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Nonionic Short Fluorocarbon Chain Surfactants for Improving Application Properties of Acrylic Resin in the Retanning of Wet-blue Leather

by

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Abstract

Acrylic resin (AR) is one of the most commonly used leather retanning agents owing to its excellent selective filling property and low cost. However, there are some defects affecting the quality of wet-blue leather in the practical application of AR, such as "excessive convergence", "detanning", and "fading". Herein, the nonionic short fluorocarbon chain surfactants (F6-m) combined with AR for retanning wet-blue goat leather to further improve the application properties of AR. In a series of comparative experiments, the grain surface state and mechanical properties of leather retanned with 4 wt% AR and 2wt% F6-400 are preferred. Moreover, after dyeing, the dye adsorption rate and a* (red-greenness) value of AR/F6-400 retanned leather are higher than that of leather retanned with AR alone. The above issues reveal that F6-400 can improve application properties of AR in the retanning of wet-blue leather to a certain extent, benefiting to further upgrade the quality of leather.

Introduction

Retanning is one of the most critical unit operations in leather manufacturing, which can significantly affect the properties of leather, such as homogeneity and fullness.[1] Currently, acrylic resin (AR) is still widely used in the retanning of leather owing to satisfactory selective filling property and low cost.[2] However, a large number of carboxyl ions on AR also yield some abominable defects in the practical application for chrome-tanned leather. For example, carboxyl ions of AR may over combine with chromium ions on the leather grain surface during the penetration, resulting in the "excessive convergence" of leather grain surface. Furthermore, chrome-free/less tanned leather has become an inevitable trend owing to the environmental pollution associated with the release of chrome.[3] Predictably, during the retanning process of chrome-less tanning leather, carboxyl ions on AR could easily capture chromium ions originally combined with collagen fibers, bring about the leather "detanning"; and compete with dye molecules (anionic dyes commonly used in leather production) for binding sites on leather, engendering the leather "fading".[4] Eventually, these unamiable issues greatly affect the property and economic value of leather.

In leather manufacturing, surfactants, appearing in almost all processes, play an important role in wetting, dispersing, emulsifying, solubilizing, etc.[5,6] The most fundamental reason is that surfactants can significantly reduce the surface tension of the solution[7] containing leather chemicals, facilitating leather chemicals to spread on the leather surface or penetrate the leather interior, thereby enhancing the production efficiency and product quality. Different from ionic surfactants, nonionic surfactants are in possession of adorable resistance for salt and pH, which can still hold stable surface activities in the attendance of electrolytes.[8] Especially, this feature of nonionic surfactants is extremely important in the face of complex electrolytes in leather processing. In addition, research[9,10] has shown that in ionic/nonionic mixed systems, the nonionic species can shield the ionic groups on ionic species via the steric hindrance effect. Inspired by this, if AR and nonionic surfactants are used together in the retanning of wet-blue leather, nonionic surfactants can not only reduce the surface tension of the bath for promoting the spreading and penetration of AR, but also shield the part of carboxyl ions on AR for inhibiting the excessive combination with chromium ions. Hence, the above advantages are expected to ameliorate defects of AR in the retanning of wet-blue leather, and ultimately further improve the leather quality.

Compared with common hydrocarbon surfactants, fluorinated surfactants usually have a higher surface activity. Since their advent in the 1950s,[11] the traditional long fluorocarbon chain surfactants, represented by perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), have been widely applied in leather, textile and other fields.[12,13] However, it has been found that PFOA and PFOS have awful disadvantages such as high persistence and bioaccumulation,[14,15] and are subsequently classified as persistent organic pollutants,[16] so they have been banned in many fields. In recent years, researchers have turned their attention to the development of short fluorocarbon chain (less than seven CF_n groups) surfactants, and these short fluorocarbon chain surfactants have been confirmed to be more environmentally friendly.[17,18] At present, although there are many reports on short fluorocarbon chain surfactants, there are few reports on their application in leather retanning.

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In this paper, the nonionic short fluorocarbon chain surfactants (F6-m) reported in our previous work[19] and AR were used together in the retanning of wet-blue goat leather.

At the same time, to better implement the current environmental protection concept of less chrome, the wet-blue goat leather was not processed with extra chrome-retanning. The effects of the type of F6-m as well as the dosage of AR and F6-m on the leather properties were systematically investigated. The grain surface and cross section morphologies of leather were carefully assessed. Furthermore, the dyeing effect of the retanned leather also was evaluated by the common color difference parameters. The results showed that when AR and F6-m were applied together in the retanning of wet-blue leather, those defects including the grain surface "excessive convergence", "detanning", and "fading" were eliminated to a certain extent, and the application properties of AR are obviously improved. This work provides a promising method for further enhancement of leather quality, and broadens the application range of fluorinated surfactants in the leather industry.

Materials and Methods

Materials

Wet-blue goat leather was purchased from the Chengdu Qingyang District Century Leather Management Department (Chengdu, China). Wetting dispersant (SWA), sulfonated fatliquor (JM), sulfited fatliquor (JMK), lecithin fatliquor (FS-90), sulfited neatsfoot oil fatliquor (DF) and AR were obtained from Sichuan Dowell Science and Technology Inc. (Chengdu, China). Sodium formate, sodium bicarbonate and formic acid were supplied by Kelong Chemical Reagent Factory (Chengdu, China). Red anionic dye (ME) was purchased from Current Tech Fine Chemical Co., Ltd (Ningbo,

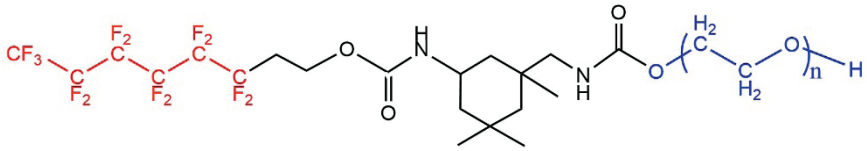

Figure 1. Chemical structure of F6-m.

Table I

Process Recipe for Leather Manufacture

Process/chemicals	Dosage(wt%)	Duration (min)	Temperature(°C)	Remarks
Rewetting				
Water	150		35	
SWA	0.2	60		Drain & Wash
Neutralization				
Water	150		35	
Sodium formate	1			
Sodium bicarbonate	1.5	60		pH 6.0 Drain & Wash
Retanning				
Water	150		35	
AR	X			X is 2, 4 or 6
F6-m	Y	90		Y is 1, 2 or 3
Formic acid	1	20 × 3 + 30		pH 4.0 Drain & Wash
Dying & Fatliquoring				
Water	150		40	
ME	1	45		Added only in the study of dye uptake
JM	6			
JMK	6			
FS-90	3			
DF	3	60		
Formic acid	0.6	20 × 3 + 30		pH 4.0 Drain & Wash
Horse up, hang-drying overnight				

China). F6-m (m is 400, 600, or 800, respectively, which represents the number average molecular weight of polyoxyethylene ether (PEO)) was synthesized according to the method in our previous work[19], whose chemical structure is described in Figure 1. And the critical micelle concentrations (CMC) of F6-400, F6-600, and F6-800 are 0.120, 0.131, and 0.136 mmol, respectively; and their surface tensions at CMC (γ_{CMC}) are 25.8, 29.4, and 32.0, respectively.

Leather Processing

In order to ensure same leather fiber woven state, the wet-blue goat leather was cut into two pieces of the same size (30 cm × 30 cm) along the backbone. One of the wet-blue leather pieces was used as the control sample (C, no retanning) and the other was used as the experimental sample (E, retanning). All leather chemicals were offered according to the weight of wet-blue goat leather pieces. The process recipe of leather manufacture is listed in Table I.

Analysis of Leather Properties

Before performing tests, the resultant leather samples were kept at 65% relative humidity and 20°C for 24 h. The thickness of leather samples was measured by a GJ9B1 digital thickness tester (Gotech Testing Machines, China) according to the Chinese standard of QB/T 2709-2005. The softness of samples was tested on a GT-303 digital leather softness tester (Gotech Testing Machines, China) according to the standard method from QB/T 1872-2004. The mechanical properties, such as tensile strength (QB/T 2710-2005), elongation at break (QB/T 2710-2005) as well as tear strength (QB/T 2711-2005), were carried out using an AI-7000 SN tensile machine (Gotech Testing Machines, China) according to Chinese standards.

Morphology

The cross sections of resultant leather samples were observed using a JSM-7500F scanning electron microscopic (SEM) (JEOL, Japan). The grain surfaces of resultant leather samples were recorded on a M50 stereomicroscope (LEICA, Germany) equipped with a digital camera.

Dye adsorption rate

The dye (ME) solution was scanned in the range of 200-700 nm via a UV-1900 UV-visible spectrophotometer (Jinghua, China) to obtain the maximum absorption wavelength of ME. The dyeing bath samples at different time points were collected, and the absorbance of their diluents was determined at the maximum absorption wavelength. The adsorption rate (A) of dye was calculated using equation (1)[20]:

$$A = \frac{(A_0 - A_t)}{A_0} \times 100\% \quad (1)$$

Where A_0 and A_t are the absorbance of dyeing baths at the beginning and other subsequent time points, respectively.

Color Difference Analysis

The color difference of dyed leather was tested on a MC-5 colorimeter (Konica Minolta, Japan). Total color difference (ΔE) was calculated from the CIE (L*, a*, b*) 1976 formula[21] (2):

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

Where L*, a*, and b* are black-white, red-green and yellow-blue color coordinates, respectively; ΔL*, Δa*, and Δb* represent the change between L*, a*, and b* values of leather samples, respectively.

Results and Discussion

Effects of Different Retanning Systems on Leather Properties

At the total dosage of 4 wt% (among them, the mass rate of AR/F6-m is 1:1), the organoleptic and mechanical properties of leather treated by different retanning systems are shown in Table II and Figure 2, respectively. It is seen clearly that the properties of leather retanned with AR or AR/F6-m are different. The thickening rates of leathers retanned with AR, AR/F6-400, AR/F6-600 or AR/F6-800 are 9.8%, 7.5%, 7.5% and 5.4%, respectively. Evidently, although the dosage of AR in the single AR system is twice as much as that of AR in the AR/

Table II

Organoleptic Properties of Control (C) and Experimental (E) Leathers Retanned with Different Retanning Systems at Total Dosage of 4 wt%.

