Juita, J., Bogdan, Z. D., Eric, M. K., John, C. M.; Oxidation reactions and spontaneous ignition of linseed oil, *Proceedings of the Combustion Institute* **33(2)**, 2625-2632, 2011.
12. Juita, J., Bogdan, Z. D., Eric, M. K., John, C. M.; Low temperature oxidation of linseed oil: a review, *Fire Science Reviews* **1(3),**1-36, 2012.
13. Suparno, O., Sa'id, E.G., Kartika, E.A., Muslich, Shiva, A.; Chamois leather tanning accelerated by oxidizing agent of hydrogen peroxide. *Teknik Kimia Indonesia* **11**, 9-16, 2012.
14. Hongru, W., Yuanyue, M., Yue, N.; An oil tanning process accelerated by oxidation with sodium percarbonate. *JSLTC* **92**, 205-209, 2008.
15. Sundar, V. J., Vedaraman, N., Balakrishnan, P. A., Muralidharan, C.; Chamois leathers - An approach for accelerated oxidation. *JSLTC* **88(6)**, 256-259, 2004.
16. Sahu, B., Alla, J.P. Rao, J.R. Sreeram, K.J. Jayakumar, G.C.; Neoteric Oxidizing Agent for Chamois Process, *JALCA* **114(9)** 344-349, 2019.
17. Sahu, B., Alla, J.P. Jayakumar, G.C., Raj, A.; Influence of Benzenecarboperoxoic Acid on chamois leather process, *JALCA* **115(2)**, 49-53, 2020.
18. IUP 7: Leather -Physical and mechanical tests- Determination of the static absorption of water, *JSLTC* **84**, 323, 2000.
19. IUP 16, Determination of shrinkage temperature up to 100°C. *JSLTC* 84, 359, 2000.
20. IUP 2, Sampling, *JSLTC* **84**, 303, 2000.
21. IUP 6, Measurement of tensile strength and percentage elongation. *JSLTC* **84**, 317-321, 2000.
22. Kerrihard, A.L., Nagy, K. Craft, B.D. Beggio, M. Pegg, R.B.; Oxidative stability of commodity fats and oils: modeling based on fatty acid composition. *J. Am. Oil Chem. Soc.* **92(8)**, 1153-1163, 2015.
23. Ahmed, M., Pickova, J., Ahmad, T., Liaquat, M., Farid, A. Jahangir, M.; Oxidation of lipids in foods. *Sarhad Journal of Agriculture* **32(3)**, 230-238, 2016.
24. Choe, E., Min, D.B.; Chemistry and reactions of reactive oxygen species in foods. *J. Food Sci* **70,** 142-159, 2005.
25. Gutowski, M., Kowalczyk, S.; A study of free radical chemistry: their role and pathophysiological significance. *Acta Biochim Pol* **60(1)**, 1-13, 2013.
26. Porter, N.A.; A perspective on free radical autoxidation: The physical organic chemistry of polyunsaturated fatty acid and sterol peroxidation. *J. Organic Chem* **78**, 3511–3524, 2013.
27. Lee, J., Koo, N. Min, D.B.; Reactive oxygen species, aging, and antioxidative nutraceuticals. Comprehensive Rev. Food Sci. *Food Safe* **3(1)**, 21-33, 2004.
28. Aidos, I., Jacobsen, C. Jensen, B. Luten, J.B. Padt A.V.D., Boom, R.M.; Volatile oxidation products formed in crude her-ring oil under accelerated oxidative conditions. *Euro. J. Lipid Sci. Technol* **104(12)**, 808-818, 2002.
29. Covington, A. D.; Tanning Chemistry – the science of leather. *Royal Society of Chemistry, Cambridge* 2009.

A Comprehensive Understanding on Sewability of Natural Biomaterial: An Insight on Process Optimization during Leather Manufacture

by
GC Jayakumar,[1] K Phebe Aaron*[2] and K Krishnaraj[2]
[1]*Centre for Academic and Research Excellence (CARE)*
[2]*Shoe & Product Design Centre (SPDC)*
CSIR-Central Leather Research Institute, Adyar, Chennai-600020

Abstract

Leather is three-dimensional matrix possessing unique properties which makes it more comfortable for daily use. Garments made from leathers are preferred choice owing to their multifaceted properties as compared to textiles in the colder regions. In the present study, an attempt has been made to evaluate the influence of phenolic syntan and synthetic fatliquor on the sewability and physical properties of post tanned leathers. From the experimental results, it is observed that the concentration of phenolic syntan and fatliquor influences leather sewability. Optical microscopic images of leathers also show that they are more compact and tighter with higher percentage of syntan. The study provides an insight in understanding the optimum usage of post tanning chemicals for better sewing properties without affecting the leather matrix adversely.

Introduction

Leather and leather-based products are termed as luxurious class owing to the comfort and multifaceted properties.[1] Though, several alternate materials to leather are available, till date their material matching properties to leather remains a great challenge. Leathers are the preferred choice of material for making products due to their impeccable physico-chemical properties.[2] Fabric used for clothing is basically a two-dimensional matrix and their properties can be fine-tuned during weaving process, whereas in leather, the three-dimensional fiber network of the natural properties of the animals are retained, refined and brought into the final texture of the products.

Sewability is the ability and ease with which fabric/leather components can be qualitatively and quantitatively seamed together for conversion into a product.[3] Fundamentally, in garment manufacturing, a two-dimensional structure is converted into a three-dimensional structure. Sewing needle penetration force is a measure of the damage which appears as a result of sewing process. A high penetration force means high resistance of the fabric and thus a high risk of damage.[4] Fabric through which a needle passes easily is expected to sew without difficulty.

Sewing of leather garments is a challenging task as compared to textile fabrics, since leather is a complex dense material with presence of different chemical constituents making it more demanding. Ease of needle penetration is highly required as it reduces the distortion of the matrix which otherwise would lead to the damage of material and in-turn affect the quality of final products.[5-7] Studies pertaining to optimization of post tanning process in line with sewability properties of leathers are very limited. Commonly used syntan in leather processing is phenolic based syntan owing to its interaction efficiency and filling ability due to availability of aromatic functional groups. Similarly, synthetic fatliquors are widely used in leather manufacture to achieve lubrication and softness. In the present study a preliminary work has been carried out to understand the influence of phenolic syntan and synthetic fatliquor on sewability and physical properties.

Materials and Methods

Phenolic based syntan was used in this study with 0-8% offer on the goat wet blue leathers. Synthetic fatliquor was used in all the trials followed by fixing with formic acid.

Post tanning process

Conventional chrome tanned leathers were shaved to a uniform thickness of 0.6-0.7 mm and neutralized to pH 5.0-5.5 through conventional method. After neutralization, leathers were completely washed and drained prior to retanning. Different percentage of phenolic syntan like 2, 4, 6 and 8% with 10% fatliquor were offered. Finally, leathers were fixed using formic acid and piled overnight. After 24 h, leathers were set, hooked to dry, staked and buffed. Based on the optimized syntan concentration, different percentages of fatliquor was offered (0, 4, 8, 12, 16 and 20%) and leathers were assessed for sewability, stiffness and softness.

Physical testing of leather samples

The samples for physical testing were obtained as per IULTCS methods (4 numbers). The samples have been conditioned at 26°C and 65% R.H. for 48 h (IUP 2, 2000).[8]-[9] Each value reported was an average of four (2 along and 2 across the backbone) measurements.

---

*Corresponding authors emails: phebe@clri.res.in & kphebejohn@yahoo.co.in

Manuscript received October 9, 2020, accepted for publication March 2, 2021.

Stiffness measurements

Stiffness was determined according to Indian standard IS 6490 test method.[10] Samples of dimensions 25 × 120 mm were cut parallel and perpendicular directions to the backbone of the leather and subjected to Stiffness measurements. For each sample, the length of slacking part of sample (L) was measured by the constant angle method with each side up, first at one end and then at the other. The mean value of (L) was attained which is a measure of stiffness.

Determination of softness

Softness is the most important physical property to be considered when assessing the quality of fabric or leather. Softness of the specimens was measured using MSA ST300 digital softness tester as per the standard IUP 36 [11] test method. Softness was measured at five different locations for leather samples. Difference in value of softness is due to difference in material, thickness, fusing and reinforcement used. High value of compression index indicates high softness.

Evaluation of sewability

The L&M Sewability Tester was used to test fabric sewability.[12] This equipment simulates a sewing machine by penetrating the fabric with an unthreaded needle, at a rate of 100 penetrations per min and measures the penetration force exerted by a sewing needle on the fabric. 34 LR needle system has been used with needle number 90 and reverse twist pointing system. The dimension of leather used was 30-40 x 350 mm. Leather sewability corresponds to the number of points that exceed the threshold previously set related to the overall tested points and expressed as a percentage. The sewability was considered good if the sewability values range between 0 and 10%.[13]

Evaluation of organoleptic properties

Crust leathers have been assessed for grain smoothness, fullness and general appearance by tactile evaluation. Three experienced tanners rated the leathers on a scale of 0-10 points for each functional property.

Optical microscopic studies

Grain surface and cross-sections of the control and experimental leathers were studied using Magnus Stereo Zoom Microscope with Trinocular Body micro imaging facility.

Results and Discussion

The selection and choice of post tanning chemicals influences the aesthetic and functional properties of post tanned leathers.

The present study explores the effect of phenolic syntan and synthetic fatliquor in imparting physical strength characteristics to post tanned leathers. Chrome tanned goat leathers have been used as the raw material and retanned with different percentage offer of phenolic based syntan and 10% synthetic fatliquor for all the trials (control and experimental) as given in Table I.

Table I

Post tanning process

Process/chemicals	%	Duration (min)	Remarks
		Washing	
Water	100	10	Drained
		Neutralization	
Water	150		
Sodium formate	1.0	10	
Sodium bicarbonate	1.0	3x15+45	pH – 5.0 - 5.5, Drained.
		Washing	
Water	200	15	Drained
		Retanning and Fat liquoring	
Water	100		
Phenolic syntan	0-8	60	
Synthetic fatliquor	10.0	30	Mixed in hot water
Formic acid	1.5	4x10+20	Exhaustion was checked. Drained.
Washing	100	15	Drained. Crust leathers were set twice, hooked to dry, conditioned, and staked.

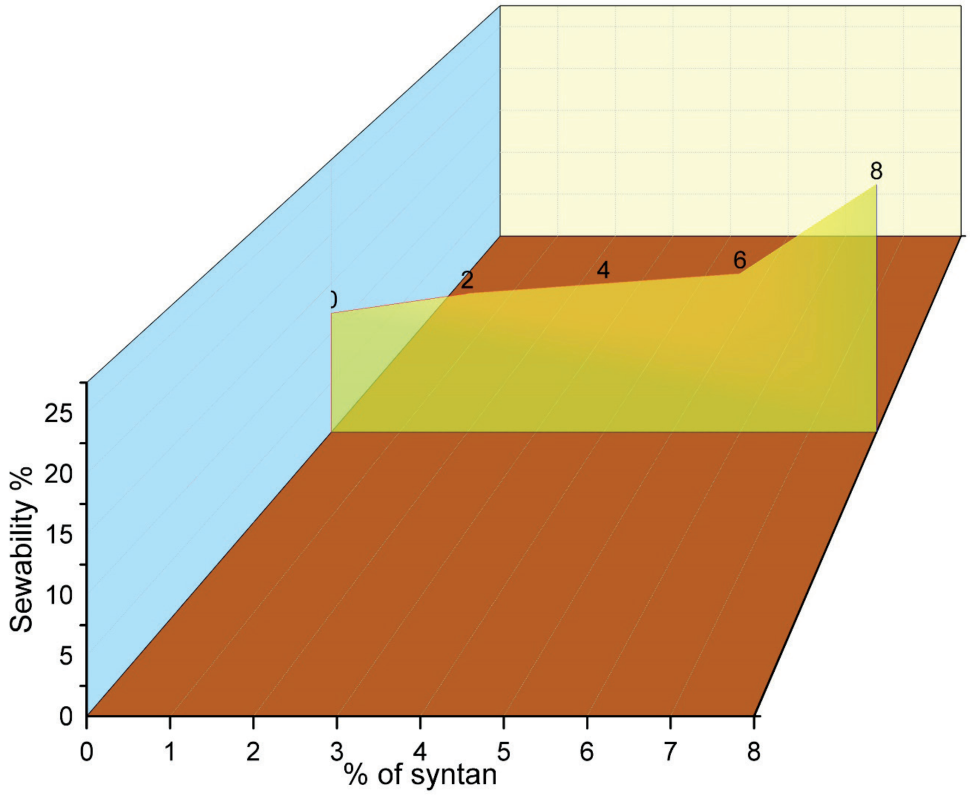


Figure 1. Sewability property of phenolic retanned leathers

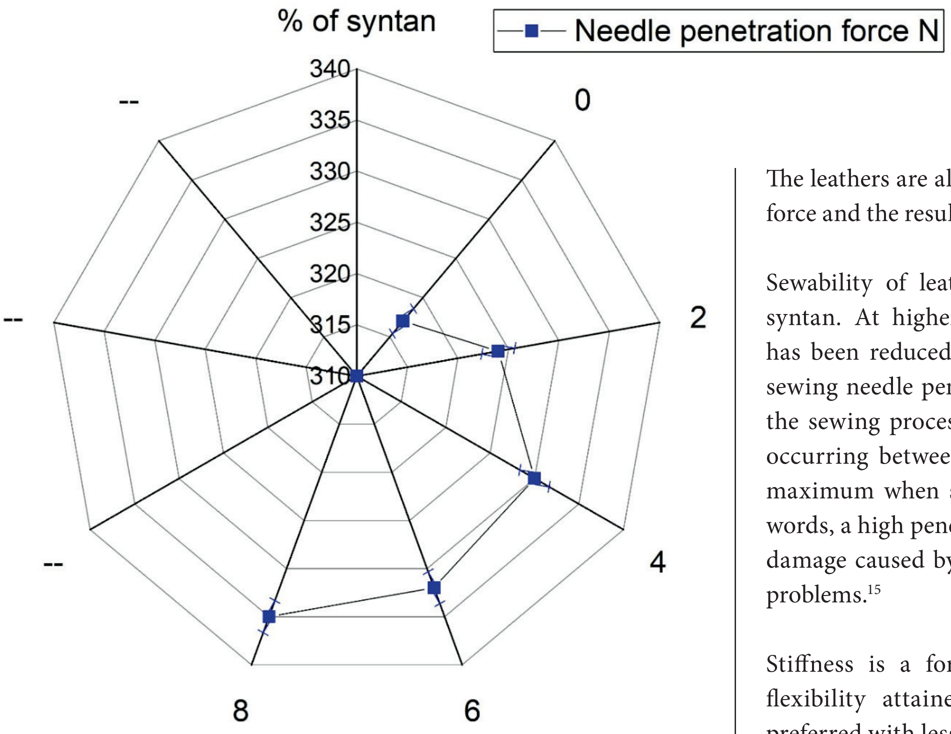


Figure 2. Needle penetration force of phenolic retanned leathers

The leathers are also assessed for sewability and needle penetration force and the results are shown in Figure 1 and 2.

Sewability of leathers is influenced with the offer of phenolic syntan. At higher concentration of phenolic syntan, sewability has been reduced which might be due to the filling nature. The sewing needle penetration force is also a significant parameter in the sewing process.[14] The penetration force is due to the friction occurring between fibers and sewing needle and is found to be maximum when sewing needle penetrates the material. In other words, a high penetration force causes a high risk of damage. Seam damage caused by needle penetration can cause severe sewability problems.[15]

Stiffness is a foremost property that defines the measure of flexibility attained by the leathers.[16-17] Garment leathers are preferred with less stiffness to achieve better drape characteristics. The stiffness properties of phenolic retanned leathers are shown in Figure 3.