Retanning agents	Groups	Thickness (mm)	Softness (mm)
AR	C	1.12	9.1
	E	1.23	8.8
AR/F6-400	C	1.34	8.5
	E	1.44	9.2
AR/F6-600	C	1.33	7.9
	E	1.43	8.6
AR/F6-800	C	1.3	8.1
	E	1.37	8.9

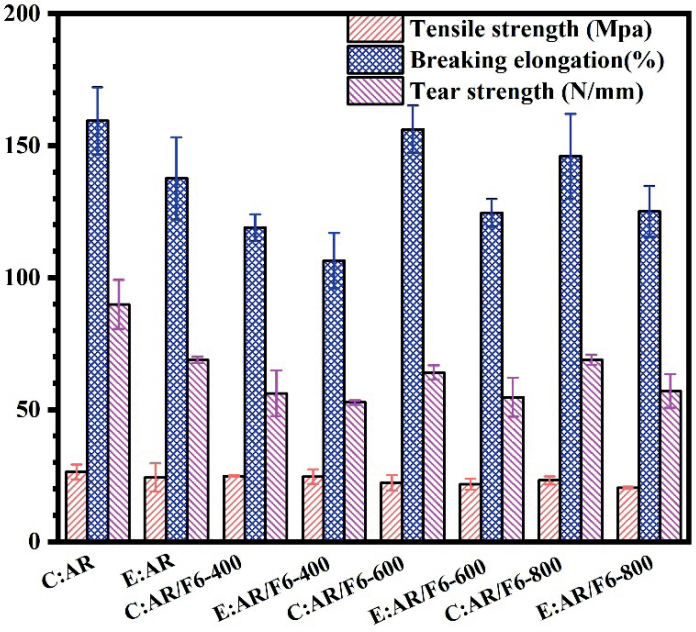

Figure 2. Mechanical properties of control (C) and experimental (E) leathers retanned with different retanning systems at total dosage of 4 wt%.

F6-m composite system, the thickening effect of single AR system does not reach twice of AR/F6-m composite system. It indicates that the combination of F6-m with AR shows a synergistic retanning effect on wet-blue goat leather.

The reasons for the synergistic retanning effect might be as follows: 1) the steric hindrance effect of nonionic F6-m shields the partially dissociated carboxyl groups on AR molecular side chains, avoiding the excessive binding of AR with chromium ions on the leather surface at the initial stage of retanning;[22] 2) F6-m with high surface activity reduces the interface tension between AR and collagen fibers, promoting more AR molecules to enter the interior of leather;[23] 3) furthermore, when the bath pH is reduced at the later stage of retanning, the hydrogen bonding between carboxy groups on AR and ether groups on F6-m is strengthened,[24] which cooperates with the hydrophobic interaction offered by the fluorocarbon chain of F6-m to drive the formation of AR/F6-m composite aggregates,[25] and further results in nonionic F6-m also being fixed and filled inside the leather. These reasons make the thickening effect of the AR/F6-m composite system better than that of the single AR system.

Meanwhile, it is noteworthy that, compared with the further deteriorated softness of AR retanned leather (-3.3%), the softness of AR/F6-m retanned leather has a significant enhancement, with approximately 9.0%. It demonstrates that these fluorinated surfactants also facilitate the absorption of subsequent fatliquoring agents by leather to improve the mobility of collagen fibers.[26] In the fatliquoring process, fatliquoring agents may further be emulsified by the partial free F6-m with high surface activity (see the material statement above); and the electrostatic repulsion between AR and anionic fatliquoring agents may inhibited by nonionic F6-m due to the steric hindrance effect. Finally, these factors make it easier for the fatliquoring agent to enter the leather and further lubricate collagen fibers, thereby enhancing the softness of leather.[27,28]

In terms of mechanical properties (as shown in Figure 2), the tensile and tear strengths of AR retanned leather exhibit a significantly decline, about 7.9% and 23.4%, respectively, which shows the obvious "detanning" effect of AR. In contrast, intriguingly, the reducing rates of mechanical strength of AR/F6-400 retanned leather are lower, and the reducing rates of tensile and tear strengths are 0.6% and 6.1%, respectively, demonstrating that F6-400 can inhibit the "detanning" effect of AR for the chrome-less tanned leather. This is probably because that the carboxyl groups on AR capture the chromium ions originally combined with collagen fibers, resulting in the reduction of crosslinking density between collagen fibers (as shown in Figures 3a and 3b). Conversely, after combined use of AR and F6-400, since F6-400 and AR may self-assemble into composite aggregates to shield some carboxyl groups on AR, the capture ability of AR to chromium ions that have been combined with collagen fibers is weakened, which still maintains a better crosslinking effect between collagen fibers (as shown in Figures 3a and 3c). In forming composite aggregates process, the possible driving forces are as follows: 1) the hydrogen bonding between AR and F6-600, intensifying the molecular chain entanglement between AR and PEO of F6-400; 2) the hydrophobic interaction from fluorocarbon chains on F6-400, driving fluorocarbon chains to form the hydrophobic microdomain, and resulting in the surrounding AR and PEO molecular chains to shrink toward the hydrophobic microdomain.

Moreover, in AR/F6-m, with the increase of PEO chain length (m increases from 400 to 800), the inhibitory effect of F6-m on the "detanning" effect of AR is weakened, and the tensile and tear strengths of AR/F6-800 retanned leather reduce 12.2% and 17.2%, respectively. This is likely due to the fact that the longer PEO chain provides more hydrogen bonding sites that can interact with carboxyl groups of AR, which increases the possibility that chromium ions are encapsulated by AR/F6-m composite aggregates (as shown in Figures 3c and 3d), and eventually weakens the cross-linking effect of chromium ions on collagen fibers. In summary, the retanning performance of AR/F6-400 is superior to the other listed retanning system. Thus, AR/F6-400 would be allowed to be used in the following studies.

Effect of the Dosage of AR on Leather Properties

Based on the above research results of AR/F6-400 (2 wt%/2 wt%), the dosage of F6-400 was fixed at 2 wt%, and effects of the dosage of AR on leather properties were studied. The results are shown in Table III and Figure 4. With increasing dosage of AR from 2 wt% to 4 wt%, the thickening rates increase significantly from 7.5% to 22.3%, and the increasing rates of softness change little and remain at about 9.0%. The higher thickening rate indicates that more AR/F6-400

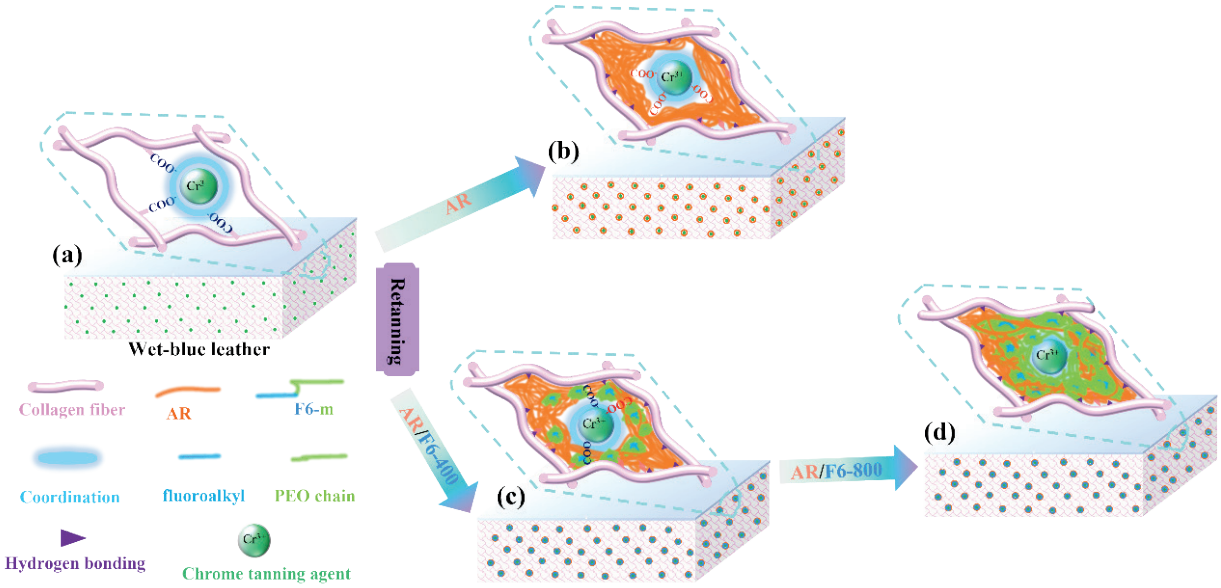

Figure 3. Schematic diagram of proposed retanning mechanism of wet-blue leather.

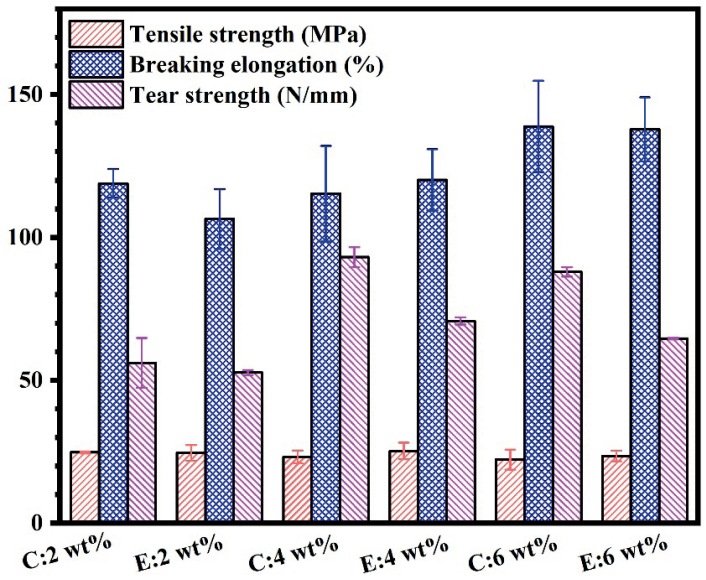

Figure 4. Mechanical properties of leathers retanned with different dosages of AR and 2 wt% F6-400.

TABLE III

Organoleptic Properties of Leathers Retanned with Different Dosages of AR and 2 wt% F6-400

Dosage (wt%)	Groups	Thickness (mm)	Softness (mm)
2	C	1.34	8.5
	E	1.44	9.2
4	C	1.12	8.2
	E	1.37	8.9
6	C	1.21	8.3
	E	1.41	8.6

Table IV

Organoleptic Properties of Leathers Retanned with Different Dosages of F6-400 and 4 wt% AR

Dosage (wt%)	Groups	Thickness (mm)	Softness (mm)
1	C	1.18	7.5
	E	1.36	8.4
2	C	1.12	8.2
	E	1.37	8.9
3	C	1.13	7.6
	E	1.17	8.2

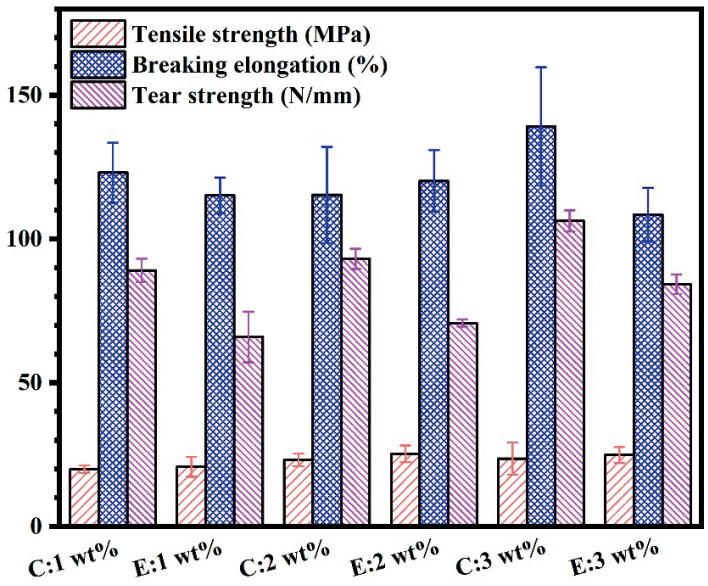

Figure 5. Mechanical properties of leathers retanned with different dosages of F6-400 and 4 wt% AR.

is filled in the gap between collagen fibers. And these AR/F6-400 would also provide more hydrogen bonding sites that can interact with carboxyl, amino, and hydroxyl groups on the collagen fibers, thus allowing AR/F6-600 to tightly cover the collagen fiber surfaces, and further increasing the maximum external force that the collagen fibers can withstand under axial stretching.[29] Ultimately, the tensile strength increases from -0.6% to 9.1%.

With the continuous increase of AR dosage to 6 wt%, the leather properties do not further improve significantly, and even deteriorate to some extent. This is likely because that when the dosage of AR is too high, the number of carboxyl anions provided by AR is higher, weakening relatively the role of F6-400. This would make AR to excessively combine with chromium ions on the superficial layer of leather, thereby preventing the penetration of retanning agent and subsequent fatliquoring agents into the leather, and affecting the improvement of leather properties. To sum up, when the dosage of F6-400 is 2 wt%, 4 wt% AR will optimize the comprehensive properties of the leather.

Effect of the Dosage of F6-400 on Leather Properties

The dosage of AR was fixed at 4 wt%, and effects of the dosage of F6-400 on leather properties were studied. The results are presented in the Table IV and Figure 5. When the dosage of F6-400 increases from 1 wt% to 2 wt%, the increasing rate of thickness raises from 15.3% to 22.3%, demonstrating that more AR/F6-400 is filled in leather. Meanwhile, the mechanical strength of leather is further improved, in which the increasing rate of tensile strength increases from 3.9% to 9.1%. There are two possible reasons that 1) when more AR/F6-400 is filled in leather, the hydrogen bonding between AR/F6-600 and collagen fibers is strengthened; 2) with growing dosage of F6-400 in AR/F6-400 composite system, the capture ability of AR to chromium ions that have been combined with collagen fibers is weakened because the possibility of carboxyl ions on AR being shielded by F6-400 increases. The above two reasons maintain the cross-linking strength between collagen fibers, but also hinder the mobility of collagen fibers, which declines the improved softness from 12.0% to 8.5%.

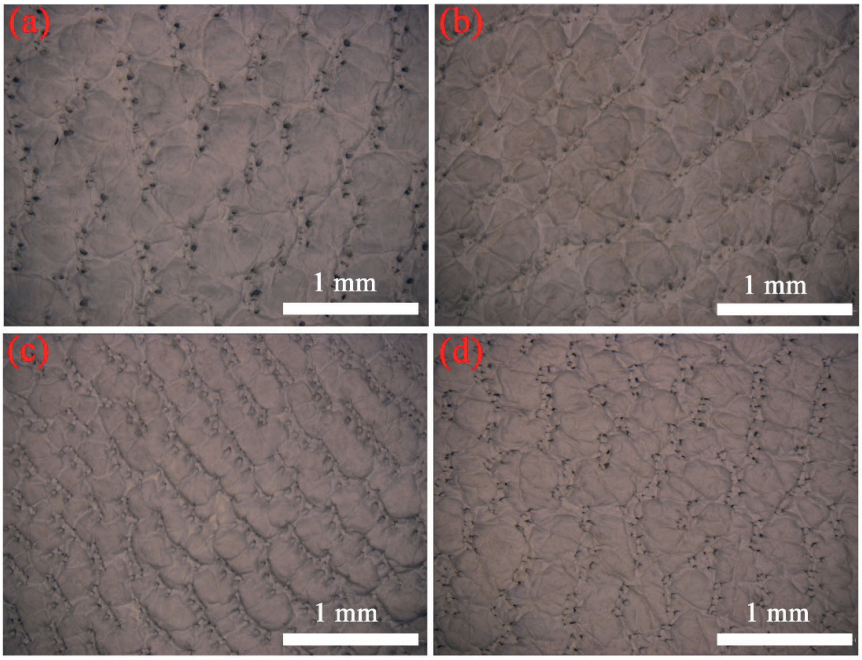

Figure 6. Images of leather grain surfaces under different retanning conditions: no retanning **(a)**; 4 wt% AR **(b)**; 2 wt% AR, 2 wt% F6-400 **(c)**; 4 wt% AR, 2 wt% F6-400 **(d)**.

In addition, when the dosage of F6-400 continuously increases to 3 wt%, the increasing rates of thickness and softness do not continue to increase, and even present a downward trend. It may be ascribed to the fact that with increasing dosage of F6-400, the hydrogen bonding between F6-400 and AR as well as AR/F6-400 and collagen fibers is also boosted, which makes AR/F6-400 easier to aggregate and adhere to the leather surface and further hinders the subsequent fatliquoring effect. Additionally, at this time, the increasing rate of tensile strength decreases from 9.1% to 5.3%. Ultimately, considering the economic cost and leather properties, the optimal result is the combination of 4 wt% AR and 2 wt% F6-400 in the retanning of wet-blue leather.

Morphology Analysis of Grain Surfaces

Morphology features of leather grain surfaces were obtained by a stereomicroscope and shown in Figure 6. It is easy to find that compared with the leather without retanning, the pores of leather retanned with AR obviously shrink, which demonstrates that AR

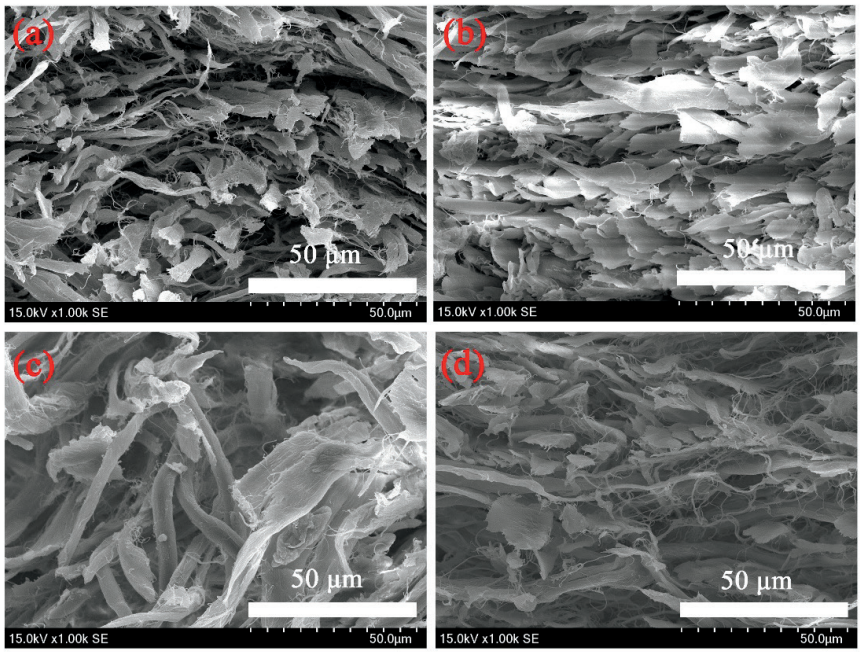

Figure 7. Images of the leather cross section under different retanning conditions: no retanning **(a)**; 4 wt% AR **(b)**; 2 wt% AR, 2 wt% F6-400 **(c)**; 4 wt% AR, 2 wt% F6-400 **(d)**.

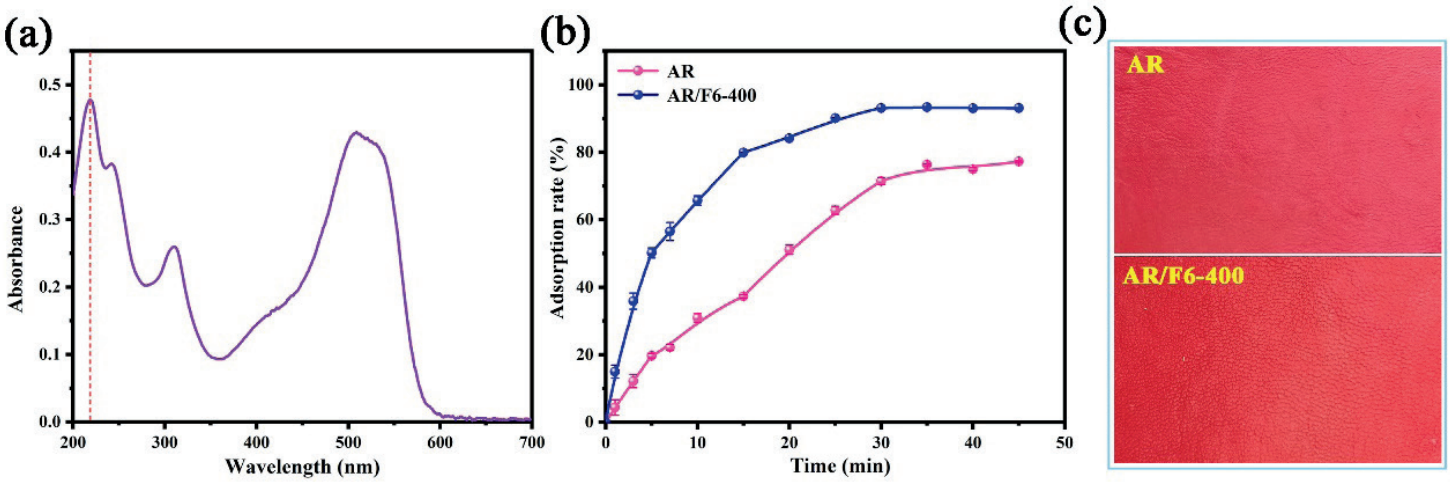

Figure 8. Full wavelength spectrum of ME **(a)**; adsorption rate of dye on leather retanned by 4 wt% AR or 4 wt% AR/F6-400 **(b)**; and the resultant leather after dyeing **(c)**.