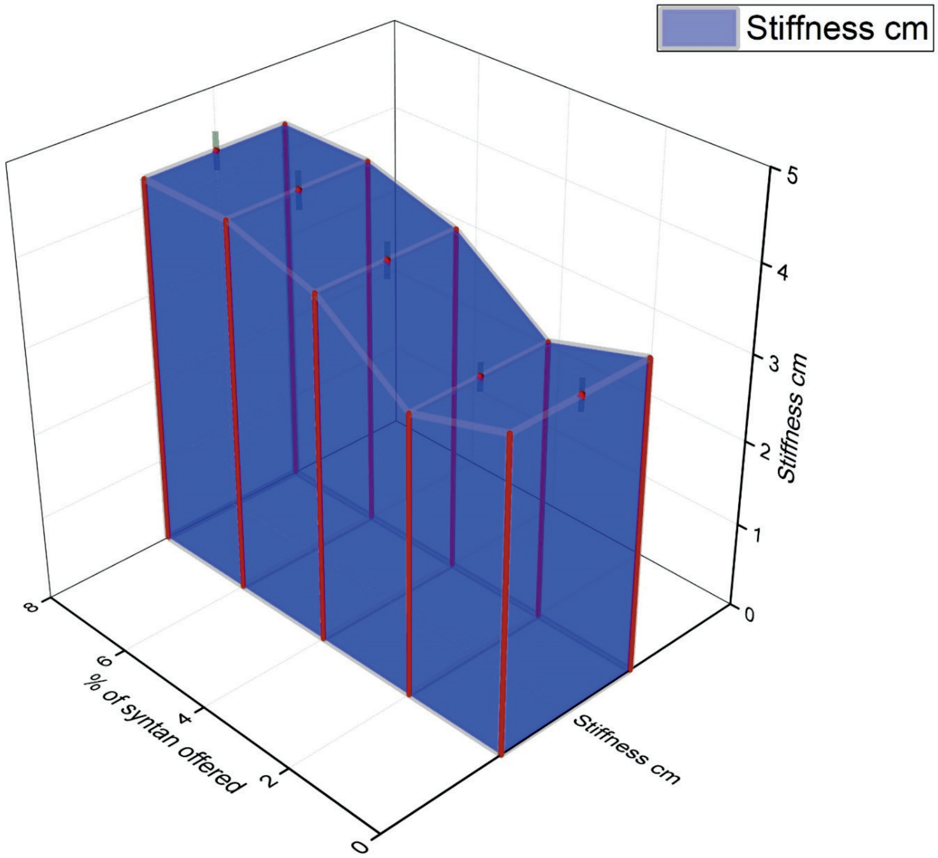


Figure 3. Stiffness measurements of phenolic retanned leathers

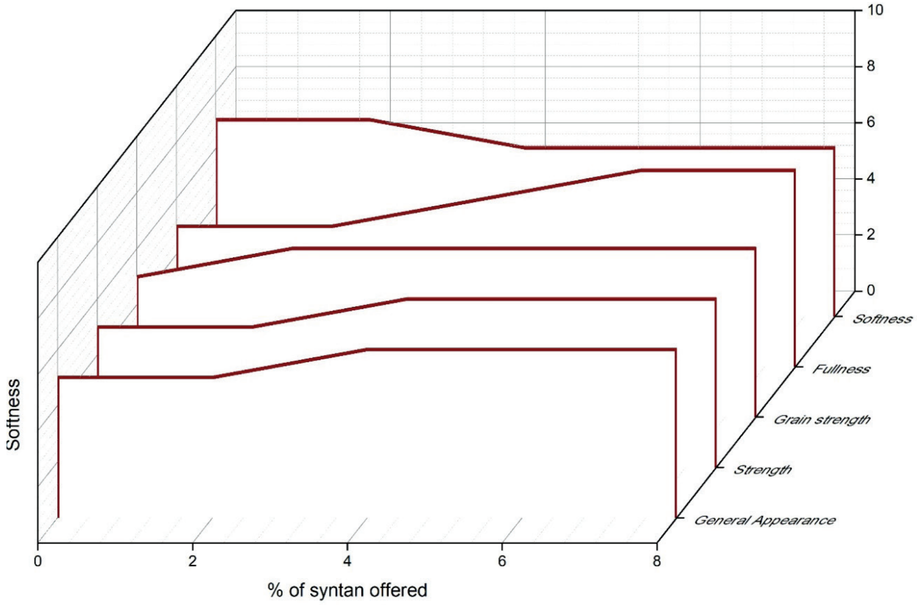


Figure 4. Organoleptic properties of leathers

Table II

Physical characteristics of different fatliquor offered leathers

Sample (Fatliquor offered)	Sewability %	Stiffness cm	Softness
Control	0	3.85	3.70
4%	0	3.5	4.15
8%	4	3.6	4.10
12%	4	3.7	4.02
16%	6	3.9	3.90
20%	34	3.7	3.50

Concentration of syntan- 6%

From the results, it can be observed that with an increase in the offer of phenolic syntan there is an influence on leather stiffness.[18] Retanned leathers were also assessed for their organoleptic properties and the results are shown in Figure 4.

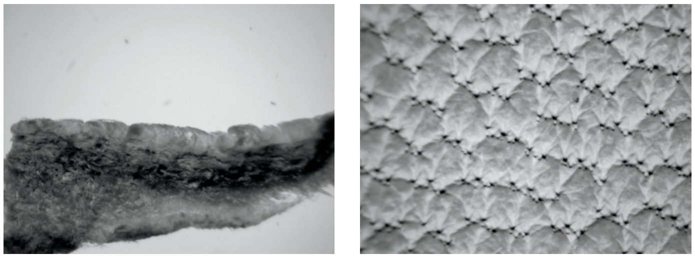
From the hand evaluation results, it can be inferred that with an increase in phenolic syntan offer, leathers were found to be full and more compact. The surface characteristic and cross-section of retanned leathers were examined using magnus stereo zoom microscope and shown in Figure 5.

From the grain and cross section images, it can be seen that there is no coarse grain characteristics and it is smooth. The experimental studies reckon that phenolic syntan has a vital role in influencing the sewability and physical properties of leathers. Leather processed without offer of fatliquor is treated as control for fatliquor optimization studies.

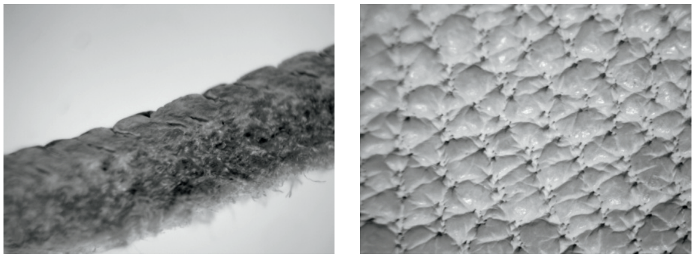
Sewability, stiffness and softness values of control and experimental leathers are given in Table II. It can be observed that synthetic fatliquor significantly influenced the sewability of leathers. Interestingly, the study provides fundamental insight on the relationship between fatliquor and sewability.[19-24]

Conclusions

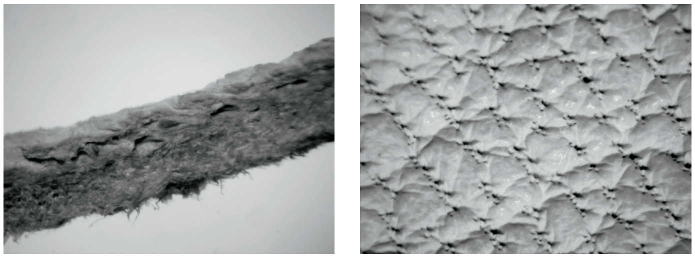
An insight of emulating the various garment leather properties and its intercalation between them had been studied to coherently emphasize the role of phenolic syntan and synthetic fatliquor. Though, there is a huge variation in phenolic syntans available in the market, nevertheless, a holistic understanding of specific syntan and fatliquor on sewability properties has been presented in this research work. Selective properties like sewability and needle penetration force, has been studied with different concentrations



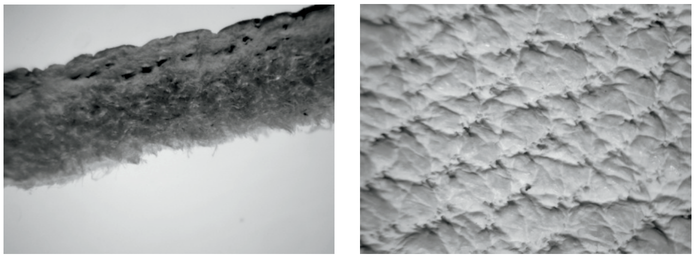
(a) Control- Cross section and Grain surface



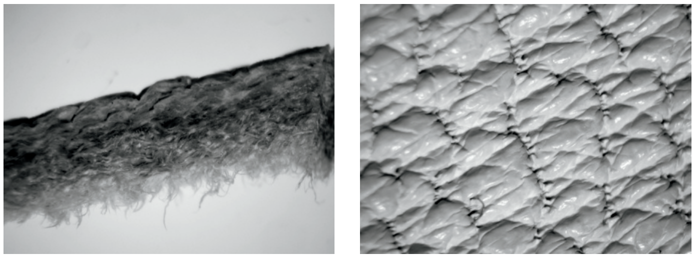
(b) 2%- Cross section and Grain surface



(c) 4%- Cross section and Grain surface



(d) 6%- Cross section and Grain surface



(e) 8%- Cross section and Grain surface

Figure 5. Optical images of leathers (cross section and grain surface)

of phenolic syntan and fatliquor. Garment properties such as sewability, stiffness and softness parameters have been influenced based on the offer of concentration. This study might surmise that selection and offer of chemicals plays a significantly influences on the leather sewability for making products. However, future studies on the synchronizing effect of post tanning chemicals needs to be evaluated.

Conflict of Interest

The authors declare that they have no conflict of interest.

Acknowledgements

Authors acknowledge the financial support from CLRI under MLP. Authors also thank CATERS for testing facilities, CSIR-CLRI communication no:1309.

References

1. Alessandro, B., Cecilia C.; The nature of luxury: a consumer perspective. *Int. J. Retail. Distrib.* **41**, 823-847, 2013.
2. Bienkewicz, K.; Physical chemistry of leather making. Robert E. Krieger Publishing Company Inc. Malabar Florida, **541**, 1983.
3. Phebe, K., Chandrasekaran, B., Mandal, A.B.; Sewability of sheep nappa garment leather. *Res. J. Textile. Apparel*, **18** (2), 49-55, 2014.
4. Gurarda, A., Meric, B.; Sewing needle penetration forces and elastane fiber damage during the sewing of cotton/elastane woven fabrics. *Textile Res. J.* **75**(8), 628-633, 2005.
5. Krishnaraj, K., Thanikaivelan, P., Chandrasekaran, B.; Relation between drape and mechanical properties of goat suede garment leathers. *J. Soc. Lea. Tech. Chem.* **93**, 1-7, 2000.
6. Manich, A.M., Domingues, J, P., Sauri, R.M., Barella, A.; Relationships between fabric sewability and structural, physical, and fast properties of woven wool and wool-blend fabrics. *J. Text. Inst.* **89**(3), 579-590, 1998.
7. Phebe, K., Chandrasekaran, B.; Performance of needles on sewability of garment leathers. *Leather Footwear J.* **11**, 2011.
8. IUP 2, Sampling. J. Soc. Lea. Technol. Chem. **84**, 303, 2000.
9. IUP 6, Measurement of tensile strength and percentage elongation. *Journal- J. Soc. Lea. Technol. Chem.* **84**, 317-321, 2000.
10. IS 6490: Method for Determination of Stiffness of Fabrics - Cantilever Test. Bureau of Indian Standards.
11. IUP 36, Leather-Physical and Mechanical tests-Determination of softness. International Standards.
12. Gurarda, A.; Investigation of the seam performance of pet/nylon-elastane woven fabrics. *Textile Research J.* **78**(21), 21-27, 2008.
13. Phebe K, Krishnaraj K, Chandrasekaran B (2016) Evaluation of Sewability of Nappa Leathers. J Fashion Technol Textile Eng 4:2.
14. Phebe, K, A., Chandrasekaran, B.; Studies on influence of stitch density and stitch type on seam properties of garment leathers. AATCC J Res. **1(6)**, 8-15, 2014.
15. Woynshet, G., Phebe, K., Thanikaivelan, P., Krishnaraj, K., Chandrasekaran, B.; Influence of sewing threads on seam pucker of sheep nappa leathers. J. Soc. Lea. Tech. Chem. **98(4)**, 158-162, 2014.
16. Krishnaraj, K., Thanikaivelan, P., Phebe, K., & Chandrasekaran, B.; Effect of sewing on the drape of goat suede apparel leathers. Intern. J. Clothing Sci. Technol. **22(5)**, 358-373, 2010.
17. Phebe, K., Thanikaivelan, P., Krishnaraj, K., Chandrasekaran, B.; Factors influencing the seam efficiency of goat nappa leathers. J. Amer. Lea. Chem. Assoc. **107(3)**, 78-84, 2012.
18. Kindlein, W., Candido, L.H.A., Guanabara, A. S.; Proposal of wet blue leather remainder and synthetic fabrics reuse. J. Clean. Prod. **16(16)**, 1711-1716, 2008.
19. Jeong, W, Y., Park, J.W., Kamijo, M., Sadoyama, T., Shimizu, Y., An, S.K.; Characteristics of artificial leather for footwear - mechanical properties and penetrating behavior of sewing needle. Soc Fiber Sci. Technol. **63(4)**, 102-107, 2007.
20. Masterma., E.A.; Functional requirements of leather in hand-sewn moccasin constructions. J. Amer. Lea. Chem. Assn. **26**, 17, 1971.
21. Ziynet, O., Emine, U., Oktay, P.; Sewability in Apparel Industry. The Fourth Edition of the International Conference of Applied Research in Textile, (CIRAT-4), At Monastir, Tunusia, 2010.
22. Nilay, O., Mehmet, M. M., Esra, Y., Oktay, P.; Sewability properties of garment leathers tanned with various tanning materials. Intern. Conf. Applied Res. Textile, 2010.
23. Yildiz, E, Z., Pamuk,O., Ondogan, Z.; A Study About The Effects of Interlinings to Sewability Properties of The Woven Fabrics", Tekstil ve Konfeksiyon, **21**, 1, 87-90, 2011.
24. Fathy, S., Abdel-Megeid, Z.M.; The relation between fabric construction, treatments and sewability, Journal of American Science, **7**, 272-280, 2011.

Hydrogen Peroxide-oxidized Soybean Polysaccharides as Novel Masking Agents for Zirconium Tanning

by

Haolin Zhu, Fang Wang, Keyong Tang,* Jie Liu, Xuejing Zheng and Shufa Qin
School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, China

Abstract

A series of hydrogen peroxide-oxidized soybean polysaccharides (HPS) were prepared using H_2O_2 and copper catalyst, which were then used as novel masking agents for zirconium tanning. The HPS samples were characterized by Fourier transforms infrared (FT-IR) spectroscopy, dynamic light scattering (DLS), and X-ray diffraction (XRD). FT-IR suggested the formation of carbonyl and carboxyl groups after hydrogen peroxide oxidation. DLS indicated that the HPS particle size decreases with increasing the H_2O_2 dosage. HPS with carbonyl and carboxyl groups and medium particle size was able to coordinate with zirconium to remarkably facilitate the tanning process. The shrinkage temperature of the tanned leather reached 92°C. Meanwhile, the fullness, softness, and mechanical properties of the leather were greatly improved by the tanning. The function of HPS and its interaction with zirconium were studied by FT-IR, XRD, and it was found that the triple helical structures of collagen fiber were not changed greatly. Scanning electron microscopy (SEM) showed that collagen fibers were dispersed and tanning agents were evenly distributed in collagen fibers. A new strategy for chrome-free tanning is suggested and a strong support for the application of zirconium tanning is provided.

Introduction

The soybean curd residue is the main surplus material, which is usually discharged as solid waste.[1] In order to reduce the cost and energy waste, it is widely reused to obtain polysaccharides.[2] Soluble soybean polysaccharide (SSPS) is an acid polysaccharide like pectin, composed of D-galactose, L-arabinose, D-galacturonic acid, and L-rhamnose. It has found a wide application in the food industry due to its excellent water solubility, oxidation property, good film-forming ability, emulsifying property, and nutritional value.[3] For example, SSPS has been used for yogurt dispersion and food packing.[4] After being oxidized by sodium periodate, dialdehyde polysaccharides can be used as a crosslinker for stabilizing collagen in leather.[5, 6]

Nowadays, the leather industry is faced with rigorous environmental pressure due to the use of chrome tanning agent.[7] The wet blues, chrome-contained wastewater, and solid waste may pose a potential harm to the environment because the Cr(III) may be converted into more toxic Cr(VI).[8] Therefore, the development of sustainable chrome-free tanning agents has become one of the focuses of researchers both in academia and in industry.[9,10]

Zirconium-tanned leather has higher shrinkage temperature, pure white color, fullness and tightness, good wear resistance, as well as high resistance to aging, sweat, and mold.[11-13] However, such shortcomings as poor tear strength, low permeability, and weak water absorption do exist for zirconium-tanned leather, compared to the chrome-tanned one.[14] A generally accepted reason is that the zirconium tanning takes place at low pH with fast hydrolysis of zirconium salt to form multimer, which destroys the collagen structure, resulting in the decrease of mechanical properties of the zirconium tanned leather.[11] On the other hand, the zirconium salt is very active to react with collagen at the initial stage of tanning, leading to the precipitation on both sides of grain and flesh, and uneven distribution of zirconium in the cross section of leather, and poor tanning performance.

Small molecular ligands with carboxyl groups, such as lactic acid, citric acid, and sulfamic acid are usually used as masking agents to coordinate with zirconium to reduce the reactivity of zirconium.[12] However, the improvement of organoleptic properties of leather is still limited. Highly-oxidation starch (HOS) was used in zirconium tanning, which effectively slowed down the hydrolysis of zirconium and improved the penetration of zirconium, with the amounts of 4.8% HOS and 6% zirconium of the pickled cattlehides in weight.[12] Unfortunately, the HOS was prepared by conventional oxidation and alcohol-precipitation process, causing a great waste of resources. Sulfonated tetraphenyl calix[4] resorcinarene (STCR) was used as a ligand in zirconium-tanning, in which STCR inhibited the hydrolysis and promoted the penetration of zirconium, which obviously reduced the zirconium consumption and improved the organoleptic properties of the zirconium tanned leather.[13]

There are abundant hydroxyl groups in soluble soybean polysaccharides, primarily in C-2, C-3, and C-6 positions of glucose unit,[15] which could be transformed into carbonyl and carboxyl groups by oxidation to form stable hydrogen bonds and metal chelation with the zirconium complexes. A potential tanning agent should have suitable viscosity for effective flow and

---

*Corresponding author email: kytangzzu@hotmail.com
Manuscript received January 24, 2021, accepted for publication March 4, 2021.

penetration to achieve uniform distribution in leather. Meanwhile, the molecular weight of oxidized soluble soybean polysaccharides could be regulated by oxidation through controlling the rupture degree of (1-4) glycosidic bond. Polysaccharides with appropriate molecular weight distribution could effectively affect the penetration of tanning agent in leather. Therefore, oxidation soluble soybean polysaccharide should be an excellent choice for the ligand of zirconium complex due to its variable coordination group, suitable viscosity, and molecular size. Moreover, compared with synthetic organic ligands, the polysaccharide-based ligand is more environment-friendly, sustainable, and economic because of the biodegradability, renewability, and cheapness of soybean polysaccharides.

In this work, HPS was prepared using hydrogen peroxide without alcohol precipitation, which was then employed in tanning as a ligand for zirconium complexes. The structures of HPS were characterized by Fourier transform infrared (FT-IR) spectroscopy, dynamic light scattering (DLS), and X-ray diffraction(XRD). The mechanical properties of leather tanned by HPS and zirconium (HPS-Zr) were studied. Then the performance of HPS as a ligand in zirconium tanning was evaluated. The synergy between HPS and zirconium was studied by FT-IR, thermogravimetric analysis (TGA), and scanning electron microscope (SEM). The possible mechanism of the tanning process was proposed and discussed.

Materials and methods

Materials

Pickled sheepskin was kindly provided by Henan Prosper Skin & Leather Enterprise Co., Ltd, China. SSPS was kindly provided by Jinjing Bio. Co. Ltd. (Pingdingshan City, Henan, China). H_2O_2 (30%), $CuSO_4{\cdot}5H_2O$, $Zr(SO_4)_2{\cdot}4H_2O$ were of analytical grade and purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China) Aladdin Reagent Co.Ltd. (Shanghai, China). The other chemicals used in tanning were of analytical grade.

Preparation of HPS

The oxidation process was carried out according to the reported work by Yu et al. with slight modifications.[12] In the 100 g/L soluble soybean polysaccharides solutions, 0.1% $CuSO_4{\cdot}5H_2O$ was added to act as catalyzer (based on the weight of soybean polysaccharides, the same below), and 30%, 60%, and 90% hydrogen peroxide of the SSPS in weight were drop-wisely added, respectively. The mixtures were allowed to react at 120°C for 2 hours to yield HPS solutions containing aldehyde and carboxyl groups, which were collected and directly used for zirconium tanning.

Tanning process

Table I shows the zirconium tanning process of pickled sheepskin. Leather tanned by pure zirconium tanning agent was used as the control, noted as "a". Leathers tanned by HPS-30, HPS-60 and HPS-90 were the b, c, and d, respectively.

Characterization of HPS

Fourier transform infrared (FT-IR) spectroscopy

The Fourier transform infrared (FT-IR) spectra of SSPS and HPS were recorded using a FT-IR spectrometer (Nicolet iS10, Thermo Scientific, USA). Samples were pressed with KBr pellet and scanned in the range of 400-4000 cm^{-1} at room temperature, with an accumulation of 32 scans and a resolution of 4 cm^{-1}.

X-ray Diffraction (XRD)

X-ray diffraction patterns of the SSPS and HPS were recorded using a Cu-Kα wide-angle X-ray diffractometer (XRD, PANalytical B.V., Netherlands). The scattered radiation was detected in the angle range of 5-90° (2θ) at a scanning rate of 0.3°/s.

Particle size analysis

Particle size analysis of samples was performed by a dynamic light scattering instrument (Nanostar, Wyatt). All the experiments were conducted at 25°C. The concentration of polysaccharide solution was 10 g/L.

Table I

The zirconium tanning process of pickled sheepskin

Process	Chemicals	Quantity/%	Duration/min	Temperature/°C	pH
Tanning	Water	300		25	
	NaCl	6	10		
	$Zr(SO_4)_2{\cdot}4H_2O$	5	240		
	HPS	5	120		
	Sodium bicarbonate	2	3*30+60		3.8-4.0
Fixation	Water	300	240	40	
Washing	Water	1000	30	25	

Characterization of leather

Thermal properties

Shrinkage temperature of leather is an important index to evaluate the tanning effect of a tanning agent, which was recorded using a digital leather shrinkage temperature instrument (MSW-YD4, Shaanxi University of Science and Technology, China). The heating rate was 2.0±0.2°C/min.

The thermogravimetric analysis was carried out using TGA (METTLER TOLEDO, Switzerland) with the nitrogen flow of 40 mL/min. The 5-7 mg sample was put in an open aluminium crucible and heated from 30 to 600°C at the heating rate of 10°/min.

Mechanical properties

The tanned leathers were cut into the shape of dumbbell (GB/T-528II, Kunshan Creator Testing Instrument Co. Ltd., China). After being air conditioned at Relative Humidity 60±5% for 48h, the samples were stretched to calculate the tensile strength and elongation at break with SMSTA.XT Plus Texture analyzer (Lotun Science Co. Ltd., British)[16].

Thickening rate

The thickness of leathers before and after tanning was measured by thickness gauges. The thickness of the sheepskin was the a_0 (mm), and that of the tanned leather was the a_1 (mm). Thus, P (thickness rate) was calculated by equation (1).

$$P/\% = \frac{a_1 - a_0}{a_0} \times 100\% \qquad (1)$$

Color

The color of different leathers was determined by a digital chromatic aberration instrument (CR-10plus, Japan). L* stands for brightness, a* stands for red and green, while b* stands for yellow and blue (L*=99.29, a* =-0.15, b* =1.34). The calculation formula of the total color difference of leather is according to equation (2).

$$\Delta E = \sqrt{(L^* - L)^2 + (a^* - a)^2 + (b^* - b)^2} \qquad (2)$$

Where ΔE stands for total chromatic aberration, L, a, and b are the parameters of the sample. All the leather samples were measured on the standard plate.

Morphological analysis

The leather samples were lyophilized after tanning. Both the cross-section and surface of the leather samples were observed using a scanning electron microscope (SEM, S4800, Hitachi, Japan) with an accelerating voltage of 10 kV.

Organoleptic properties

Organoleptic properties such as fullness, grain tightness, and grain smoothness were assessed and rated by three experts independently, which were rated on a scale of 1-10, with 10 of the best.

The structures of leather

FT-IR spectra of leathers were obtained using a TENSORII spectrometer (Nicolet iS10, Thermo Scientific, USA) equipped with universal attenuated total reflection (ATR) sampling accessory. For each spectrum, the transmittance was recorded from 400 to 4000 cm^{-1} with an accumulation of 32 scans and a resolution of 4 cm^{-1}.

XRD measurements were performed on an Empyrean X-ray diffractometer (PANalytical B.V., Netherlands) at 40 kV, 40 mA, with CuKα (λ = 1.5406 Å) as radiation source. The leather samples were irradiated in the range from 5 to 60° at a scanning rate of 0.3°/s.

Results and discussion

Structure of polysaccharides

FTIR and XRD analysis

The FT-IR spectra of SSPS, HPS-30, HPS-60, and HPS-90 are shown in Figure 1. Two characteristic peaks around 3200-3500 cm^{-1} and 2927 cm^{-1} are attributed to the stretching vibration of –OH and C-H. The intense band at 1640 cm^{-1} is assigned to the bending vibration of water molecules contained in polysaccharides. The characteristic peaks near 1000 cm^{-1} in the fingerprint region are ascribed to the bond stretching of –OH with some contributions from the rhamnogalacturonan moiety in the samples. The new peak at 1740 cm^{-1} which corresponds to the stretching vibration of carbonyl groups was found in both HPS-30, HPS-60 and HPS-90. Furthermore, the intensity of this absorption peak was enhanced with increasing the H_2O_2 dosage by oxidation. This result further confirmed that carbonyl and carboxyl groups were introduced in the molecular structure of HPS by the oxidation with H_2O_2.

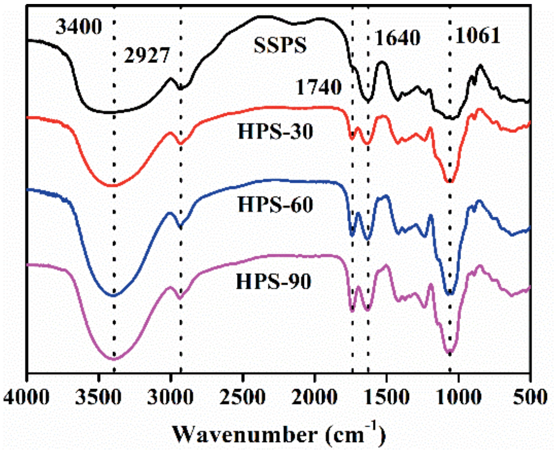


Figure 1. FT-IR spectra of SSPS, HPS-30, HPS-60 and HPS-90

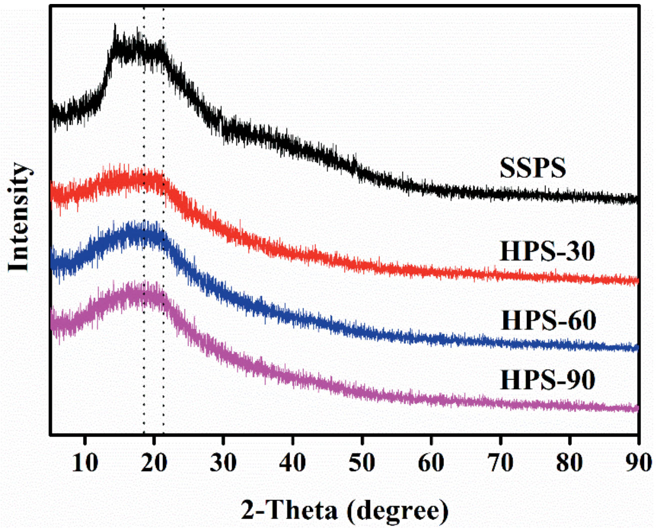


Figure 2. X-ray diffraction (XRD) patterns of SSPS, HPS-30, HPS-60, and HPS-90

Figure 2 shows the XRD pattern of soybean polysaccharide before and after H_2O_2 oxidation. The obvious diffuse broad peak of SSPS at 19° (2θ) indicated a low crystallinity of polysaccharides with an amorphous structure. The lower crystallinity suggests the lower chain stiffness of polysaccharides. High crystallinity and chain stiffness would affect the accessibility of oxidation agent to the crystal region, and thus the degradation mainly takes place in the amorphous region. XRD patterns indicated that SSPS could be degraded by the oxidation with hydrogen peroxide. For the samples of HPS-30, HPS-60, and HPS-90, obvious diffuse broad peaks at 21° and dispersion broad peaks are basically consistent with those of SSPS, indicating an amorphous structure in the oxidized polysaccharides.

Particle size of HPS

DLS was used to determine the average particle size of SSPS and HPS. Figure 3 shows the particle size distribution of HPS, and the intensity average diameter and intensity calculated from the particle size distribution are shown in Table II. For SSPS, the major set of particles was observed, in which 89.6% had an intensity average diameter of 901.8 nm. The particles of HPS-30 distributed over a larger range with three part sets. The intensity average diameter of the main set (539.0 nm, intensity 74.3 %) was smaller than that of SSPS. With increasing the amount of hydrogen peroxide used in the oxidization, the average particle size of the polysaccharide gradually decreases. The average particle size of HPS is significantly smaller than that of SSPS, indicating that hydrogen peroxide could probably degrade the soybean polysaccharides by destroying the glycosidic bonds of soybean polysaccharides to depolymerize the molecular chains of soybean polysaccharides. So the average particle size of the polysaccharides was reduced. The reduction in average particle size is conducive for the penetration of polysaccharide ligands into leathers. Furthermore, the full-component polysaccharide has a wide particle size distribution, and it could act as a masking agent for zirconium tanning and serve as a good filling agent, which was further confirmed by the results of the thickening rate in Figure 6.

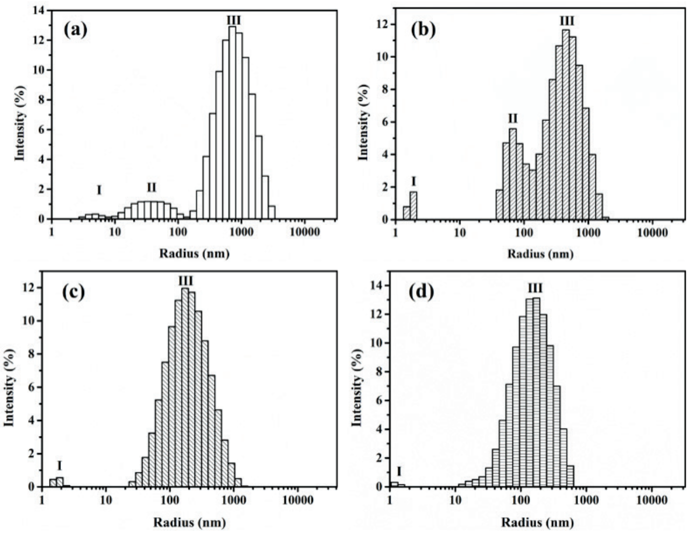


Figure 3. Particle size distribution of different polysaccharides (**a:** SPSS; **b:** HPS-30; **c:** HPS-60; **d:** HPS-90)

Table II

Particle size distribution (A-intensity average diameter, B-intensity) of HPS.

	SSPS		HPS-30		HPS-60		HPS-90	
	A/nm	B/%	A/nm	B/%	A/nm	B/%	A/nm	B/%
I	5.0	1.1	1.8	2.5	1.8	1.1	1.2	0.7
II	43.4	9.3	80.8	23.2	-	-	-	-
III	901.8	89.6	539.0	74.3	243.7	98.9	176.2	99.3

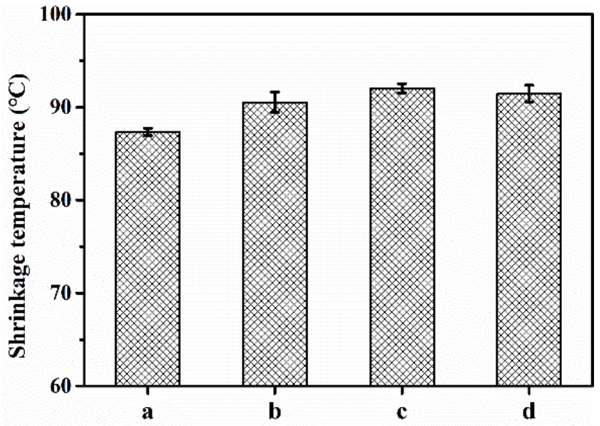


Figure 4. Shrinkage temperature of samples for different tanning processes

(Note: **a**-Zirconium-tanned leather; **b**-HPS-30-zirconium-tanned leather; **c**-HPS-60-zirconium-tanned leather; **d**-HPS-90-zirconium-tanned leather)

Structure and properties of leather

Thermal properties of leather

The shrinkage temperature (T_s) of leathers is usually used to evaluate the hydrothermal stability and performance of leathers.[17] High shrinkage temperature of leather means good hydrothermal stability and good tanning effect. The shrinkage temperature of leathers is closely related to the degree of tanning. Figure 4 shows the shrinkage temperatures of leather samples tanned by different zirconium tanning processes. The shrinkage temperature of the tanned leather was 87°C for the control, which reached the highest of 92°C with HPS-60. So the HPS with medium oxidation degree and particle size does good in zirconium tanning. This could be ascribed to the better penetration, distribution, and crosslinking of HPS-Zr complexes in the collagen fiber network of leather. So the introduction of HPS-60 could significantly improve the hydrothermal stability of leather.

Thermogravimetric analysis (TGA) and differential thermal gravity (DTG) analysis could be used to characterize the thermal stability of leather samples.[18] The TGA and DTG curves of the samples by different tanning processes were shown in Figure 5. Similar three stages exist in the TGA curves of the four samples. The first weight loss at 30-100°C was approximately 10% by the volatilization of free water and bound water in leathers. There are a large number of hydrogen bonds in the collagen fibers, which play an important role in stabilizing the collagen fiber and the whole structure of leather. At 100-400°C, some hydrogen bonds might be damaged and the triple helical structure of the collagen fibers might be unwound, resulting in the breakage of the polypeptide chain of collagen in leathers. On the other hand, tanning agent could react with collagen fibers by van der Waals forces, covalent bonds,and hydrogen bonds to form crosslinking and increase the thermal stability of leather. At high temperatures, great damage will take place for collagen fiber, and the weight fell sharply to 33% of the original weight. Finally, at a temperature above 400°C, the TGA curve turns smooth, mainly by the degradation of carbide slag at high temperatures.

The maximum weight loss rate temperature (T_{max}) of the leather sample reflects the structural stability of leather. The higher the maximum weight loss rate temperature means the better thermal stability of leather. By comparing the T_{max} in the second stage of the four samples, the ones of HPS-Zr tanned leathers are higher than that of Zr-tanned leather, indicating that HPS with medium size and a moderate degree of oxidation could improve the thermal stability of leather. This should be ascribed to the good penetration, distribution, and crosslinking of HPS-Zr complexes in the fiber network of leather.