Table V
Chroma Color Difference Values of Dyed Leather

	L*	A*	B*	ΔE*
4 wt% AR	50.3±0.3	48.7±0.4	32.8±0.6	4.6
4 wt% AR/F6-400	46.4±0.7	50.2±0.4	34.7±0.7	

shows an apparent "convergence" to leather grain surface. While the pores of AR/F6-400 retanned leathers shrink slightly, and they are still clear. This additionally proves that F6-400 promotes the penetration of AR in leather, thereby weakening the combination of AR and chromium ions on the leather grain surface and avoiding "excessive convergence" of leather grain surface.

Morphology Analysis of Cross Section

The fiber weave structure of leather cross section was observed by SEM, and the results are shown in Figure 7. It can be clearly seen that the fibers of leather without retanning are thicker and the fiber gap is uneven; and the gap between fibers of AR retanned leather is narrower. By contrast, the space between fibers of AR/F6-400 retanned leathers is wider, and their arrangement is looser, which indicates that F6-400 promotes the penetration and absorption of subsequent fatliquoring agents in leather and is consistent with the former softness result.

Dyeing

It can be obtained from Figure 8a that the maximum absorption wavelength of dye (ME) is 219 nm. The dye adsorption rate calculated by measuring the absorbance of the dying bath at 219 nm is shown in Figure 8b. Under the same operation time and total dosage with 4 wt%, the dye adsorption rate of AR/F6-400 (1:1) retanned leather is higher than that of AR retanned leather, with dye adsorption rates reaching 93.1% and 77.3% at the end of dying, respectively. Simultaneously, as expected, Figure 8c indicates that compared with AR, AR/F6-400 retanned leather shows a higher adsorption capability to dye. The main reason is that the steric effect of nonionic F6-400 weakens the electrostatic repulsion between AR and anionic ME, and some incompletely fixed F6-400 also further promotes the dispersion and penetration of ME in leather.

The color of dying leathers is evaluated by the CIE Lab 1976 standard colorimetric system. As shown in Table V, L* (black-whiteness) and a* (red-greenness) values of AR/F6-400 retanned leather are lower and higher than those of the AR retanned leather, respectively, which indicates that the AR/F6-600 retanned leather is brighter and redder. And ΔE* (total color difference) value is 4.6 and higher than the industrial color difference approving limit of 1.0,[30] revealing that there is obvious color difference between two samples. These results show that the dyeing effect of AR/F6-400 retanned leather is better as compared to the AR one, and F6-400 improves the "fading" defect of AR in the retanning of wet-blue leather.

Conclusions

In this work, the nonionic short fluorocarbon chain surfactants (F6-m) and AR were used in combination to retan wet-blue goat leather. The results showed that the combination of 4 wt% AR and 2wt% F6-400 is the optimal retannage ratio. After retanning, the grain surface state and mechanical properties of AR/F6-400 retanned leather were better than that AR retanned leather, illustrating that F6-400 could greatly improve the application properties of AR, and correspondingly avoid the occurrence of defects like the grain surface "excessive convergence" and "detanning", in the retanning of wet-blue leather. Furthermore, the dying effect of AR/F6-400 retanned leather was better than that of AR retanning leather, which indicates that F6-400 can ameliorate the "fading" effect of AR. Most importantly, it provides a promising ideal for further improving application properties of AR in the retanning of wet-blue leather, which is conducive to further enhance leather quality and broaden the application range of fluorocarbon surfactants in leather industry.

Acknowledgements

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A Bibliometric Study of the Unhairing and Liming of the Leather Tanning Process

by

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Abstract

Unhairing and liming are the most polluting operations of the leather tanning process. Over the years, this sector has been investigated increasingly. Hence, this paper aims to explore and analyze the scientific activity of this field of research with a new view, applying bibliometrics techniques. The method of the study is based on a search and collection of publications indexed in Scopus. Subsequently, bibliometric data were extracted from the corresponding publications. Graphics and bibliometric maps were made to obtain quantitative results and the relationships between countries, authors, journals, and keywords. The results show an upward trend over the last 100 years or so, where the topic of most of the publications has reversed from being purely about engineering and process to focus on the big environmental issue generated by traditional unhairing. At the same time, research in this field has shifted to countries with the biggest tanning industry, such as China and India. In conclusion, bibliometrics has been a good method to know the current state of scientific literature and the timeline of this field of research, which will allow for a deepening in alternative methods to traditional unhairing and advance of the environmental concern caused by these polluting operations.

Introduction

Leather tanning can be divided into three different stages. The first one is called Wet or Beamhouse stage due to a large amount of water present and used in each of the included operations, such as soaking, unhairing, deliming, pickling, etc.

Unhairing and liming have always been treated as a single process. Due to their compatibility, both operations can be performed together in the same float, although each one has specific objectives.[1] On the one hand, unhairing consists of removing from the soaked skin the hair or wool, and the epidermis, to hydrolyze keratin (the hair protein). On the other hand, liming has the objective to hydrolysate collagen, causing a loosening of its fibrous structure. Traditional unhairing and liming are achieved using sodium sulfide (Na_2S), sodium hydrosulfide (NaHS) and calcium hydroxide. Due to its reductive nature, unhairing with sulfides helps to break disulfide bonds of cysteine, leading to the subsequent hydrolysis of keratin. That occurs due to the combination of hydrosulfide (HS^-) and hydroxyl (OH^-) ions, resulting from the reduction of sodium sulfide in an aqueous solution.[2] Together with calcium hydroxide, the hydrogen bonds between the collagen fibers get broken. The skin swells, the fibers loosen, and the chemical reactivity points increase, making the products added in later stages penetrate the skin correctly. This effect is called lyotropic swelling.[3] Unhairing and liming are easy to control, and it is an inexpensive process.[4]

One of the challenges that tanners face is to reduce the environmental impact generated by the tanning process. Concretely by reducing the high-water consumption produced by the Beamhouse process, and particularly unhairing and liming operations. Reductive unhairing (with sulfides) is the most effective and traditional, but it is the most polluting. Not only does it entail an extremely high consumption of water and chemical products. It also generates highly polluting and waste of water due to the hair and other dirt and fats present in the water, which contributes to the increase of polluting parameters such as Chemical Oxygen Demand (the amount of dissolved oxygen that must be present in water to oxidize chemical organic materials), Biochemical Oxygen Demand (the amount of oxygen required to breakdown organic pollutants biologically with microorganisms),[5] Total Suspended Solids (organic and inorganic particles larger than 2 microns found in water), sulphides (S^{2-}), and so on.[6,7] Moreover, the use of sodium sulfide in this type of unhairing does not only affect the wastewater. When working at pH values below 10, sodium sulfide is released in the form of hydrogen sulfide (H_2S), causing a stink, and in sufficient quantities, severe respiratory problems, or even death.[8,9]

Therefore, due to this enormous environmental problem caused by traditional unhairing, this sector has evolved over the years, looking for less polluting and alternative methods to traditional unhairing.[9] Oxidative unhairing uses hydrogen peroxide as an oxidative agent and sodium hydroxide as a source of alkali in the same float to hydrolyze the hair, with the advantage of working with less water and reducing the polluting parameters of the wastewater.[10] In addition, research in recent years focused on a type of enzyme that allows the replacement of sodium sulfide as an unhairing agent. Although enzymatic unhairing is a suitable alternative because of its advantages (diminution of sulfides in water and the amount of water used, recovery of good quality hair), enzymes, in general, are

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expensive and need much more accurate control in comparison to other products.[11] Nor a process has been found that can be carried out only with enzymes, giving results comparable to traditional unhairing. Another alternative that many factories have already started to use is hair-save unhairing. It significantly reduces the pollution load of the resulting water, especially in terms of solid waste (hair and sludge generated in the process), even though it uses the same chemicals as the traditional process (sodium sulfide and lime). Recently, recirculation systems for wastewater floats have also started to reduce water consumption. However, there is not yet a satisfactory solution.[12]

Scientific and technological research and the divulgation of the resulting knowledge are fundamental activities to satisfy the growing needs of society, and there is also a need to analyze and evaluate this scientific production. It is at this point that Information Science comes in, developing techniques to measure and value postgraduate scientific activity. Among the different metric disciplines within Information Science is Bibliometrics, which is a part of Scientometrics. Bibliometrics is the science that uses mathematical and statistical methods to study the nature and scientific activity of a specific line of research. This field of Scientometrics aims to investigate and evaluate the quality and quantity of published scientific literature. To know the trend of publications, the most relevant journals where these documents are published, the most active authors in the subject, and the relationship and contribution between countries and institutions in a particular field, and the most used keywords in the publications.[13]

Around the 1960s, the curiosity to understand scientific development led to the first works on Bibliometrics. Price created the concept of "Science of Science", and it was then that the application of scientific methods for the analysis of science began. Due to the digitalization of databases and the great demand to evaluate the effectiveness of the policies of science planning authorities, there was an important boom in bibliometric studies. Bibliometrics took a step forward in 1978, with the foundation of the journal Scientometrics, when research articles related to scientometrics, the science of quantitative analysis of scientific research activity, began to be published.[14] However, it was not until two decades ago that J. M. López Piñero and M.L. Terrada introduced bibliometric studies in Spain.[15]

To develop bibliometric research, it is essential to have bibliographic information on scientific publications, such as the author/s, the title of the publication, the year of publication, the journal, etc. To obtain this, bibliographic databases are used, which are formed of an extensive number of registers stored and managed through computer systems. Some of the most used databases are Scopus, Web of Science, Journal Citation Reports, Google Scholar, etc..[16,17] Once the bibliographic information is obtained from the selected publications, it is extracted and converted into a specific format. To value this information, the application of bibliometric indicators is useful. For years, these numerical parameters have been decisive in analyzing the impact of scientific papers, valuing the research activity of an author, an institution, or a specific country.[18] In general, some of the aspects that can be determined using bibliometric indicators are the chronological evolution of scientific production, the productivity of authors or institutions by measuring the number of their works, the collaboration between scientists and institutions, the analysis of sources that distribute published works and their evolution, etc. There are many distinct categories used to distinguish the bibliometric indicators currently in use. Generally, there is a difference between qualitative indicators, which evaluate the scientific quality of the work, and quantitative indicators. Within this group, a distinction is made between those of scientific activity and those of scientific impact.[19,20] Depending on the purpose of the study, these indicators can be unidimensional or multidimensional. Unidimensional indicators study a single characteristic of publications, such as which journals they have been published in, which authors have produced the papers, etc., while multidimensional indicators investigate the relationships between characteristics, such as co-authorship relationships, co-citation relationships, or keyword co-occurrence relationships.[21] Bibliometric maps are a sort of multidimensional bibliometric indicator that provides a preliminary view of the quality and evolution of a particular line of research through representative diagrams of connected within words, ideas, or concepts.[22-24] For creating bibliometric maps, it is necessary to have software capable of constructing this type of complex graphics, such as VOSviewer. One of the advantages provided by this software is that it allows visualizing the maps created in three different ways, network visualization, density visualization and overlay visualization. That makes it easier to explore the maps in detail, which is especially useful and essential when working with maps containing many elements. Some of the most common maps that could be created are co-citation networks, co-authorship networks, keyword co-occurrence networks, etc.[25-28] One last outcome of using Bibliometrics to analyze a scientific topic is the possibility to find literature gaps, that is, to identify topics or areas of research still to be fully explored.