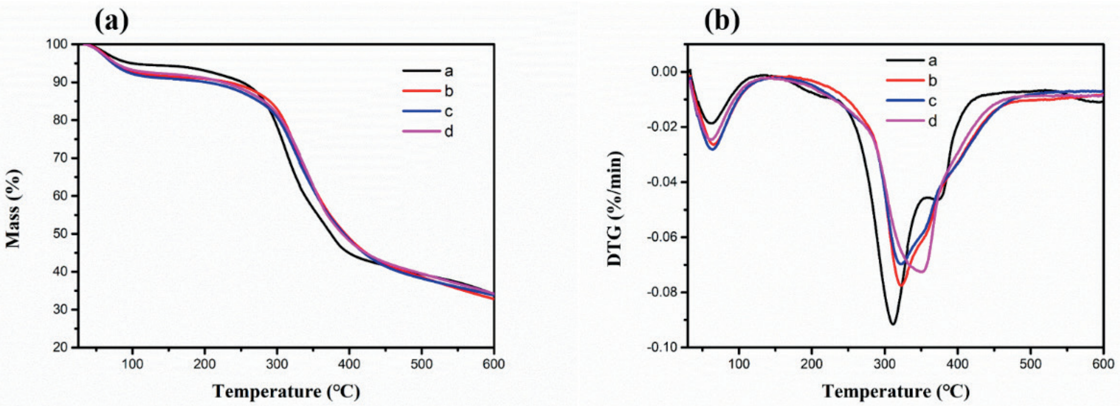


Figure 5. TGA **(a)** and DTG **(b)** curves of leather samples for the different tanning process

(Note: **a:** pickled sheepskin, **b:** zirconium-tanned leather, **c:** HPS-30-zirconium-tanned leather, **d:** HPS-60-zirconium-tanned leather)

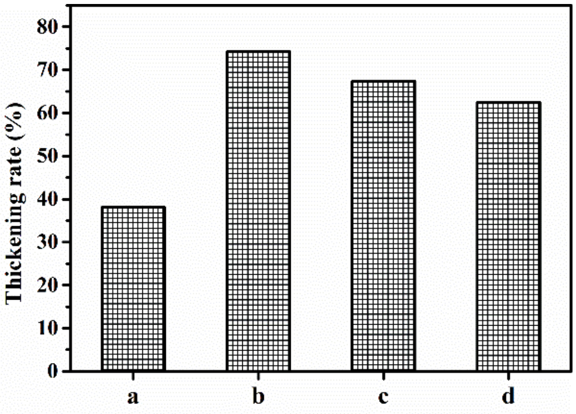


Figure 6. Thickness rate of leather samples for different tanning processes

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

Filling effect of leather

The thickness rate suggests the filling properties of polysaccharides for leather.[12] The higher the thickening rate, the better the filling ability of the polysaccharides. The thickness rate of leathers with different tanning processes is shown in Figure 6. The thickness rates of zirconium, HPS-30, HPS-60, and HPS-90 were 38.1%, 74.2%, 67.35%, 62.46%, respectively. Compared with that of the control, the one with pure zirconium tanning, the thickness rates of all the other samples with HPS are greatly increased, with the highest for the HPS-30. So the filling effect with oxidized polysaccharide as masking agent of zirconium tanning is very good. It could be explained by the particle size of oxidized polysaccharides, which is suitable for the penetration in leather and conductive to the absorption by collagen fibers. All the components were kept in HPS solution, which was directly used in the tanning process. The wide particle size distribution provided the oxidized polysaccharide solution with a very good filling effect.

Mechanical properties

Tensile strength and elongation at break are important for leathers, which are commonly used to evaluate the mechanical properties of leather.[5, 10] Table III shows the mechanical properties of leather tanned by different processes. The tensile strength of the leather with HPS-60 is the best. Compared with the one with pure zirconium tanning, the tensile strength of HPS-60 was increased from 13.23 MPa to 18.9 MPa. However, the tensile strength of HPS-90 is only 9.83 MPa, the possible reason is that the smaller ligands are not enough to coordinate and stabilize the Zr complexes. Furthermore, Zr complexes may be too small to sufficiently crosslink the collagen fibers, resulting in decreased tensile strength and increased elongation at break. By the addition of oxidized polysaccharide, the aldehyde and carboxyl group are introduced to bind with collagen fiber and zirconium tanning agent, and the crosslinking degree is increased, resulting in an increased tensile strength.

Color and area yield

For zirconium tanned leather, generally called wet-white, the whiteness is important because good whiteness is preferable for tanners to make either natural color or light colored products.[6] Thus, the colorimetric values of pickled sheepskin and different tanned leathers were measured to evaluate the whiteness, with the results shown in Table IV. The total color difference (ΔE) value was calculated

Table III

Mechanical properties of leather samples for different tanning processes

Sample	Tensile Strength (MPa)	Standard (MPa)	Elongation (%)	Standard (%)
a	13.23±1.2	≥12	137.66±11.9	≥25
b	14.65±1.2	≥12	109.28±8.6	≥25
c	18.90±1.1	≥12	111.85±11.0	≥25
d	9.83±0.6	≥12	122.34±1.3	≥25

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

Table IV

Area yield, chromaticity and color difference of different samples

Sample	Area yield/%	L	a	b	ΔE
sheepskin	100.0	77.1	5.3	11.6	25.0
a	101.2	81.2	1.3	5.9	18.8
b	103.5	83.7	3.4	13.8	20.3
c	102.8	82.7	2.9	15.6	21.1
d	103.1	81.1	1.5	14.6	22.6

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

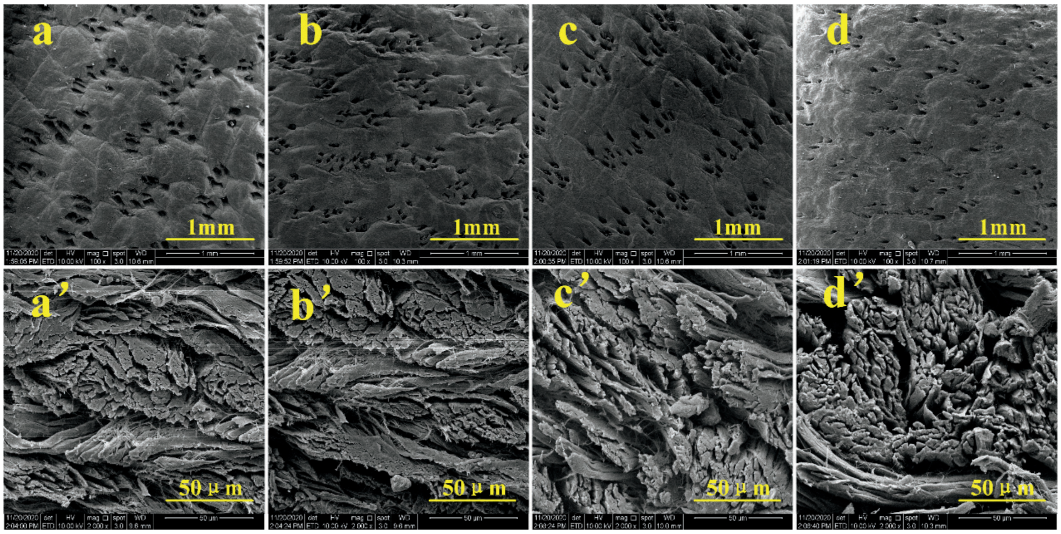


Figure 8. SEM images of grain surface **(a, b, c, d,)** and cross-section **(a', b', c', d')** of leathers

(Note: **a** and **a'**: pickled sheepskin, **b** and **b'**: zirconium-tanned leather, **c** and **c'**: HPS-30-zirconium-tanned leather, **d** and **d'** HPS-60-zirconium-tanned leather)

by subtracting the corresponding values for standard white (L=99.29, a =-0.15, B =1.34), and a lower ΔE value means higher whiteness. The ΔE of zirconium-tanned leather with polysaccharides is close to that of pickled sheepskin, indicating that the addition of polysaccharide does not significantly change the whiteness of the leather. As can be seen from Table IV, the introduction of polysaccharide could improve the leather yield of zirconium tanned leather, which is good from viewpoint of economic profits.

Morphological analysis

The performance is closely related to the microstructure of leathers.[19] By the changes in the microstructure of samples, we could know the effect of oxidized polysaccharides on the combination, distribution of tanning agent in leather. Leathers dried by different ways were compared for morphological study, and it was found that the SEM images of the lyophilized samples could better explain the degree of collagen fiber dispersion. So the lyophilized samples were used in the study. In Figure 8(a), for the pickled sheepskin before tanning, the collagen fiber bundle is tight and bonded together, with clear grain surface pores. After being tanned with pure zirconium tanning agent, the collagen fiber bundles are better dispersed with clear grain surface pores. In Figure 8(c) and (d), the collagen fiber bundles of leather tanned with zirconium and HPS-30 or HPS-60 were well dispersed with clear surface pores and flatter grain surface. So it can be concluded that the synergism of zirconium and HPS could provide leathers with good fiber dispersion and strong cross linking on collagen fibers, yielding excellent leather.

Organoleptic properties

The organoleptic properties of zirconium-tanned leathers with and without different HPS are given in Table V, in which the leather tanned with zirconium and HPS-60 exhibited the best organoleptic properties, including softness, fullness, and grain smoothness, compared to those tanned with pure zirconium tanning agent. Generally, compared with vegetable-tanned and aldehyde-tanned leathers, the zirconium tanned leather has better fullness, because of the large polymeric zirconium complex formation. Here in this study, the samples were tanned with zirconium tanning agent with different masking agents of HPS. The fullness evaluation of pure zirconium tanned leather is 5, which is much worse than the 9 of zirconium with HPS-60. Furthermore, the softness and grain smoothness of leather tanned with zirconium and HPS-60 is also 9, indicating that it has good organoleptic properties. The fullness of leather tanned with zirconium and HPS-60 is in accordance with the thickening rate results in Figure 6. The fullness and tightness were found to be enhanced by the introduction of HPS with wide particle size distribution. So the introduction of HPS might provide zirconium tanned leathers with good organoleptic properties.

Table V

Organoleptic properties of leather samples for different tanning process

	a	b	c	d
Softness	5	9	9	8
Fullness	5	8	9	7
Grain smoothness	5	9	9	8

(Note: **a:** Zirconium-tanned leather; **b:** HPS-30-zirconium-tanned leather; **c:** HPS-60-zirconium-tanned leather; **d:** HPS-90-zirconium-tanned leather)

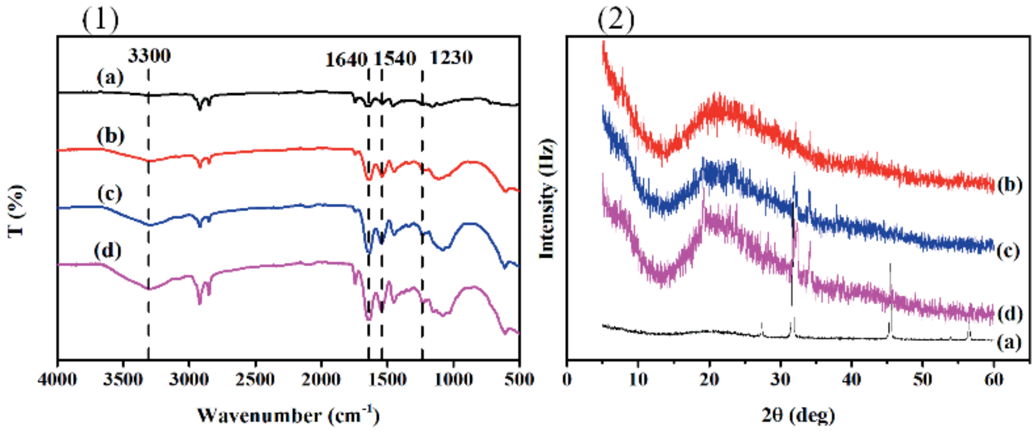


Figure 9. **(1)** FTIR and **(2)** XRD of pickled sheepskin **(a)**; zirconium-tanned leather **(b)**; HPS-30-zirconium-tanned leather **(c)**; HPS-60-zirconium-tanned leather **(d)**

Tanning mechanism

Collagen in leather has a special triple helical structure and is usually characterized by the amide bands in the infrared spectrum. Figure 9(1) shows the infrared spectra of leathers tanned by different tanning processes, which might indicate the tanning mechanism. For the control, the peak at 3300 cm^{-1} was attributed to the N-H stretching vibration in collagen. The bands at 1640 cm^{-1}, 1540 cm^{-1}, and 1230 cm^{-1} in both the control and tanned leathers using polysaccharide were assigned to the carbonyl stretching vibration (amide I band), C-N stretching vibration (amide II band), and C–N stretching vibration and N-H of the amide group in the peptide bond (amide III band),[20] respectively.

The amide I band of collagen is particularly sensitive to the secondary structure of collagen. The amide I band peaks of collagen tanned with pure zirconium tanning agent, HPS-30 with zirconium, and HPS-60 with zirconium, were 1643 cm^{-1}, 1640 cm^{-1} and 1642 cm^{-1}, respectively. The results showed that the secondary structure of collagen did not change significantly after tanning, suggesting that the triple helical structure of collagen was not destroyed by tanning. Besides, the increase in peak intensity at 1640 cm^{-1} in Figure 9 was contributed to the carbonyl group in the oxidized soybean polysaccharide, demonstrating the existence of HPS in leather.

Figure 9(2) shows the XRD patterns of the samples. Collagen fibers have triple helical structures with good orientation and high crystallinity, which can be characterized by XRD. After tanning, the original two characteristic peaks at 7.6° and 21° were not changed, indicating that the triple helical structure of collagen had not been destroyed in the tanning process. By tanning, the peak at 21° turned broader and the intensity turned weaker, probably because the regularity of collagen fibers was decreased by the interaction between collagen, tanning agent, and HPS. The results showed that both zirconium sulfate and HPS can penetrate into the leather to react with collagen fibers, increasing the distance between collagen fibers and dispersing collagen fibers.

Based on the above results, interaction mechanism in the tanning process of HPS with zirconium was proposed, as shown in Figure 10. The FT-IR spectra and XRD patterns proved that the tanning agent penetrates into the leather and react with the collagen fiber, with the triple helical structure of the collagen not changed. Schiff base reaction could take place between the aldehyde group of HPS and the amino group of collagen.[21] Traditional zirconium tanning had been proven to crosslink with the amino and carboxyl groups of collagen through coordination bonds.[12] HPS and zirconium could form complexes through coordination bonds, by the coordination of zirconium with the carboxyl group of HPS.[11] Therefore, it was speculated that the HPS-Zr tanning agent is bound to collagen through hydrogen bonds, ionic bonds, and coordination bonds.

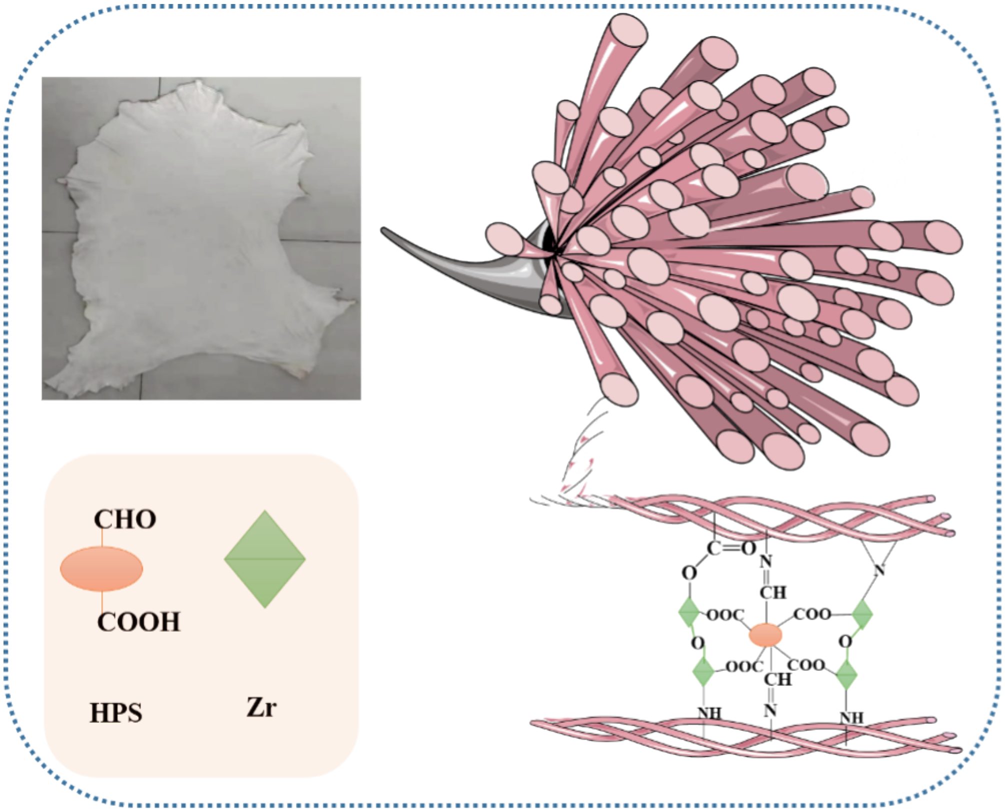


Figure 10. Proposed crosslinking reaction between collagen, HPS and zirconium

Conclusion

By hydrothermal reaction, soybean polysaccharides were oxidized by hydrogen peroxide to yield polysaccharides with aldehyde and carboxyl groups. The oxidized polysaccharide solution was directly used in zirconium tanning. The carboxyl group in the oxidized polysaccharide could act as a ligand with zirconium sulfate to crosslink the collagen fibers to improve the mechanical strength, thermal properties, and organoleptic properties of the leather. With the introduction of HPS, the collagen fibers are dispersed better, which is more beneficial for leather chemicals to penetrate into leathers for efficient tanning. No damage in the triple helical structure of collagen in leathers was found by the HPS and zirconium tanning. The oxidized polysaccharides are suggested a potential application in chrome-free tanning.

Acknowledgment

The financial supports from the National Key R & D Program of China (No.2017YFB0308500) and National Natural Science Foundation Commission of China (No. 51673177) are greatly appreciated.

References

1. Khare, S. K., Jha, K., Gandhi, A. P.; Citric acid production from Okara (soy-residue) by solid-state fermentation. *Bioresour. Technol.* **54**, 323-325, 1995.
2. Jia, X. J., Chen, M. W., Wan, J. B., Su, H. X., He, C. W.; Review on the extraction, characterization and application of soybean polysaccharide. *RSC Advances*. **5**, 73525-73534, 2015.
3. Liu, C., Huang, J., Zheng, X., Liu, S., Lu, K., Tang, K., Liu, J.; Heat sealable soluble soybean polysaccharide/gelatin blend edible films for food packaging applications. *Food Packag. Shelf Life*. **24**, 2020.
4. Salarbashi, D., Tajik, S., Ghasemlou, M., Shojaee-Aliabadi, S., Shahidi Noghabi, M., Khaksar, R.; Characterization of soluble soybean polysaccharide film incorporated essential oil intended for food packaging. *Carbohydr. Polym.* **98**, 1127-1136, 2013.
5. Ariram, N., Madhan, B.; Development of bio-acceptable leather using bagasse. *J. Clean. Prod.* **250**, 119441, 2020.
6. Ding, W., Wang, Y. N., Zhou, J. F., Shi, B.; Effect of structure features of polysaccharides on properties of dialdehyde polysaccharide tanning agent. *Carbohydr. Polym.* **201**, 549-556, 2018.
7. Simon, C., Pizzi, A.; Tannins/melamine-urea-formaldehyde (MUF) resins substitution of chrome in leather and its characterization by thermomechanical analysis. *J Appl Polym Sci*. **88**, 1889-1903, 2003.

8. Zuriaga-Agustí, E., Galiana-Aleixandre, M. V., Bes-Piá, A., Mendoza-Roca, J. A., Risueño-Puchades, V., Segarra, V.; Pollution reduction in an eco-friendly chrome-free tanning and evaluation of the biodegradation by composting of the tanned leather wastes. *J. Clean. Prod.* **87**, 874-881, 2015.
9. Chattopadhyay, B., Aich, A., Mukhopadhyay, S. K.; Chromium in the tanning industry: An odyssey from cradle to grave. *JSLTC*. **96**, 133-140, 2012.
10. Ding, W., Yi, Y. D., Wang, Y. N., Zhou, J. F., Shi, B.; Preparation of a Highly Effective Organic Tanning Agent with Wide Molecular Weight Distribution from Bio-Renewable Sodium Alginate. *ChemistrySelect*. **3**, 12330-12335, 2018.
11. Cao, S., Zeng, Y., Cheng, B., Zhang, W., Liu, B.; Effect of pH on Al/Zr-Binding Sites Between Collagen Fibers in Tanning Process. *JALCA*. **111**, 242-249, 2016.
12. Yu, Y., Wang, Y.-n., Ding, W., Zhoua, J., Shi, B.; 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.
13. Li, W. B., Ma, J. Z., Zhou, Y. X., Sun, X. D., Gao, D. G.; The application of sulfonated tetraphenyl calix[4] resorcinarene as a novel, multi-functional and eco-friendly ligand in zirconium tanning system. *J. Clean. Prod.* **280**, 2021.
14. Sizeland, K. H., Wells, H. C., Edmonds, R. L., Kirby, N., Haverkamp, R. G.; Effect of Tanning Agents on Collagen Structure and Response to Strain in Leather. *JALCA*. **111**, 391-397, 2016.
15. Salarbashi, D., Tajik, S., Shojaee-Aliabadi, S., Ghasemlou, M., Moayyed, H., Khaksar, R., Noghabi, M. S.; Development of new active packaging film made from a soluble soybean polysaccharide incorporated Zataria multiflora Boiss and Mentha pulegium essential oils. *Food Chemistry*. **146**, 614-622, 2014.
16. Tang, K., Tang, Z., Wang, F., Liu, J., Ferah, C. E.; Effect of Cyclic Stress on the Structure and Mechanical Properties of Leather. *JSLTC*. **104**, 163-169, 2020.
17. Qiang, T. T., Gao, X., Ren, J., Chen, X. K., Wang, X. C.; A Chrome-Free and Chrome-Less Tanning System Based on the Hyperbranched Polymer. *ACS Sustain. Chem. Eng.* **4**, 701-707, 2015.
18. Hu, Y. D., Liu, J., Luo, L., Li, X. M., Wang, F., Tang, K. Y.; Kinetics and Mechanism of Thermal Degradation of Aldehyde Tanned Leather. *Thermochim. Acta*. **691**, 178717, 2020.
19. Krishnamoorthy, G., Sadulla, S., Sehgal, P. K., Mandal, A. B.; Greener approach to leather tanning process: d-Lysine aldehyde as novel tanning agent for chrome-free tanning. *J. Clean. Prod.* **42**, 277-286, 2013.
20. Gao, D. G., Cheng, Y. M., Wang, P. P., Li, F., Wu, Y. K., Lyu, B., Ma, J. Z., Qin, J. B.; An eco-friendly approach for leather manufacture based on P(POSS-MAA)-aluminum tanning agent combination tannage. *J. Clean. Prod.* **257**, 2020.
21. Zhang, L., Liu, J., Zheng, X., Zhang, A., Zhang, X., Tang, K.; Pullulan dialdehyde crosslinked gelatin hydrogels with high strength for biomedical applications. *Carbohydr. Polym.* **216**, 45-53, 2019.

Preparation and Properties of Thermally Expandable Microspheres for Leather Foam Coating

by

Guodong Huang,[1] Zhixian Lin,[1] Haojun Fan,[1]* Jun Xiang,[1] Chong Zheng[2] and Zhiqing Luo[2]
[1]*Key Laboratory of Leather Chemistry and Engineering of Ministry of Education, Sichuan University*, Chengdu 610065, China
[2]Qingyuan Qili Synthetic Leather Co, Qingyuan, China, 511510

Abstract

A type of thermally expandable microspheres (TEMs) for foam coating was prepared by suspension polymerization with acrylonitrile (AN), methyl methacrylate (MMA), vinyl acetate (VAC) as shell polymer monomers and i-pentane as core foaming agent. The effects of an aqueous additive (Sodium Chloride, NaCl) on the size and distribution of TEMs, and the effects of crosslinking degree, i-pentane dosage and monomer mass ratio on the expansion property, expansion temperature and solvent-resistance of TEMs were investigated. The results showed that when the dosage of NaCl was close to the saturation solubility (30%), the dosage of crosslinking agent and alkane were about 0.09% and 7.4%, and the mass ratio of AN/MMA/VAC w rm distribution and good solvent resistance, the expansion diameter ratio was 5 times under 110~120°C, which meets the application requirements for foam coating of leather or synthetic leather.

Introduction

Thermally expandable microspheres (TEMs) are polymer particles at micrometrical scale, prepared by microencapsulation technology.[1] TEMs are composed of a polymer shell with good gas tightness and an inner core of an alkane which has a low boiling point. Figure 1 demonstrates its expansion process: when heating, the internal alkanes create vapor pressure as the temperature rises. As it comes to the correct temperature to soften the polymer shell, TEMs begin to expand; once the temperature decreases, the polymer shell is in a rigid state, and expansion of TEMs remains, which exhibits a foaming effect.[2-3] Because of these characteristics, TEMs have been widely used in many industrial fields, such as plastic foaming,[4-5] adhesives,[6] ink printing,[7] etc. For example, TEMs are added to crystalline polymers, such as polyethylene, to make low density and high heat-resistant foaming composites. When TEMs were blended with adhesives and expanded after fabric and paper being coated and heated, the treated substrates were found to have the advantage of being skid resistant and easy to color. In leather manufacture, TEMs can also be used to prepare foam coating for split leather. Specifically, TEMs are blended with water based polyurethane resin firstly, then followed by a coating process on the corresponding substrate, and accompanied with the procedure of pre-drying and foaming, a foam coating layer can be achieved. The split leather products made by this method not only have a fluffy effect of high quality, an exquisite feel and a tender lustre[8-9] but also possess enhanced fullness, air-permeability and moisture-penetrability.[10] In addition, TEMs can be used as matting and mending materials for grain damaged leather.[11] The damaged grain repaired by this foaming coating shows obvious matting effect, excellent fullness, and polishing performance which will greatly improve the grade of inferior leather products.[12]

Currently, great efforts have been done to investigate the TEMs. Hou et al.[2] used vinylidene chloride (VDC), AN, and MMA as the shell polymer monomers, and isobutane as the internal alkane to prepare such TEMs with the diameter approximately 20μm, the temperature of expansion was 110°C-120°C, and the greatest ratio of expansion was 3 times. Even though VDC is a cryogenic monomer, equipped with the advantage of heat and corrosion resistance, and good gas tightness,[13] it is an extremely toxic substance, in the process of decomposing, it produces harmful substances. Up to now, there are few reports about TEMs on their application in foam coating of leathers, synthetic leathers and textiles.

As a foam coating for leather or synthetic leather, TEMs should meet the technical requirements as below: (1) the polymer shell must be of good gas tightness, pliable, and tough (with proper cross-linking) to avoid the volatilization of the internal alkanes at a low boiling point and assure the morphological stability of TEMs during the expansion process instead of untimely breaking; (2) the internal alkanes of low boiling point should generate enough vapor pressure and should not penetrate the polymer shell during the heating process;[14] (3) because TEMs are blended with resin, which often contains organic solvents, [15] such as *N,N*-dimethylformamide(DMF) and acetone, the polymer shell should be solvent and chemical corrosion resistant; (4) the expansion temperature of TEMs should be higher than the pre-drying temperature (≈100°C) so as to evaporate the moisture and prevent the untimely breaking of microspheres.

Given the aforementioned requirements and taken the expansion performance and temperature, particle size and distribution as well as the solvent resistance of the TEMs into account, a type of TEMs were designed and prepared by optimizing the type of monomers,

---

*Corresponding author e-mail: fanhaojun@scu.edu.cn
Manuscript received January 19, 2021, accepted for publication March 3, 2021.

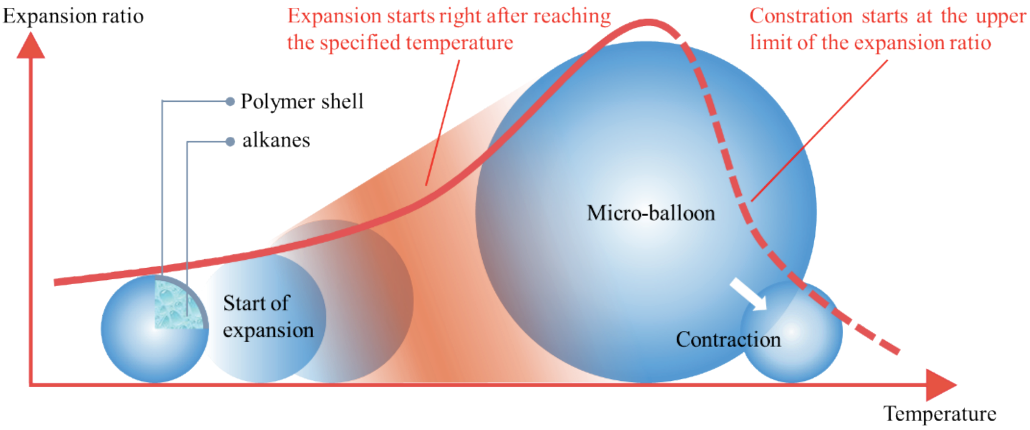


Figure 1. The foaming diagram of TEMs

aqueous additive (NaCl) concentration, cross-linking degree, alkane dosage together with the monomer mass ratio. Furthermore, the expansion ratio, temperature, and the solvent-resistance of resultant TEMs were investigated. The aim of this research is to provide a novel foaming agent and foam technology for leather, synthetic leather and textile coating.

Materials and Methods

Experimental materials

Acrylonitrile (AN), methyl methacrylate (MMA), vinyl acetate (VAC), ethylene glycol dimethacrylate (EGDMA), 2,2'-azobisisobutyronitrile (AIBN), isopentane (i-pentane) were all analytically pure and purchased from Shanghai Adamas Reagent Co., Ltd; Polyvinylpyrrolidone (PVP K30) was analytical pure and purchased from Aladdin China Chemical Reagent Co., Ltd.; sodium dodecyl sulfate (SDS), magnesium chloride hexahydrate($MgCl_2{\cdot}6H_2O$), sodium hydroxide(NaOH), sodium nitrite($NaNO_2$), sodium chloride(NaCl) were chemical purity and purchased from Chengdu Kelong Chemical Reagent Co., Ltd; deionized water was obtained by laboratory-self-made; Waterborne polyurethane(WPU) with 53% solid content was purchased from Liulian New Material Co., Ltd.

Preparation of TEMs

The basic formula for preparing TEMs is shown in Table1.

Aqueous phase preparation: a certain amount of NaOH and NaCl were fully dissolved in deionized water. The aqueous solution of $MgCl_2{\cdot}6H_2O$ containing SDS was first added slowly under stirring, and then stirred vigorously for 30 minutes to obtain the basic dispersion solution, then small amounts of $NaNO_2$ and PVP K30 were added to the mixture to obtain the final dispersion solution by dissolving the mixture evenly. The dispersion solution was put into a refrigerator to cool down.

Table I

The basic formula for preparing TEMs

Phase state	Substance	Dosage/(%)[a]
Aqueous phase	Deionized water	100
	NaCl	0~30
	NaOH	3.70
	$MgCl_2{\cdot}6H_2O$	11.30
	SDS	1.50
	$NaNO_2$	0.03
	PVP K30	0.30
Oil phase	AN	21.5~26
	MMA	7.4~11.1
	VAC	1.9~6.3
	AIBN	0.29
	EGDMA	0~0.19
	i-pentane	3.7~14.8

a: The mass fraction of raw material in the aqueous phase and oil phase were based on the water content.

Oil phase preparation: a certain amount of EGDMA, AIBN, i-pentane were dissolved in weighted mixed monomer (AN, MMA, VAC), and then placed in the refrigerator to cool down.

Emulsification and reaction: The cooled oil phase was mixed with the aqueous phase, and emulsified at 8000 rpm for 3 mins, then quickly poured into the reactor to seal, deoxygenated with nitrogen for 3 mins, and then pressurized to 0.4~0.6Mpa with nitrogen. The rotating speed of the agitator was adjusted to 300 rpm, and the reaction temperature was raised to 60°C. After 20 hours of reaction, the reactor was heated to 70°C for curing for 30 mins, then the temperature was cooled down, and the material discharged.

Post-treatment operation: The pH of the obtained product was adjusted to 2 by dilute hydrochloric acid to remove the magnesium hydroxide deposits on the surface of the microspheres, then washed, filtered and dried at 50°C for 24 hours, the TEMs were obtained.

Preparation of foaming coating

TEMs were added into WPU, and a certain amount of leveling agent, thickening agent and other additives were added under the stirring condition to prepare the coating slurry. The slurry with moderate viscosity was evenly coated on the leather, synthetic leather or textile substrate by roller coating method. The coated substrates were pre-dried in the oven at 100°C for 1 min, followed by a foaming process at 120°C for 1 min, finally, the foaming products were taken out and analyzed.

Finishing of split leather and damaged grain leather

Quantitative TEMs, WPU and other additives were mixed uniformly, and the viscosity of size was increased to a range of 3000~5000 cps, then the size was coated on the surface of split leather and damaged grain leather by roll coating, and pre-dried in the oven at 60°~80°C for 1 min, followed by a hot foaming process at 120°C for 3s, the foamed split leather or repaired leather was obtained.

Characteristics of TEMs

Determination of particle size and distribution

One to two grams of TEMs after the post-treatment were added to 20~30ml of deionized water and dispersed by ultrasonic wave for 2 minutes. The average particle size of TEMs was measured by laser particle size analyzer(LPS), and the size distribution of microspheres was calculated by the formula: $(D_{90}-D_{10})/D_{50}$, where D_{90}, D_{50}, and D_{10} represented the particle size of the sample when the percentage of cumulative particle size distribution reached 90%, 50%, and 10%, respectively, and their physical meaning indicated that the proportions of the number of particles inferior to this particle size out of the total number of particles were 90%, 50%, and 10%, respectively.

Observation on surface morphology

A small amount of dried TEMs were coated on the conductive adhesive, sprayed gold in a vacuum, and then was put under the scanning electron microscope to observe its surface morphology.

Determination of expansion property and temperature

The expansion property of the TEMs was measured by thermal mechanical analysis (TMA). The appropriate amount of the TEMs were placed in an aluminum crucible, being loaded with 0.06 N and heated to 250°C at 15 K/min in a nitrogen atmosphere. Observed the change of probe displacement (dimension change) with temperature to obtain the initial expansion temperature (T_{start}), the maximum expansion temperature (T_{max}), as well as the greatest expansion height (D_{max}).

The endothermic enthalpy(ΔH) of the microsphere in expansion process was measured by using the differential scanning calorimeter (DSC) as the temperature was increased from 20° to 200°C at a rate of 15 K/min under the protection of nitrogen to determine the amount of alkane contained in the TEMs.

Thermogravimetry (TG) analysis was carried out from 35° to 600°C at a heating rate of 15 K/min under the protection of nitrogen. The weight loss rate of TEMs during the expansion process was reflected by differential thermogravimetry (DTG) and used to analyze the change of the polymer shell during the expansion process.

Results and Discussion

Structure design of TEMs

As mentioned above, the polymer shells of TEMs for foam coating require good gas tightness and heat resistance, so the polymer shell of TEMs must be tough, tensile and solvent resistant. There are many available polar monomers with a double bond and heat resistance, such as acrylonitrile(AN), methyl acrylonitrile, methlacrylic acid, and vinylidene chloride, etc. among which AN has a strong interaction between molecules due to the presence of a strong polar cyanogen group in its structure, thus PAN has the advantage of high strength, good gas tightness, good solvent resistance, and high heat resistance.[16-17] Therefore, acrylonitrile was chosen as the main monomer for preparing TEMs. However, it is so susceptible to semi-crystalline that the polymer shell will become too rigid when AN is used as the polymer monomer alone, so the PAN must be modified by copolymerization so as to increase flexibility of the polymer shell.[15] Taken the heat-resistance into account, MMA was selected as a co-monomer. Copolymerization of AN and MMA will decrease the regularity of polymer molecular arrangement and thus decrease the crystallinity of polymer and increase the flexibility of polymer shell.[18] In the expansion process, the volume of microspheres will enlarge many times, so the polymer shell must have a certain of elasticity. On the other hand, the foaming temperature should not be too high, otherwise the grain leather will shrink. On this basis, VAC with a flexible side groups and low toxicity was chosen as the third copolymer monomer, its purpose was to improve the extensibility of the shell and control the expansion temperature.[19] Furthermore, a proper cross-linking can make the polymer shell form a network structure, which can further improve its heat resistance, gas tightness and strength. The alkane contained in TEMs requires a low boiling point, high vapor pressure generated at the expansion temperature, and low permeability from the polymer shell. According to the vapor pressure calculation formula proposed by Magnus Jonsson et al. [14] where vapor pressure (in Bar) = $\exp [C1 + (C2/T) + C3 * \ln (T) + C4 * TC5] * 10^{-5}$, the vapor pressure generated by i-pentane, iso-octane, n-heptane, n-octane and methylcyclohexane at different temperatures was investigated. It was found that the vapor pressure of i-pentane was 1.1 MPa at 122°C, and the temperature could just satisfy the ideal expansion temperature range of TEMs for foam coating of leather, synthetic leather and textiles and the vapor pressure was large enough to ensure the rapid expansion of TEMs. Moreover, the molecular structure of i-pentane is of a branched-chain type, it is difficult to penetrate the polymer shell, this steric hindrance is beneficial to the improvement of expansion performance, that is why the i-pentane was chosen as the inner core for TEMs in this experiment. Just as mentioned above, the particle size and distribution, surface morphology, expansion temperature, expansion ratio and solvent resistance of TEMs play a key role in its application performance in foaming leather-making. Therefore, the effect of parameters on the particle size and distribution, the surface topography, the expansion temperature, expansion ratio of TEMs and other performances of resultant leather were discussed in detail.