This science has been applied to research a wide variety of fields of current interest, e.g., Big Data, energy efficiency, and sustainability, biomedicine, mobile technology, etc. To the best knowledge of the authors, there is not any bibliometric analysis or publication on the unhairing and liming of leather tanning. Therefore, this paper aims to apply bibliometric analysis techniques to explore and evaluate the current status of this scientific and industrial process and its evolving trends in recent years. The results should help the research community to accentuate the find new lines of investigation to improve the sustainability of this process.

Experimental

The function of bibliometric studies is to analyze and evaluate the results of lines of scientific research. For its realization, it is essential to have one or more databases. In this paper, Scopus is used, accepted by the international scientific community as the largest database of citations and abstracts of scientific literature to analyze scientific publications.[29,30] However, like all databases, Scopus presents a limitation, it does not consider national journals as they do not meet some of the requirements to be in the database.[30] The methodology followed to perform this bibliometric analysis in this study is shown schematically in Figure 1. The first step consists of an advanced search and data collection in Scopus. Through the advanced search, one could obtain more technical information about the topic of interest in comparison to a basic search. Like most databases, Scopus works with subfields (title, abstract, keyword, etc.) and Boolean operators (AND, OR, AND NOT, etc.), elements that allow combining and establishing relationships between the keywords chosen to perform the search.[31] Initially, a first advanced search was carried out at the end of 2020, using the following keyword string:

TITLE-ABS-KEY (("unhairing" OR "liming")
AND ("hide" OR "skin" OR "leather")
AND NOT ("parchment*" OR "clinic*"))

In this initial search, a total of 363 documents resulted, from 1926 to 2020. The keywords "unhairing" and "liming" appeared in the investigation. Additionally, the terms "hide", "skin", and "leather" were key in this study. It was necessary a general reading of each of the publications to get accurate understanding and to keep in the query only those that deal with the topic of interest.[32] Thus, using the AND NOT operator, the keywords "parchment*" and "clinic*" were excluded from the search. In March 2021, 22 new documents were added in the same query, a result of a total of 383 papers. Following the same method as with the initial query, the abstracts of the new documents and those already included in the query were reviewed. Finally, after excluding some unwanted terms, the final query is of a total of 291 documents from 1927 to 2021:

TITLE-ABS-KEY (("unhairing" OR "liming")
AND ("hide" OR "skin" OR "leather") AND NOT
("parchment*" OR "clinic*" OR "fisheries" OR
"rat" OR "pear*" OR "sanitary" OR "demod*" OR
"leather shavings" OR "coriagen" OR "preparation of
gelatin" OR "nose" OR "liritan" OR "hysteresis" OR
"genotoxicity" OR "bacterial sp*" OR "fatliquoring
agent*" OR "ammonia removal" OR "waterproofing"
OR "organic nanofiltration" OR "anionic
polyelectrolyte" OR "glutaraldhyde" OR "skate" OR
"reverse tanning process" OR "decorin content" OR
"alkaline lipase" OR "fungus growth" OR "growth
factor" OR "fish skin" OR "growth performance"
OR "slaughtering industry" OR "alkylphenol"
OR "bone" OR "air filter" OR " plasma" OR "fruit
quality" OR "bullfrog" OR "red mud" OR "short
term" OR "agroecology" OR "resilient" OR "shaving
operations" OR "interweaving" OR "climate" OR
"biodiesel" OR "adsorption" OR "cowhide fleshings"
OR "proteobacteria" OR "the linear" OR "detergent
tolerance" OR "laboratories*" OR "wet blue leather
manufacture" OR "limed fleshing" OR "relative
elongations" OR "cattle breedings" OR "papermaking"
OR "green productivity" OR "expansive soil"
OR "rabbit skins*" OR "keratose" OR "brines*"
OR "substrate concentration" OR "infusion" OR
"furniture" OR "deamination"))

The next step was to extract and convert bibliometric information of the 291 publications, such as the year of publication, author/s, journal,

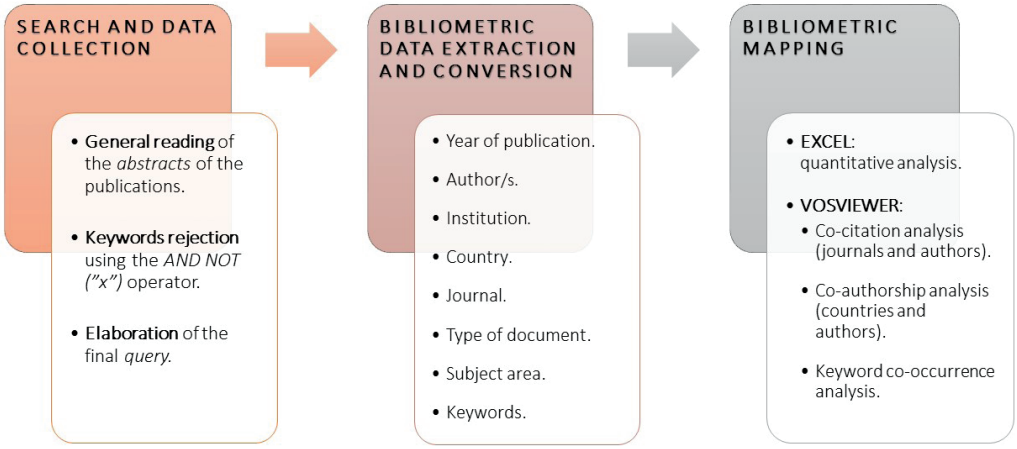

Figure 1. Methodology used for the bibliometric analysis.

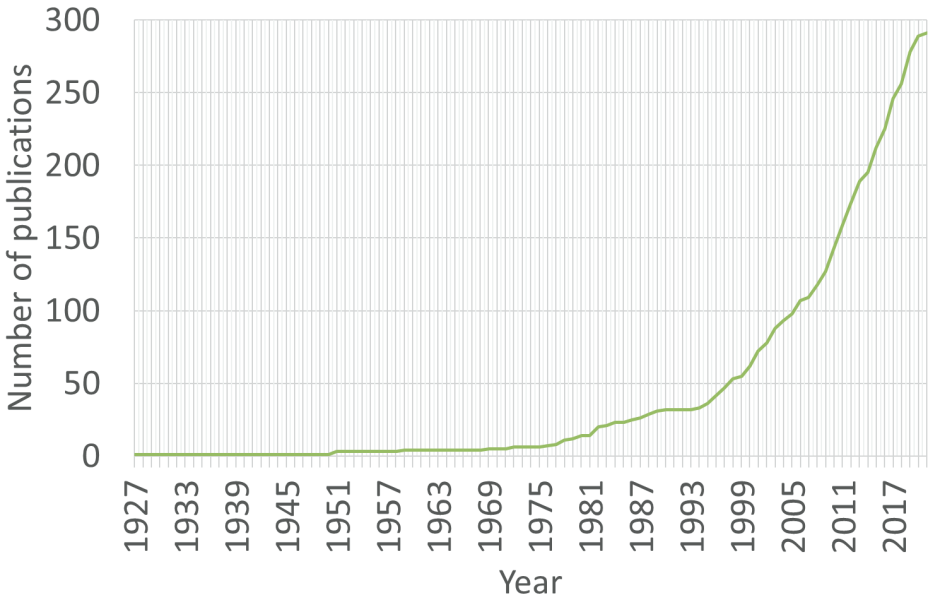

Figure 2. Accumulated annual trend of publications.

country, keywords, etc. Scopus has the advantage of exporting these data in different formats, either through Mendeley, RIS format, CSV, BibTeX, etc. With all the information obtained various graphs and bibliometric maps were elaborated. The spreadsheet Excel was used to perform a quantitative analysis. That is to study the trend, distribution, and quantity of publications according to the year, journal, type of document, subject area, institution, country, and author/s. The software VOSviewer was used to study the diverse relationships and connections between authors, countries, journals, and keywords.

Results and Discussion

This section shows the results of the bibliometric analysis of the 291 publications selected in the Scopus database, from 1927 to 2021, following the methodology described previously. This bibliometric study is divided into 4 large parts. The first part shows the results of quantitative analysis on the trends and distribution of publications. The second section presents the co-authorship analysis. The analysis of co-citation and co-occurrence of keywords are shown in the third and fourth sections, respectively. The results of these last three sections were obtained with VOSviewer.

Quantitative analysis. Trends and distribution of publications

In this first analysis, the trend and distribution of publications were studied, according to the year of publication, the journal, type of document, thematic area, institution, country, and author.

Figure 2 shows the cumulative annual trend of publications extracted from Scopus. According to this database, Henry Baldwin Merrill was the first author who published the first document about unhairing and liming of skins, in 1927.[33] As it can be seen, only 10 documents were published in the early 1980s. From then on, the trend began to increase. By the late 1990s, more than 50 documents had already been published, which some of them began to deal with alternative methods to traditional unhairing and liming operations, emphasizing enzymatic unhairing. Specifically, in 1996, a total of 6 documents were published, of which 4 dealt with the action of enzymes as an alternative to the use of traditional chemical products. Then, the trend is increasing, reaching a total of more than 140 Publications in 10 years elapsed.