Effect of NaCl concentration on the size and distribution of TEMs

There are many aqueous phase additives in the synthesis of TEMs, such as NaCl, $NaNO_2$, PVP K30, SDS, etc. among them NaCl is the issue factor which affects the size and distribution of TEMs. During suspension polymerization, each monomer droplet contained three type polymeric monomers, AN, MMA and VAC, among them AN and MMA were slightly soluble in water, while VAC had a solubility of 20g/L. As the reaction proceeds, the water-soluble monomers will form secondary particles that cannot expand, and finally reducing the expansion properties of the TEMs. Fortunately, this tendency can be inhibited by addition of NaCl in the aqueous phase. Compared with monomers, NaCl has a stronger affinity with water, which will change the monomer-water chemical equilibrium due to the salting out effect, thus reducing the solubility of monomers in the aqueous phase.[20] Under the premise of fixed monomer ratio, the effect of NaCl concentration on the particle size, distribution and the surface morphology of TEMs is shown in Figure 2 and Figure 3, respectively. As can be seen from Figure 2, the prepared TEMs without NaCl show a small particle size and wide distribution. This is because, with the progress of the reaction, the monomers that dissolve in the aqueous phase undergo polymerization, generating fine particles with different sizes. Further observation through SEM indicated that these fine particles attached to the surface of TEMs, resulting in a non-smooth surface of TEMs (Figure 3a). When the concentration of NaCl is increased to 15%, the particle size of TEMs increase and the distribution becomes significantly narrower. When the concentration of NaCl is close to its saturation solubility (30%), there is no significant change in the particle size and distribution of the TEMs, but the surface morphology of TEMs become smoother and more regular (Figure 3c). This is because the increase in the dosage of NaCl breaks the chemical equilibrium of monomer-water, thus reducing the water solubility of AN, MMA, and VAC, which inhibits the polymerization of monomers in the aqueous phase.

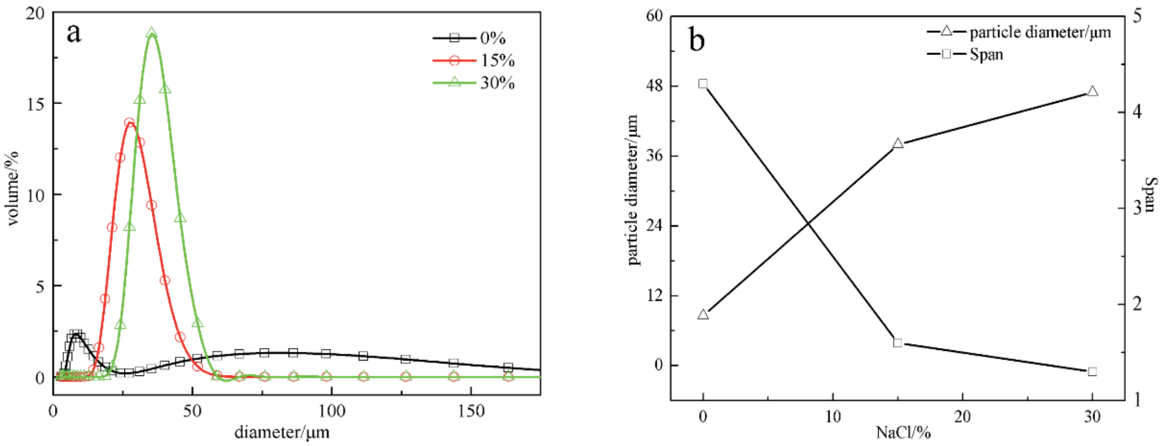


Figure 2. particle size distribution and mean particle size of TEMs with different content of NaCl: **(a)** Particle size distribution, **(b)** mean particle size.

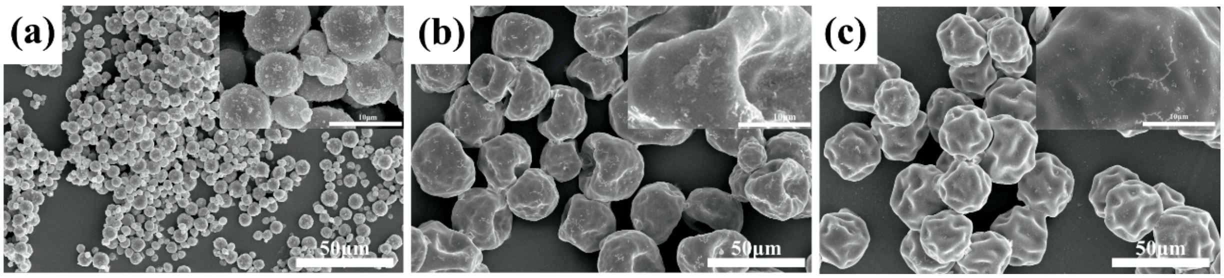


Figure 3. The SEM of the TEMs with different content of NaCl: **(a)** 0%, **(b)** 15%, **(c)** 30%.

Effect of crosslinking degree on the expansion property and temperature of TEMs

The addition of crosslinking agent was believed to increase of polymer flow viscosity at higher temperatures,[21-22] and a suitable crosslinking degree make the polymer shell more ductile to deform under the vapor pressure resulting from the evaporation of internal alkane as well as help TEMs change from their original core-shell structure into larger, hollow spheres. Herein, EGDMA was used as a crosslinking agent, and the effect of crosslinking degree on the expansion performance and expansion temperature of TEMs was investigated via the single variable method.

Table II shows the effect of the dosage of EGDMA on the expansion performance and expansion temperature of TEMs. As can be seen with the increase of cross-linking agent, the T_{start} of TEMs tend to increase slightly, while the T_{max} shows an obvious increase. Besides, the expansion ratio increases firstly and then decreases. According to the thermogravimetric (TG) curve in Figure 4a, no obvious weight loss has been observed in the low-temperature range for TEMs samples without crosslinking, which corresponds to the foaming height of 0μm in the static Thermomechanical Analysis (TMA, Figure 4b). The indicates that TEMs do not contain alkane in absence of crosslinking agent. When the dosages of crosslinking agent are 0.046%, 0.093% and 0.19%, the TG curve shows two stages of weight loss, the first weight loss corresponds the escape of alkanes. Moreover, the higher the degree of cross-linking, the more alkane it contains. Compared with the first weight loss curve of TEMs with 0.19% and 0.093% crosslinking agent, it was found that the slope is much steeper for the former than for the latter, which reveals that the release rate of alkane inside TEMs is rapid for 0.19% cross-linking agent than for 0.093% cross-linking agent in the process of expansion. Correspondingly, the greatest expansion height (D_{max}) also decreases from 1240μm to 857μm as shown in Table II. This is because too much higher crosslinking density increases the rigidity of the polymer shell whilst decreases its flexibility. As a result, even though more alkanes are enclosed inside, the excessive cross-linked shell limits the expansion of TEMs, and finally the TEMs rupture under the volatilization of alkanes, resulting in a low expansion ratio. On the contrary, when the shell is not cross-linked, the gas tightness of TEMs is too low to withstand the pressure generated by expansion.

Table II

Foaming properties and Foaming temperature of TEMs with different content of EGDMA

Crosslinker concentration/ (%)	T_{start}/ (°C)	T_{max}/ (°C)	Expansion ratio/ (d/d_0)	D_{max}/ (μm)
0	-	-	-	0
0.046	109	126	4.1	1021
0.093	110	127	5.0	1240
0.19	112	136	3.4	857

a: No expansion was observed during heating.

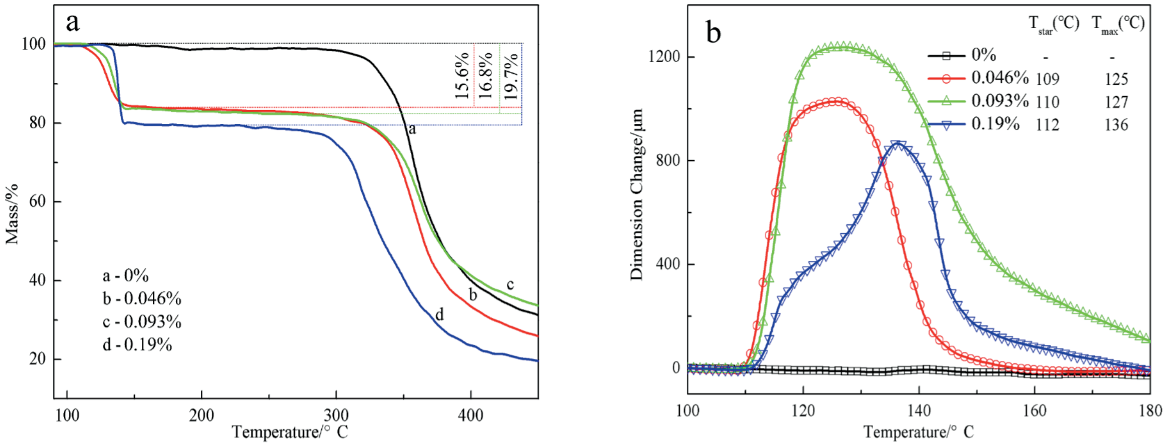


Figure 4. Thermodynamic analysis of TEMs with different dosage of EGDMA: **(a)** TG curve, **(b)** TMA curve.

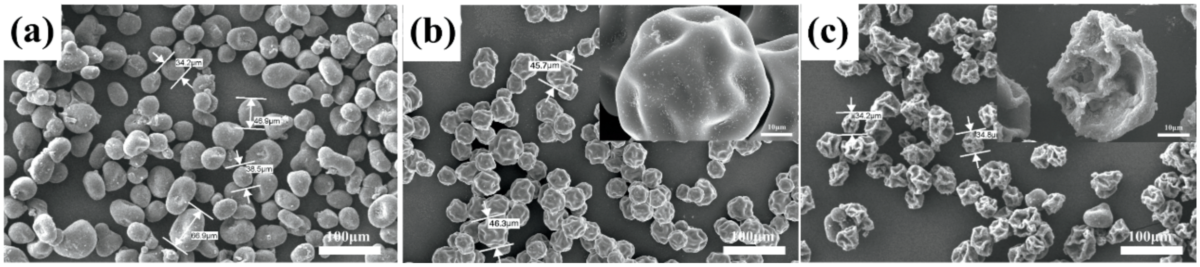


Figure 5. SEM of TEMs with different content of EGDMA: **(a)** 0%, **(b)** 0.093%, **(c)** 0.19%.

In addition, the cross-linking density also affects the surface morphology of the TEMs. As shown in Figure 5, with the increase of EGDMA, TEMs gradually transforms from regular spheres to irregular particles. This is because the shrinking force generated by the non-crosslinked polymer shell is smaller, and the internal pressure generated by the volatilization of i-pentane inside the microsphere is dominant, therefore, the TEMs show a smoother morphology and higher sphericity (Figure 5b). Further increase the crosslinking agent density, the shrinking force gets bigger, while the internal pressure is relatively small, so the surface morphology of the TEMs gets irregular gradually.

Effect of dosage of alkane on expansion property and temperature of TEMs

Keeping other parameters unchanged, the effect of i-pentane concentration on expansion property and temperature of TEMs was investigated. Figure 6a is the DSC curve of TEMs prepared with the concentration of 3.7%, 7.4%, 11.1%, and 14.8% i-pentane, and the endothermic enthalpy(ΔH) during the expansion of TEMs were listed in Table III. It can be seen that with the increase of i-pentane (3.7%, 7.4% and 11.1%), the ΔH increases, which means the content of i-pentane enclosed by TEMs increased. However, when the dosage of i-pentane reaches 14.8%, the content of i-pentane in TEMs decreases instead. This may be due to the excessive i-pentane with low boiling point leads to the excessive internal pressure in the polymerization process, which makes the microspheres unable to seal the i-pentane perfectly.

Dosage of alkane also influences the T_{start} and T_{max}. As shown in Table III, both the T_{start} and T_{max} decrease with the increase of i-pentane contained by the TEMs. This is because when the dosage of i-pentane contained inside TEMs was small, the polymer shell of TEMs was relatively thick. At the same temperature, the pressure inside TEMs containing less i-pentane is lower. In order to make TEMs expand, the temperature needs to be increased continuously. On the contrary, when TEMs contain more i-pentane, they would expand rapidly at a lower temperature, so the T_{start} and T_{max} shifts to the lower temperature range. Figure 6b reveals the relationship between expansion ratio and i-pentane concentration, when the dosages of i-pentane are 7.4% and 11.1%, TEMs show more high expansion heights, but TEMs with 11.1% dosage of i-pentane exhibits a very sharp expansion curve, which indicates that even though TEMs have achieved a satisfied expansion height, it could not withstand the high internal pressure and rupture prematurely at a lower temperature, reducing its foaming stabilization.

Table III

Effect of foaming agent dosage on the expansion property and foaming temperature of thermally expanded microspheres

Isopentane concentration/(wt%)	T_{start}/(°C)	T_{max}/(°C)	Expansion ratio/ (d/d_0)	D_{max}/(μm)	ΔH/(J/g)
3.7	114	138	2.3	253	12.76J/g
7.4	110	128	5.0	1240	47.8J/g
11.1	109	116	5.2	1341	51.32J/g
14.8	106	111	3.4	619	30J/g

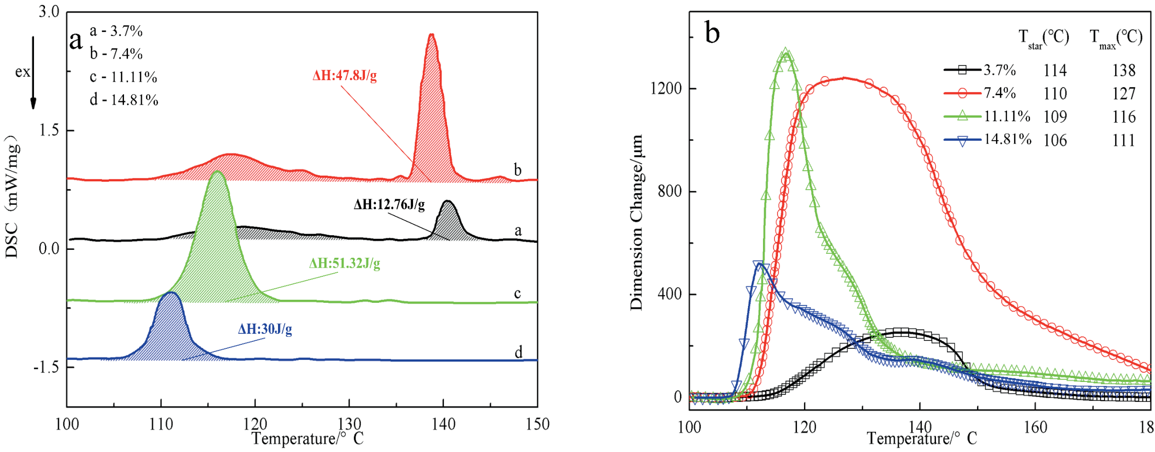


Figure 6. Thermo dynamic analysis of TEMs with different content of Isopentane: **(a)** DSC curve, **(b)** TMA curve.

Effect of monomer mass ratio on expansion property, temperature and solvent resistance of TEMs

As well known to all, each monomer has its own function, so the resultant properties such as gas tightness, heat-resistance, toughness, and solvent-resistance of TEMs are directly determined by the monomers in different proportions. The effects of AN, MMA and VAC mass ratio on the expansion properties and temperature of TEMs were shown in Table IV.

Table IV

Effect of monomer ratio on the expansion property and expansion temperature of thermally expanded microspheres

AN/MMA/VAC[a] (%)	T_{start}/(°C)	T_{max}/(°C)	Expansion ratio/ (d/d_0)	D_{max}/ (μm)
5/3/1	107	111	3.1	784
6/3/1	109	115	2.9	722
7/3/1	110	128	5.0	1240
8/3/1	111	129	4.8	1198
7/1/1	106	111	3.2	787
7/2/1	110	129	3.3	810
7/3/1	110	128	5.0	1240
7/4/1	111	117	2.3	549
7/3/0.5	112	116	1.6	402
7/3/1	110	128	5.0	1240
7/3/1.5	103	116	11	2730
7/3/2	98	118	3	752

a: AN/MMA/VAC is the mass ratio of the three monomers

Generally, for the heating process of the TEMs, the TG reflects two weight loss stages, the first is ascribed to the volatilization of alkane at low boiling point contained in the TEMs, with a temperature range of 100°~150°C, and the second is the weight-loss of the polymer shell, which usually occurs above 300°C. Here, the first stage corresponds to the expansion process of the TEMs. Differential thermogravimetry(DTG) can be used to reveal weight loss rate and fine structure of TEMs. It can be seen from the DTG in Figure 7b, with the increase of AN, the weight loss rate of TEMs decreases, and the peak of the maximum weight loss moves toward higher temperature, and meanwhile, the weight loss rate curve shows obvious double peaks for 5/3/1, 6/3/1, 7/3/1. This is because the lower content of AN results in the leakage of low boiling point alkanes at low temperature. In this case, TEMs have not fully expanded, so the weight loss rate curve becomes sharper and the corresponding D_{max} (Figure 7a) is very low. With the increase of AN, the weight loss rate exhibited a double-peak curve. This is because the increase of AN strengthens the gas tightness and the heat-resistance of polymer shell, resulting in more TEMs expand in the high-temperature region and relatively fewer TEMs expand in the low-temperature region. That is why the weight loss curve shows a double-peak in the DTG (Figure 7b) and the D_{max} in Figure 7a increases rapidly. However, when the mass ratio of three monomers reached 8/3/1, the polymer shell becomes too rigid and most of TEMs expand in the high-temperature region. Therefore, the weight loss rate curve (Figure 7b) changes again from a double-peak to a single-peak. Accordingly, the expansion ratio of TEMs decreases from 5.0 to 4.8 times (Table IV).

Keeping the proportion of AN and VAC constant, the effects of MMA concentration on T_{start} , T_{max} and D_{max} of TEMs were shown in Figure 8. It can be seen that the T_{start} of TEMs tends to rise gradually but the T_{max} of TEMs first increases and then decreases with the increase of MMA content until the mass fraction of MMA reaches

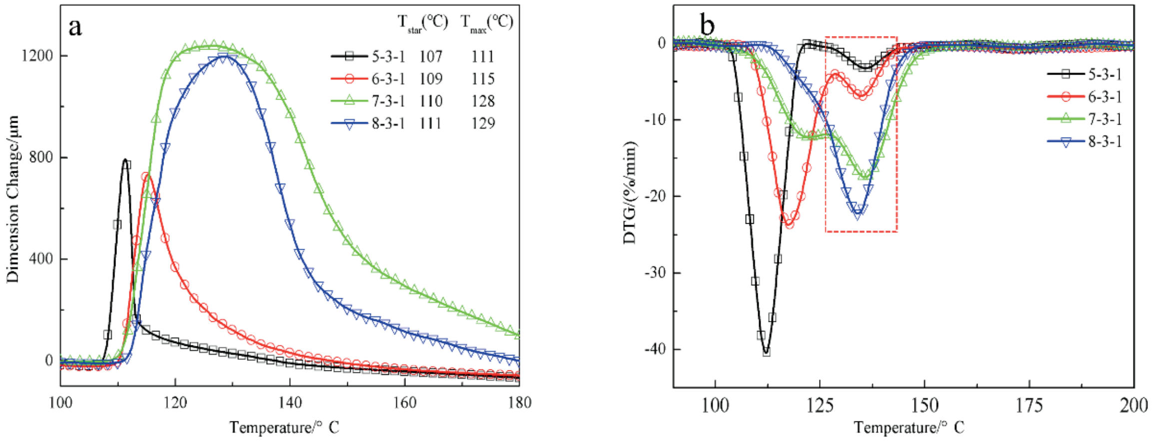


Figure 7. Thermo dynamic analysis of TEMs with different content of AN: **(a)** TMA curve, **(b)** DTG curve.

4, meanwhile, the maximum expansion height (D_{max}) of TEMs firstly increases and then decreases where the turning point occurs in the case of mass fraction of MMA increases to 3.When the mass fraction of MMA is 1, TEMs have poor expansion properties and the lowest expansion temperature. Because the mass ratio of AN is relatively higher in this case that the polymer shell of TEMs shows higher rigidity and lower flexibility, as a result, TEMs are easy to rupture during the expansion process. Correspondingly, a sharp weight loss peak can be observed in DTG in Figure 8b. With the increase of MMA mass fraction, the double-peak occurs and the second peak enlarged and the first peak weakened gradually in Figure 8b. Because copolymerization of MMA and AN can break the regularity of PAN, imparting the polymer shell of TEMs a certain of flexibility, therefore, the curve of the weight loss rate becomes flat and the D_{max} increases gradually. Besides the addition of MMA can also enhance the heat-resistance of the polymer shell, the T_{start} of TEMs show an increasing tendency (Figure 8a). But excessive MMA has a negative effect on the expansion property and temperature of TEMs, when the mass fraction of MMA increases to 4, a sharp weight loss peak occurs again in DTG, and the D_{max} shift to the lower temperature range. The reason is that the excessive MMA weaken the intermolecular force of the polymer shell, thereby reduces the gas tightness of the TEMs. This is not beneficial for the expansion of the TEMs, from the data in Table IV, the expansion ratio of TEMs is also reduced from 5 times to 2.3 times.

Similarly, the mass fraction of VAC also influences the T_{start} ,T_{max} and D_{max} of TEMs. It can be observed from TMA in Figure 9a that the T_{start} of TEMs shows a declining tendency with increasing in mass fraction of VAC; whilst the D_{max} and expansion ratio of TEMs increases (Table IV). Because the addition of VAC improves the ductility of the polymer shell, which means the polymer shell is easier to soften and deform during expansion. Therefore, a smoother curve of the weight loss rate in DTG (Figure 9b) and a greater expansion ratio are obtained. However, as the soft part of the polymer shell, excessive mass fraction of VAC will decrease the T_{start} of the TEMs, for example, when the mass fraction of VAC was up to 2, the T_{start} of TEMs is only 98°C (Figure 9a), which will cause the TEMs expansion ahead before pre-dried.

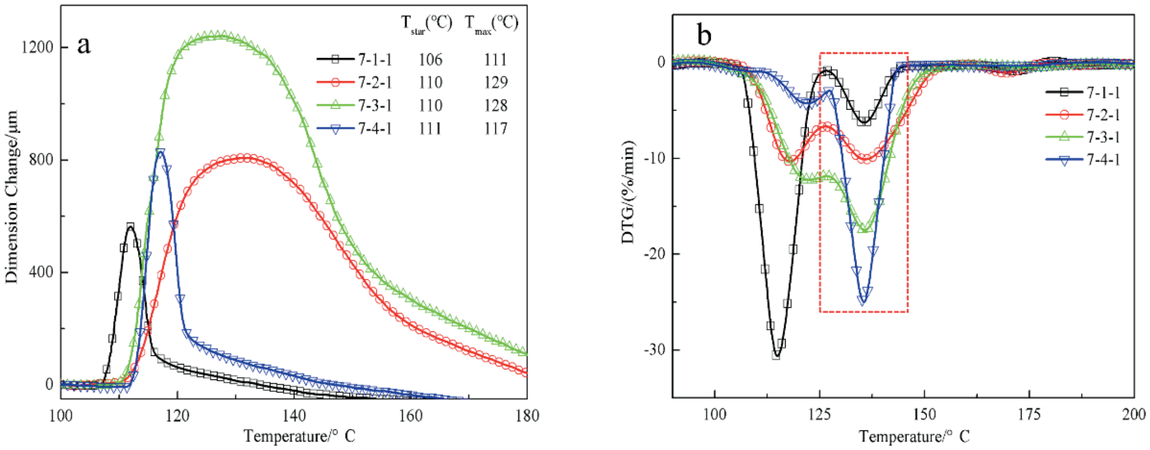


Figure 8. Thermo dynamic analysis of TEMs with different mass fraction of MMA: **(a)** TMA curve, **(b)** DTG curve

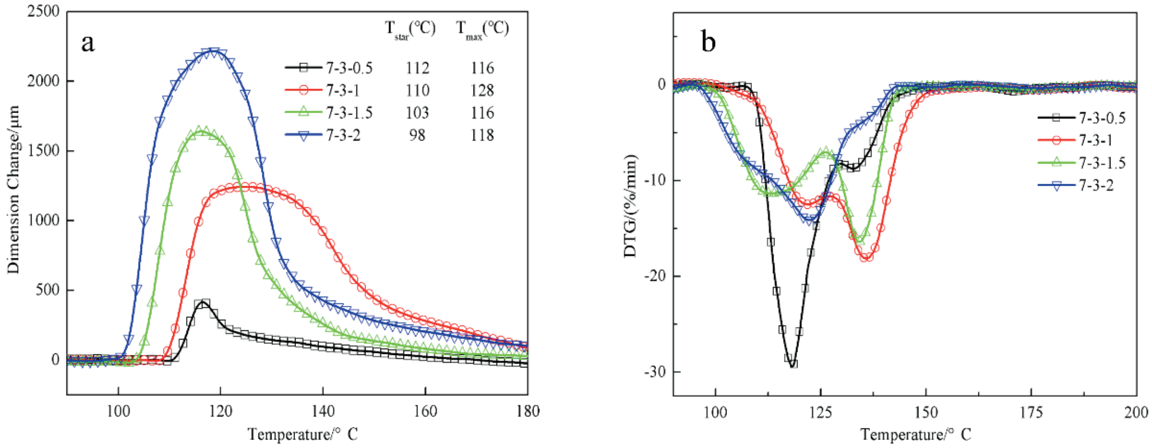


Figure 9. Thermo dynamic analysis of TEMs with different content of VAC: **(a)** TMA curve, **(b)** DTG curve.

In a real foam coating system, TEMs are frequently applied together with polyurethane or acrylic resin. The solvent-based resins always contain some solvents such as *N,N*-dimethylformamide (DMF), acetate esters, acetone and so on. Similarly, water-based resin sometimes also contain acetone and/or DMF. Therefore, the polymer shell of TEMs should have a resistance to solvents. In this experiment, 2wt% aqueous acetone, 2wt% aqueous DMF and 98wt% ethyl acetate were used to simulate water-base and solvent-base resins. TEMs with the mass fraction of AN/MMA/VAC of 7/3/1 were selected and soaked for 4 hours in these simulation systems, and then the expansion property of the corroded TEMs was tested by DSC and shown in Figure 10. It can be observed that all of the corroded TEMs shows endothermic peaks, indicating that TEMs have preferable solvent-resistance and expansion characteristics. Besides, the T_{start} of the corroded TEMs (the part in the red circle) decreases while the intensive expansion temperature (the part in the blue circle) increases slightly compared with control sample and the corresponded endothermic enthalpies also shows a declining trend, This revels that the polymer shell of TEMs are swelled to some degree by organic solvents so they cannot prevent the inner blowing agent from escaping before TEMs expand. From SEM in Figure 11, it is found that ethyl acetate has little effect on state of TEMs but DMF and acetone caused the soaked TEMs aggregating together and their surface become smoother (Figure 11c), indicating that the solvent resistance of TEMs is better for ethyl acetate than for DMF and acetone.

Morphology of split leather foam coating

The as-prepared TEMs were blended with WPU in proportion as well as other additives, and then the mixture was coated on split leather, pre-dried at 80°C for 1 min, and then foamed at 120°C to obtain foam coating layer. The SEM of the surface (Figure 12a) and

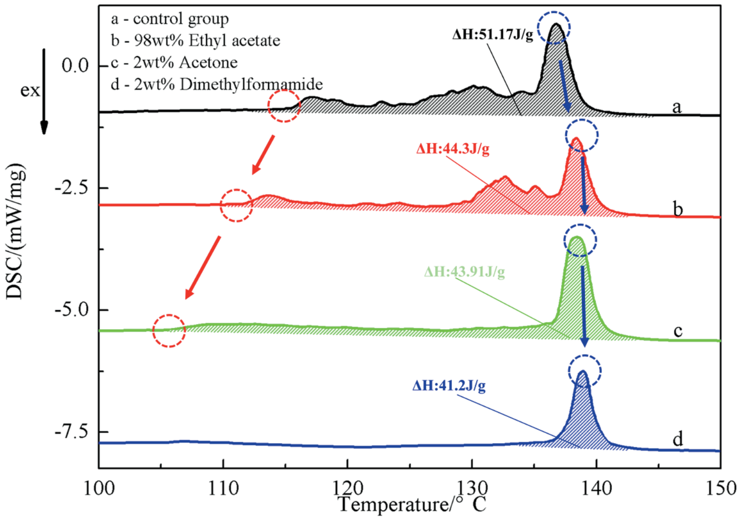


Figure 10. DSC curves of TEMs immersed in different solvent systems for 4h

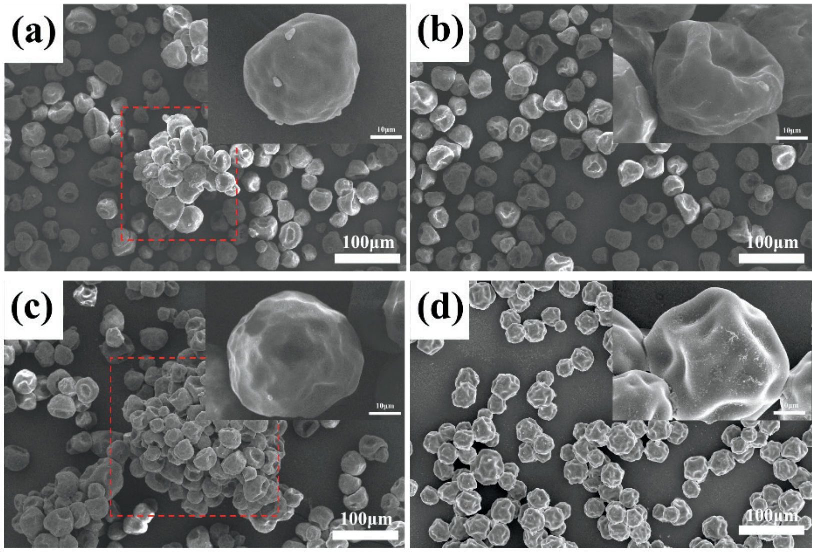


Figure 11. SEM of TEMs immersed in different solvents for 4h: **(a)** 2wt% acetone solution, **(b)** 98wt% ethyl acetate, **(c)** 2wt% DMF, **(d)** control group.

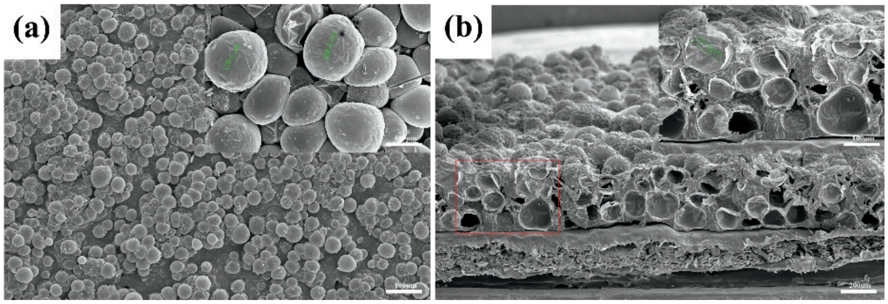


Figure 12. SEM of split leather foam coating: **(a)** surface, **(b)** cross section.

cross section (Figure 12b) of the foam coating are shown in Figure 12. It can be seen that the thickness of the foam coating is increased and hollow spheres with relatively uniform size are formed in the coating. Moreover, the cell walls are regular and compact, and few broken cells, combined cells, or large cells can be observed, which guarantees the resilience, fullness, air and moisture permeability of the coating layers.

Matting and mending effect of foaming coating

The as-prepared TEMs were mixed with WPU in proportion as well as other additives, and then the mixture was coated on the leather with scratches on the grain surface, pre-dried at 100°C for 1 min, and then foamed at 120°C for 3s to obtain the repaired leather. The leather surface before and after the repair is shown in Figure 13. It can be seen that the finished leather before foaming (Figure 13b) has obvious surface defects. After foaming (Figure 13c and Figure 13d), the coating basically covered all the original damages. Further study, found that the coating consists of two foaming layers (Figure 13d), showing a stronger covering performance. At the same time, the surface of the foamed leather is uniform and compact (Figure 13d), and good matting effect was also obtained

Conclusion

A kind of TEMs for foam coating was prepared and the effects of aqueous additive, crosslinking degree, alkane content, and mass fraction of comonomers on diameters and distribution, expansion ratio, expansion temperature and solvent-resistance of resultant TEMs were investigated. The conclusions are shown below:

(1) The additive NaCl can decrease the solubility of monomers in the water phase and then affect the diameter distribution and size of microspheres. At saturation concentration, the diameter of prepared TEMs is up to 47 μm with uniform distribution and more regular shapes.

(2) A proper crosslinking degree can improve the expansion properties and expansion temperature of microspheres, but the excessive crosslinking degree will restrain the expansion of TEMs. Appropriate expansion temperature (120°C) and maximum expansion ratio (5.0) can be obtained simultaneously for TEMs with 0.09% crosslinking agent.

(3) The i-pentane amount influences the expansion temperature and expansion ratio. Too low amount of i-pentane increased the expansion temperature but decreased the expansion ratio. Whilst too much i-pentane will result in the decrease of expansion temperature and break ahead of TEMs, the suitable foamability and expansion temperature occurred in a case of alkane amount was up to 7.4%.

(4) The mass fraction of co-monomers (AN/MMA/VAC) was controlled to 7/3/1, the resultant TEMs show designable T_{start}, T_{max} and expansion ratio together with good solvent resistance.