Figure 3 shows the annual trends of published documents in different journals, congresses, and other sources from 1972, the decade when the trend of publications starts to increase little by little. The Journal of the American Leather Chemists Association is one of the first journals where more documents on unhairing and liming began to be published, reaching a total of 68 published documents. The second one with more published documents (48) on the topic of study is the Journal of the Society of Leather Technologists and Chemists, which began to publish in 1996. Table I shows the top journals with at least 3 publications on the topic of the study. Figure 3 also shows that it was not until 2001 when the Journal of Cleaner Production (17) began to publish about the subject of study. Similarly, the Journal Clean Technologies and Environmental Policy (5) did so in 2004. As their proper title says, these Journals also publish documents about cleaner environmental technologies. Therefore, when the environmental concern caused by traditional unhairing began, many authors also decided to publish their documents there.

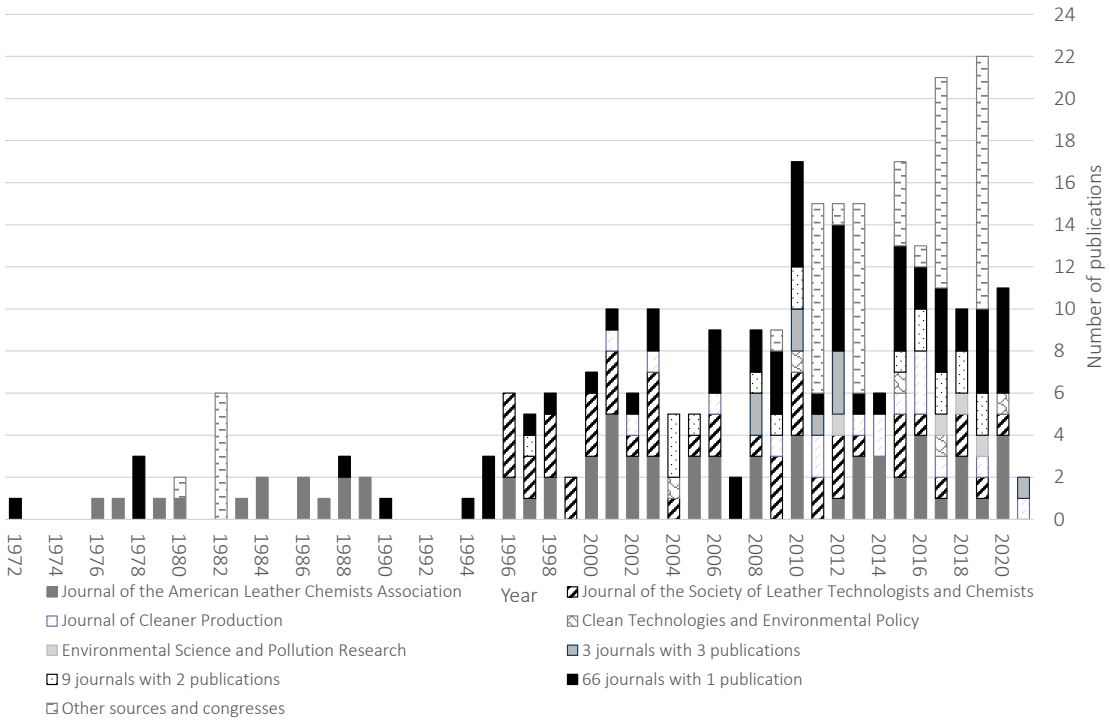

Figure 3. Annual trend of publications by journal.

Table I

Top journals with at least 3 publications on the topic

Journal	Number of publications
Journal of the American Leather Chemists Association	66
Journal of the Society of Leather Technologists and Chemists	48
Journal of Cleaner Production	17
Clean Technologies and Environmental Policy	5
Environmental Science and Pollution Research	4
Advanced Material Research	3
Brazilian Journal of Chemical Engineering	3

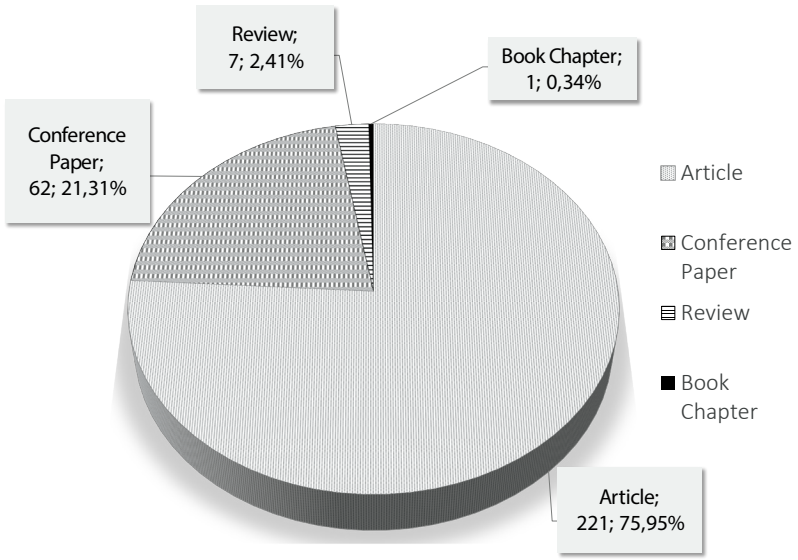

Figure 4. Percentage distribution of the document type of publications.

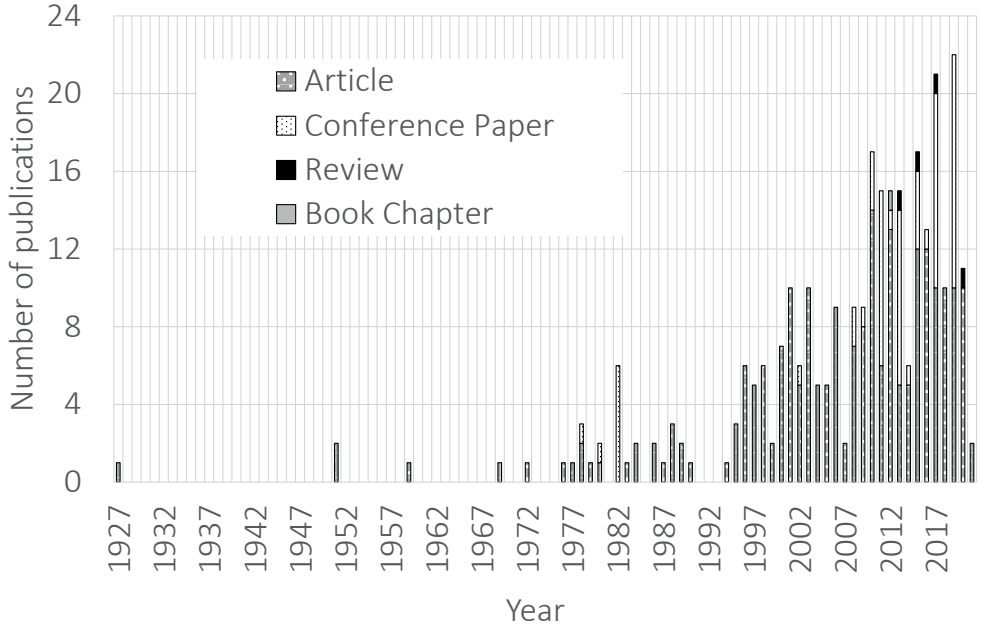

Figure 5. Annual trend of publications by document type.

Figure 4 shows the percentage distribution of publications classified by document type. It is observed that most publications are articles (221), followed by conference papers (62). As for the rest of the documents, 7 reviews have been published and a single book chapter related to unhairing and liming.

Figure 5 presents the annual trend and distribution of publications according to the type of documents, from 1927 to 2021. As mentioned above, the most common format of publications is the article. It is observed that it was not until the late 1970s that conference papers began to be published, but it was not until the end of the first decade of the 21st century that they were published again. On the other hand, it was not until 2013 that documents were published in the form of review. Finally, the only document in book chapter format was published in 2012.

Figure 6 presents the percentage distribution of the documents published according to their thematic area. There is so much diversification of subject areas because some journals deal with various topics at the same time, so some documents may be assigned in more than one thematic area. Chemical Engineering is the subject with the highest percentage of published documents (23%), followed by Chemistry (22%), and Materials Science (19%).

According to the query used and the documents extracted from Scopus, the main institutions and affiliations that have published more than 5 documents on the topic of interest are ordered in Table II. As it can be seen, the Council of Scientific and Industrial Research India (also called the Central Leather Research Institute India) tops the list, being the most active institution on the subject, followed by two Chinese institutions, Sichuan University and the Ministry

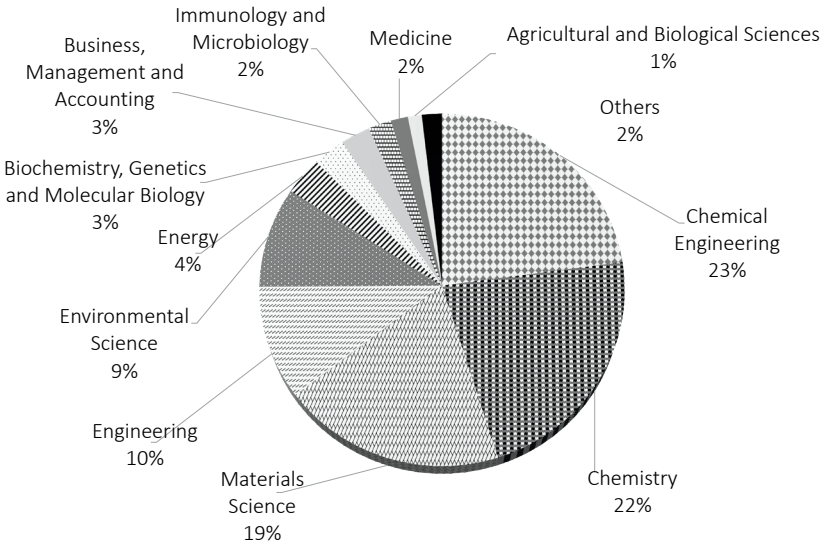

Figure 6. Percentage distribution of publications by subject area.

Table II

Top 10 institutions and their corresponding country

Affiliation/Institution	Country	Number of publications
Council of Scientific and Industrial Research India	India	42
Sichuan University	China	33
Ministry of Education China	China	22
The Federal University of Rio Grande do Sul	Brazil	18
Kaunas University of Technology	Lithuania	16
United States Department of Agriculture	United States	14
Polytechnic University of Catalonia	Spain	8
Ege University	Turkey	7
Leather Research Centre CITEC	Argentina	6
Shaanxi University of Science and Technology	China	6

of Education China, with 33 and 22 publications, respectively. This suggests that India and China are the main most active countries in the subject of interest. Other countries interested on the topic are Brazil, Lithuania, United States, and Spain It is also observed that most institutions are universities or research centers (independent or belonging to governments).