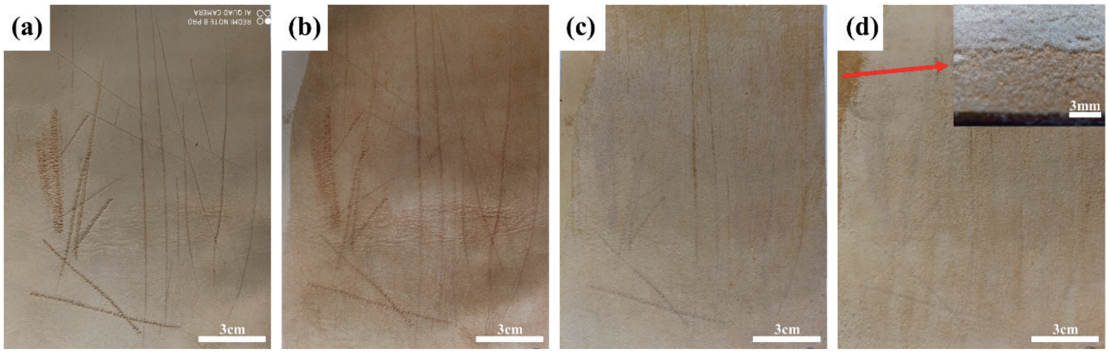


Figure 13. Surface of the finished leather: **(a)** control sample, **(b)** Before foaming, **(c)** One layer foaming, **(d)** Two layers foaming.

(5) TEMs can be used make foaming layer of split leather and matting and mending layer of damaged grain leather. The former can improve the resilience, fullness, air and moisture permeability of split leathers, and the latter can cover the damage of leather and impart the repaired leather suitable matting and mending effect.

Acknowledgement

We are grateful for the financial support from national key R&D (2017YFB0308600), innovation and entrepreneurship team project of Qingyuan (QK [2018] No.31) and key R&D of Shandong (major scientific and technological innovation project) project (2019jzzy010355)

References

1. Zhang X, Wang P F, Sun D W, et al. Dynamic plastic deformation and failure mechanisms of individual microcapsule and its polymeric composites. *Journal of the Mechanics and Physics of Solids*, **139**: 25, 2020.
2. Hou Z, Xia Y, Qu W, et al. Preparation and Properties of Thermoplastic Expandable Microspheres With P(VDC-AN-MMA) Shell by Suspension Polymerization. *International Journal of Polymeric Materials & Polymeric Biomaterials*, **64**(8), 427-431, 2015.
3. Nordin O, Malmström E, Hammer] C. Suspension polymerization of thermally expandable core/shell particles. *Polymer*, 2006.
4. Xue B, Zhang J, Bao Y. Acoustically and Thermally Insulating Epoxy Foams Prepared by Non-traditional Expandable Microspheres. *Polymer Engineering & Science*, 2018.
5. Zhang R Z, Chen J, Huang M W, et al. Synthesis and Compressive Response of Microcellular Foams Fabricated from Thermally Expandable Microspheres. *Chinese Journal of Polymer Science*, 2018.
6. Nishiyama Y, Uto N, Sato C, et al. Dismantlement behavior and strength of dismantlable adhesive including thermally expansive particles. *International Journal of Adhesion & Adhesives*, **23**(5), 377-382, 2003.
7. Ahmad M. Flexible vinyl resiliency property enhancement with hollow thermoplastic microspheres. *Journal of Vinyl & Additive Technology*, **7**(3), 2001.
8. Fan H, Chen Y, Yan J, et al. Artificial leather / synthetic leather materials and technology. China Light Industry Press, 2017.
9. Cheng G, Cheng H, Cheng Y, et al. A kind of YangBuck resin for leather and its preparation method. Chinese patents: CN107603194A, 2017.09.30.
10. Preparation and Application of Conductive Polyaniline-Coated Thermally Expandable Microspheres. *Polymers*, 2018.
11. Lin H, Chen H, Shi M, Kron A L, et al. Covering finishing agent for leather primer. *Leather and Chemical*, **32**(04):1-4+39.2015.
12. Chen Y, Lu A, Liu H, et al. Study on Micro Foam Finishing Technology and foaming agent. *Asia International Leather Science and technology conference. China Leather Industry Association*. 1998.
13. Xie G, Wang Z, Bao Y. Expansion Properties and Diffusion of Blowing Agent for Vinylidene Chloride Copolymer Thermally Expandable Microspheres. *Materials*, **13**(17), 3673, 2020.
14. Jonsson M, Nordin O, Kron A L, et al. Thermally Expandable Microspheres with Excellent Expansion Characteristics at High Temperature. *Journal of Applied Polymer Science*, **117**(1), 384-392, 2010.
15. Olle L, Bou J, Shendrik A, et al. Sustainable solvent-free finishing of patent leather using carbonyl-functional resins. *Journal of Cleaner Production*, **65**(FEB.15), 590-594, 2014.
16. Liu J. Preparation and foaming properties of core-shell thermoplastic expanded microspheres. *Hefei University of Technology*, 2015.
16. Jiang, Y, Synthesis and research of thermal expansion microspheres with excellent foaming properties. *Yangzhou University*, 2015.
18. Yi Q, Li J, Zhang R, et al. Preparation of small particle diameter thermally expandable microspheres under atmospheric pressure for potential utilization in wood. *Journal of Applied Polymer Science*, 49734, 2020.
19. Ji L, Jiang Y, Qiao W, et al. Synthesis of Low-temperature Expanding Microspheres under Atmospheric Pressure. *Journal of Acta Polymerica Sinica*, (**08**), 40-46, 2015.
20. Fu H, Gong W, Chen B, et al. Influence of electrolytes on thermal expansion microcapsules. *Journal of Macromolecular Science Part A*, **56**:1,104-114, 2019.
21. Kawaguchi Y, Oishi T. Synthesis and properties of thermoplastic expandable microspheres: The relation between crosslinking density and expandable property. *Journal of Applied Polymer Science*, **93**(2): 505-512, 2010.
22. Jonsson M, Nordin O, Kron A L, et al. Influence of crosslinking on the characteristics of thermally expandable microspheres expanding at high temperature. *Journal of Applied Polymer Science*, **11**, 1219-1229, 2010.

Lifelines

Bindia Sahu, see JALCA 114, 359, 2019

Jay Prakash Ala, see JALCA 109, 411, 2014

Gladstone Christopher Jayakumar, see JALCA 106, 68, 2011

K. Phebe Aaron, see JALCA 107, 102, 2012

K. Krishnaraj, see JALCA 107, 102, 2012

Haolin Zhu is a Master's degree student in School of Materials Science and Engineering at Zhengzhou University, Zhengzhou, China, majoring in leather chemistry and engineering. His research is focused on green leather chemicals for cleaner leather making.

Fang Wang graduated from Zhengzhou University with a Bachelor's degree in 1991. She has been working in School of Materials Science and Engineering at Zhengzhou University since 1993. She is now a senior engineer, with the research field of leather structure and properties.

Keyong Tang received his PhD degree in 1998 from Sichuan University, Chengdu, China. He is a professor in School of Materials Science and Engineering at Zhengzhou University, Zhengzhou, China. He worked as a visiting scientist in Texas Tech University in 2008-2009. His research interests include the leather structure and properties, as well as cleaner leather making. He has published more than 100 papers, co-authored 4 books and edited 1 book in the field of leather chemistry and engineering.

Jie Liu received his PhD degree in 2007 from Institute of Mechanics, Chinese Academy of Sciences, Beijing, China. He currently is an associate professor in the School of Materials Science and Engineering at Zhengzhou University, Zhengzhou, China. From 2016 to 2017, he worked as a visiting scientist at ERRC, USDA in Cheng-Kung Liu's group. His current research interests focus on green composite materials based on natural polymers and their applications in packaging, biomedical and environmental fields.

Xuejing Zheng received her PhD degree in 2002 from the Institute of Chemistry, Chinese Academy of Sciences, Beijing, China. She is now a professor in School of Materials Science and Engineering at Zhengzhou University, Zhengzhou, China. Her current research interests are focused on green composite materials based on natural polymers.

Shufa Qin was graduated from School of Materials Science and Engineering, Zhengzhou University, China, with a Master's degree in Leather Chemistry and Engineering in 2005. He is currently a senior engineer with the research interest on cleaner leather making.

Guodong Huang is currently studying for Master's degree with Prof. Haojun Fan at Sichuan University, and his research mainly focuses on synthetic leather and thermal expansion microspheres.

Zhixian Lin is currently studying for Master's degree with Prof. Haojun Fan at Sichuan University, and his research mainly focuses on synthetic leather and water-based polymer materials.

Haojun Fan, see JALCA 100, 29, 2005.

Jun Xiang, Ph.D., associate researcher, PhD degree in Chemistry from University of Sherbrooke, Canada in 2018, and his research mainly focuses on design, synthesis and application of stimulus response functional polymer materials, inorganic/organic hybrid functional materials and new materials for green manufacturing of synthetic leather.

Chong Zheng works at Qingyuan Qili Synthetic Leather Company. His research mainly focuses on synthetic leather and water-based polymer materials.

Zhiqing Luo works at Qingyuan Qili Synthetic Leather Company. His research mainly focuses on synthetic leather and water-based polymer materials.

Corrigendum

Corrigendum for manuscript "Influence of Ultrasound on the Adsorption, Diffusion and Kinetics of Leather dyeing process: Mechanistic Insight" in JALCA 115(7), 239-247, 2020.

The corrections for this manuscript "Influence of Ultrasound on the Adsorption, Diffusion and Kinetics of Leather dyeing process: Mechanistic Insight" are as follows:

Page 239: The portion of the abstract discussing the Freundlich constant and the Langmuir parameter should read:

> "The Freundlich constant (K_f), Langmuir parameter (Q_m), Intra Particle diffusion rate constant (K_d) Apparent Diffusion coefficient (D) and Pseudo First order kinetic constant, K_1 have been calculated to be 18.67 mg/g , 50 mg/g, **1.7 mg/g min$^{0.5}$, 1.89 * 10^{-6} cm^2/s** and **0.006 min^{-1}** respectively for ultrasound assisted leather dyeing as compared to that of 0.1 mg/g, 26.67 mg/g, 0.733 **mg/g min$^{0.5}$**, 0.19 * 10^{-6} cm^2/s and 0.003 **min^{-1}** respectively for control process."

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

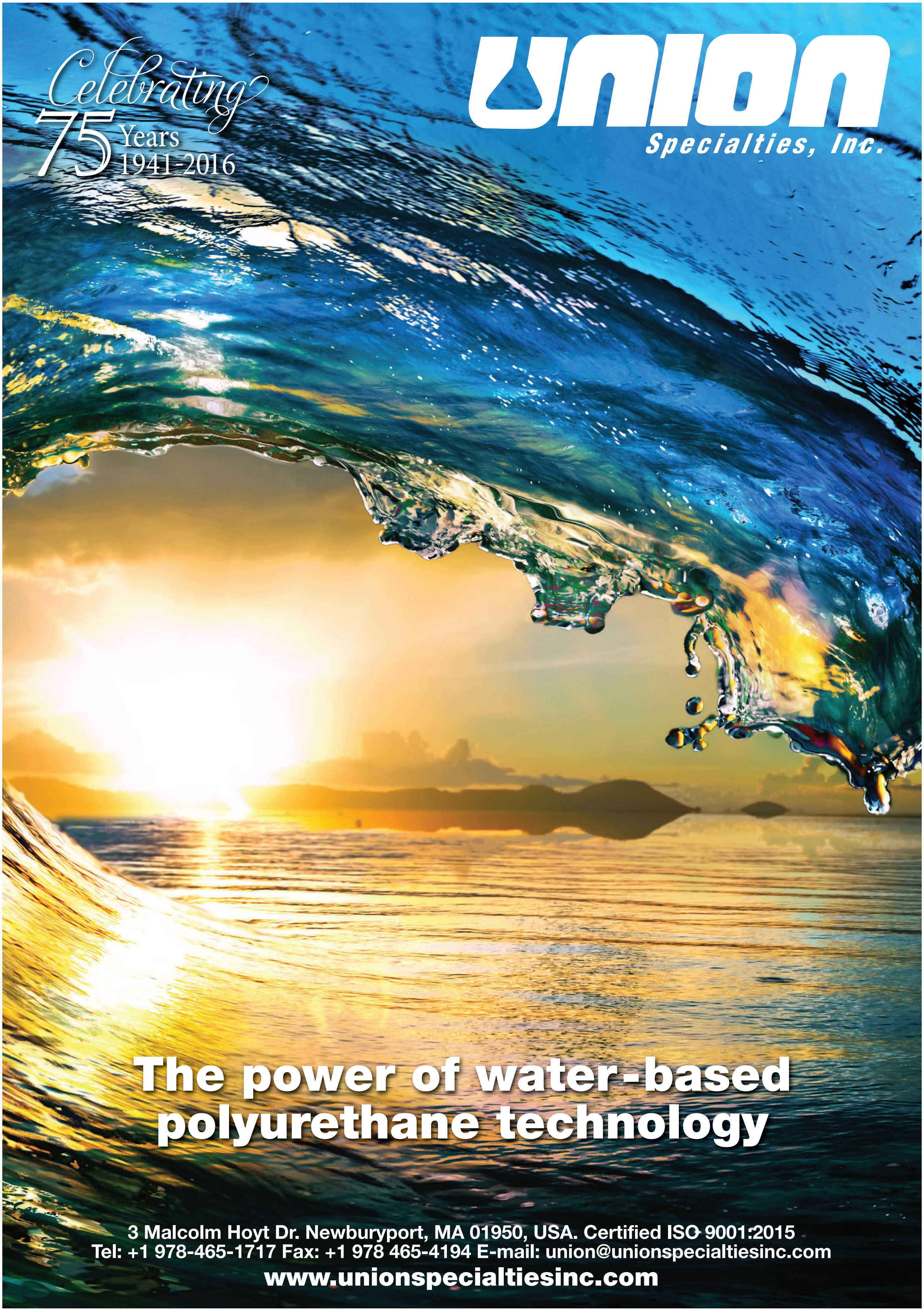
Stay Clean

Low-VOC

PolyMatte®

stahl

www.stahl.com


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

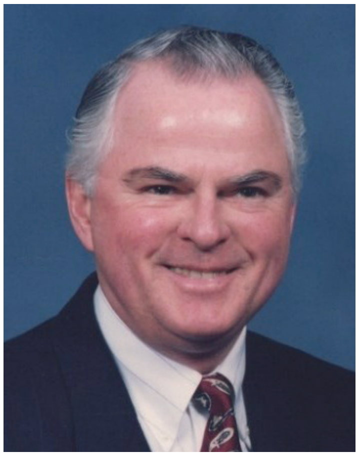
COLD
Milling

Smooth Leather Milling

Erretre
Tannery Innovations

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

Obituary



Leo Devarenne, age 84, of Rockford, Michigan, peacefully passed into eternity while at home surrounded by his family on June 6, 2021. He stoically outlived the prognosis of esophageal cancer in these last few years. Leo was born on August 4, 1936, the youngest of six siblings, in Danvers, Massachusetts. Leo is lovingly remembered by Sue, his wife of 58 years, and his family Brian and Sandy Devarenne, Mike and Kathleen Devarenne, Tim Devarenne, and grandchildren Catherine, Emma, Sophie and Anna. After graduating from Danvers High School in 1953, Leo studied leather chemistry at Lowell Technological Institute. He went on to work in the leather industry his entire career. His first job out of college was in New York City in chemical sales for the leather industry. That job later took him to Chicago, where on a Young Catholics outing at Buckingham Fountain, he met Sue Miller, who would become his wife. They married in 1962, and after their honeymoon at Niagara Falls, continued on to their first home in Massachusetts. Leo's next job brought him to Wolverine World Wide, the maker of Hush Puppies shoes, in Rockford, Michigan. Leo was a dedicated Wolverine employee for 35 years. He started as a leather chemist, and then technical director. Later, he enjoyed traveling the world as a consultant in countries such as Brazil, Russia, and China. His business travel introduced him to adventurous food and drink which he enjoyed sharing with his family.

Leo joined the American Leather Chemists Association as a student member in 1958. In 1959 his membership was changed to associate and then he became a regular active member in 1971. In 1998 he was awarded life membership in the Association. He served the Association in many positions including the following: Council Member from June of 1979 to June of 1981 and again from June of 1989 to June of 1992; Chair of the Committee on Leather from September 1979 to June of 1981; Methods Committee from 1981 to 2002; Research Liaison Committee for 1982 and then Chair from February 1986 to February 1995; Selection Committee for O'Flaherty for 1984 and then Chair for 1995; Nominating Committee 1985, 1987, 1993 and 1997; Chair of Board of Tellers for 1985; Co-Chaired the 1978 symposium on Garment Leather; Specifications Review from 1988 to 2002; Chaired the 1988 and 1989 symposiums on Dyestuff and Pigments – their Use in Coloring Leather; Representative on IULTCS Colorfastness Commission (I.U.F.) 1992 to 1994; and O'Flaherty Award Recipient for 1992;

Although Leo left Boston, he retained his accent and love for the Red Sox, Patriots, lobster, and fried clams. Leo enjoyed fishing, birding, and gardening, but his favorite activity was cutting, splitting, and precisely stacking wood for winter fires in the hearth. With a young family, Leo towed a pop-up camper to state and national parks. As a retiree, he piloted a motorhome from coast to coast and from Alaska to Mexico. Leo was a kind, philanthropic, generous man who supported his entire family throughout their many pursuits and delighted in family gatherings. He was also a dedicated Catholic who never missed weekly mass no matter where he was in the world. Visitation was on June 11 at 10:00 am at Our Lady of Consolation Catholic Church, 4865 11 Mile Rd., Rockford. A Funeral Mass followed at 11:00 am. In lieu of flowers, please consider a donation to the Cornell Lab of Ornithology.

INDEX TO ADVERTISERS

116th ALCA
ANNUAL CONVENTION
Change of Date:
June 21–24, 2022
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, June 21

Golf Tournament, Opening Reception and Dinner

Wednesday, June 22

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

Thursday, June 23

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


www.CHEMTAN.com
Made with
WATERPROOF
TECHNOLOGY
CHEMTAN
Tel: (603) 772-3741 • Fax: (603) 772-0796 • www.CHEMTAN.com