Figure 7 presents the accumulative annual trend of the publications of the first 10 institutions (Table II). From 1927 to 1958, none of these institutions published documents about the topic of interest. It was not until 1959 when the United States Department of Agriculture published its first paper on the subject. Then, in 1995, so did the Leather Research Centre CITEC institution. It should be noted that most of these institutions, their trend of publications begins in the late 1990s, publishing between 2 and 5 documents per year.

Figure 8 presents a world map of the different countries that have published more documents on unhairing and liming between 1927 and 2021. Search results in Scopus show that only 45 countries are involved in the topic of interest. As it can be seen, countries with the highest number of publications are colored with more intense orange, such as China and India (60 and 53 publications, respectively), compared to other countries with fewer published documents, for example, Spain (12) and Turkey (10).

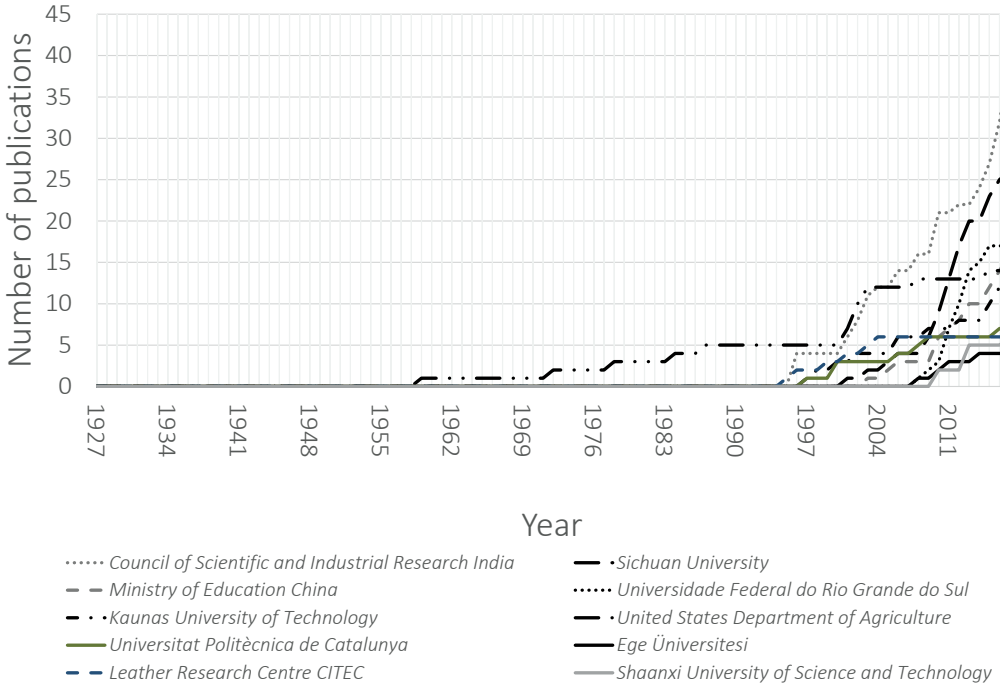

Figure 7. Annual trend of publications by institution or affiliation.

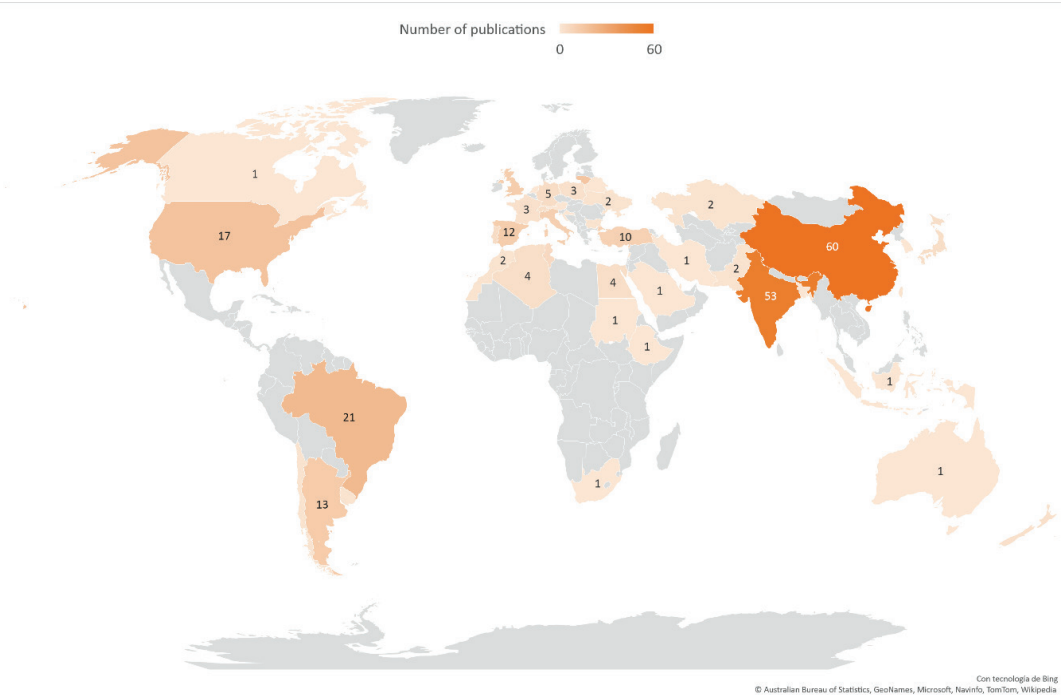

Figure 8. World map of the publications distributed for each country.

Figure 9 shows the cumulative annual trend of the top 10 countries with the highest number of published documents. According to the data extracted from Scopus, the United States was the first to publish an article about unhairing and liming operations, specifically in 1927 (Action of Ammonia on Calfskin). The following countries to publish their first paper on the topic of the study were United Kingdom and China (which is not seen in the graph since it is overlapping with England), specifically in 1988: *Enzymes in the tannery - catalysts for progress?*[34] and *Improvement of Unhairing Enzyme for Leather Processing*,[35] respectively. As it can be seen, these two documents study the influence of enzymes on leather tanning.

It can also be seen that the two countries with the most documents published so far are China and India. This is due to the large increase in the publication of papers due to the development of the tanning industry. Italy is the third country to publish documents on the topic of study in 1990 (*Environmental impact of the tanning industry*[36]).

Table III presents the top 10 authors with the highest number of documents published on the topic of study. Mariliz Gutterres leads the list, with 18 documents published, followed by Virgilijus Valeika and Kçstutis Beleška, with 16 and 15 publications related to unhairing and liming, respectively. Both authors are from the

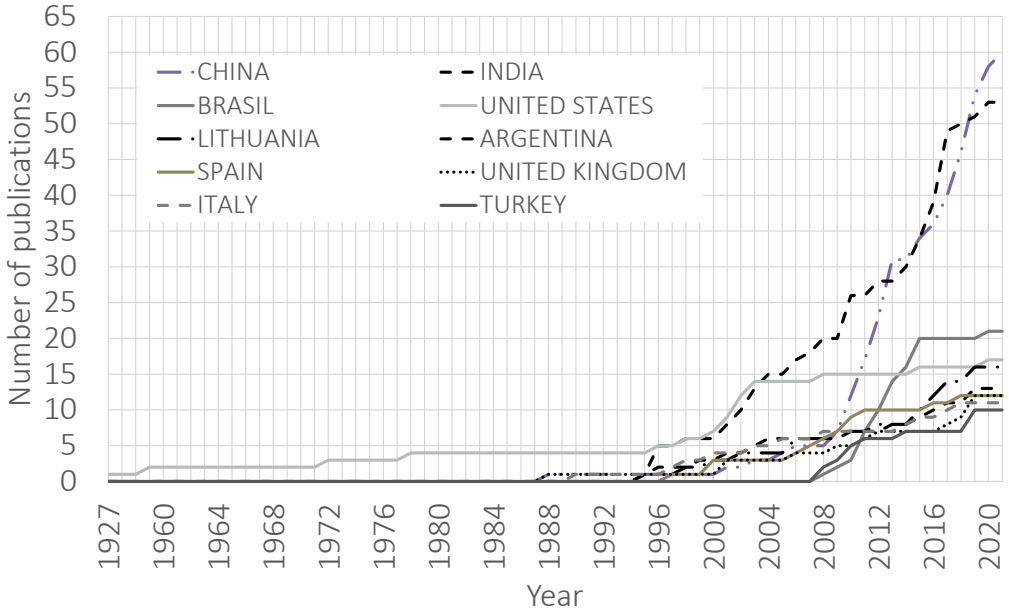

Figure 9. Accumulated annual trend of publications by country.

Table III

List of the top 10 authors including institution, country, total publications on Scopus and h-index

Author	Affiliation/Institution	Country	Publications (Topic of study)	Publications (Totals)	h-index (Scopus)
Gutterres, M.	Federal University of Rio Grande do Sul	Brazil	18	118	21
Valeika, V.	Kaunas University of Technology	Lithuania	16	40	11
Beleška, K.*	Kaunas University of Technology	Lithuania	15	32	9
Rao, J.R.*	Central Leather Research Institute India	India	14	186	24
Shi, B.	Sichuan University	China	11	270	39
Muralidharan, C.	Central Leather Research Institute India	India	10	70	19
Valeikiene, V.	Kaunas University of Technology	Lithuania	10	22	7
Dettmer, A.	Federal University of Rio Grande do Sul	Brazil	8	47	13
Cantera, C.S.	Leather Research Centre CITEC	Argentina	7	21	10

*Authors presents in the database with more than one different name.

same institution, with a total of 40 and 32 published documents, and an h-index of 11 and 9, respectively. In fourth place is the author Jonnalagadda R. Rao, from India, with 14 documents published on the subject. Table III shows that Lithuanian authors have published the most documents on unhairing and liming operations, compared to their total publications. The same can also be said of the author Carlos Santos Cantera, who has published 7 documents about the topic of interest from a total of 21 publications.

Figure 10 presents the accumulated trend from the documents published by the authors of Table III, year by year, from the early 1990s to the current year (2021). Indeed, the years before the 90's were not contemplated because, among these authors, until 1995 only Carlos Santos Cantera was the first one to publish a document about unhairing, specifically aiming to recycle the effluents from the hair-saving chemical unhairing process.[37] The following year, Chellapa Muralidharan published his first document on the subject,

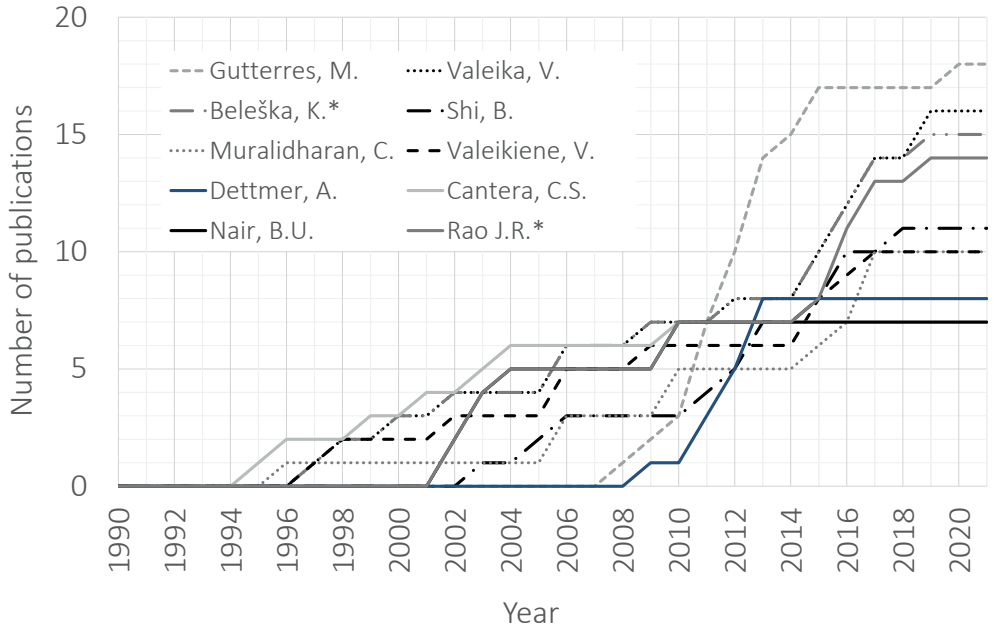

Figure 10. Accumulated annual trend of publications by author from 1990 to 2021.

with the aim to study an alternative non-enzymatic but sulfide free unhairing of goat skins[38] and again C.S. Cantera published one more document that year, focusing on a hair saving enzyme-assisted unhairing.[39] As it can be seen, the main common topic of these 3 documents is the study of alternative methods to traditional unhairing, free of sulfides: hair-save unhairing and enzymatic unhairing. Mariliz Gutterres began publishing in 2008, a few years later compared to other authors, but its trend has been increasing, becoming the author with more documents published so far (a total of 18 publications on this field of research), as seen in Table III.

Co-authorship analysis

Most scientific research projects are increasingly being developed in groups. Currently, completing research on a particular topic individually is quite difficult. Co-authorship analysis is essential for any bibliometric study, as it helps to know the level of collaboration and interaction existing between different authors who research the same specific field.[40] In this section, two types of co-authorship analyses are presented: by country and by author.

Figure 11 shows the co-authorship relationships between the countries that have published on the topic of study. The size of the circles determines the number of published documents in a country on the topic.[41] Then, the main countries with the highest number of publications are China, India, and Brazil. It seems to be no link between the countries that make up the graph. It is true that countries such as Austria, Chile, Egypt, etc., do not have any co-authorship relationship with other countries. However, in Figure 12 it can be seen in more detail the collaboration between different groups of countries (or clusters). China is not only one of the countries with the most published documents, but it is also one of the countries with the most co-authorship relations with countries such as the United Kingdom, Turkey, New Zealand, and Taiwan. Similarly, in

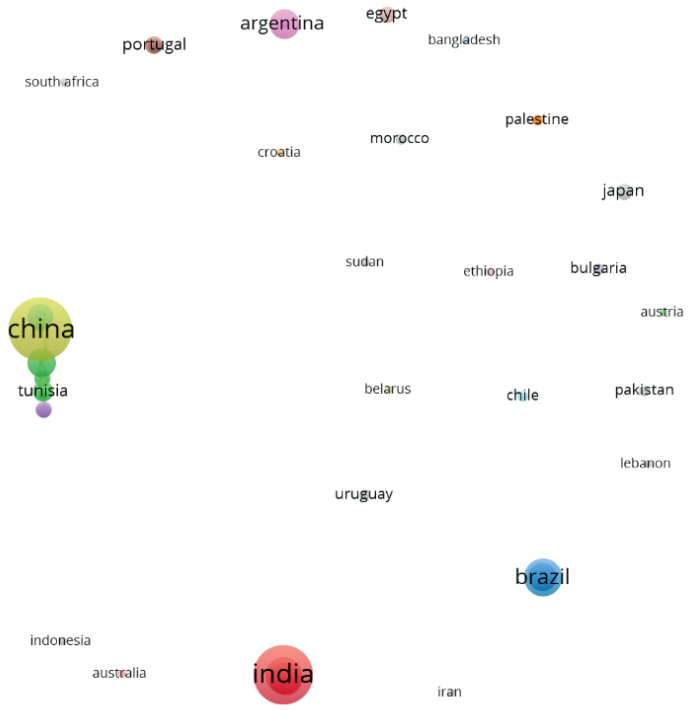

Figure 11. Country co-authorship network.

the red cluster, the relationship between Ukraine and Lithuania is very close, although only Ukraine has shared authorship with the United States. The last blue cluster shows that each country is connected only to two other countries. Brazil has shared authorship with Italy and Germany, but not with Spain.

As it can be seen, countries very close to each other such as China and India do not have any co-authorship relationship. As mentioned before, in these two countries, there has been a large increase in publication production due to the rapid and very important development of the tanning sector in recent years, so their tradition

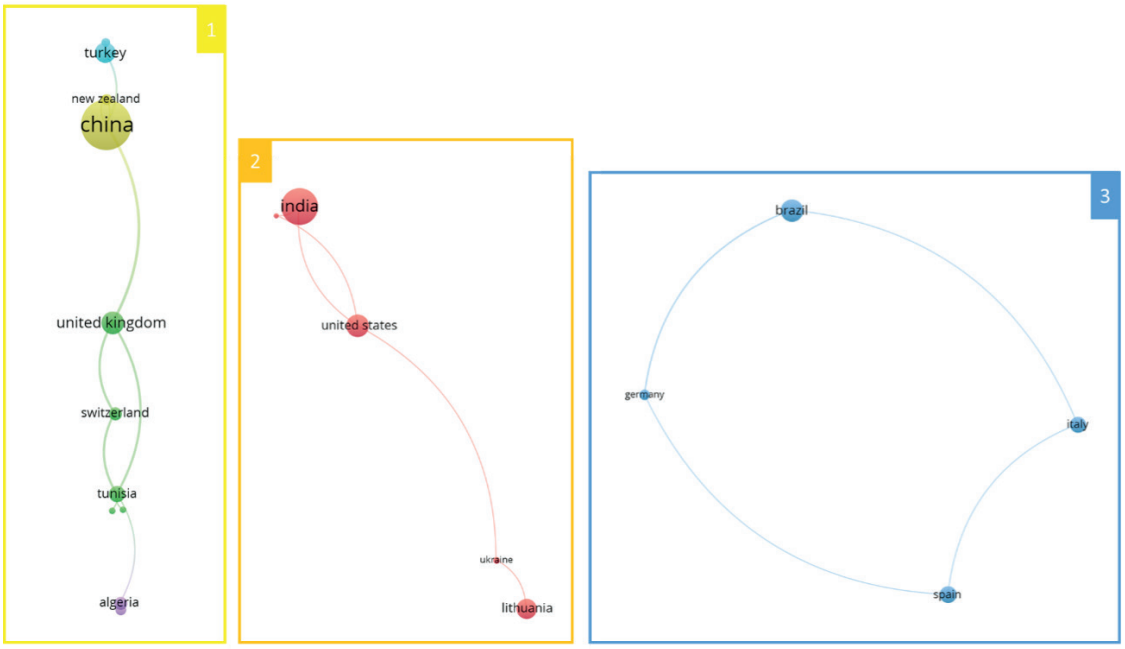

Figure 12. Co-author links between different countries.

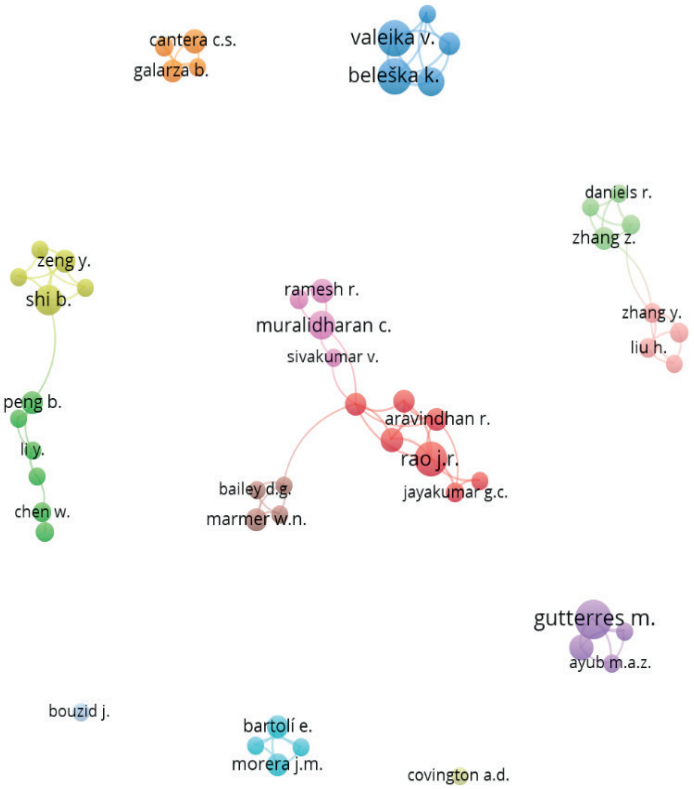

Figure 13. Author co-authorship network.

of research in this field is quite new. That is why they collaborate with other countries where there is a strong tradition of research for years but with very little production at an industrial level, such as the United States or United Kingdom.

The analysis of co-authorship by authors allows us to know the main links that exist between the most outstanding authors with publications on the subject in question. It broadly reflects social relations and interactions between members of different institutions.[42]

Figure 13 shows the relationship between the different authors who have published a minimum of 4 documents on the subject. As can be seen, there are a total of 13 clusters, most of them linked to each other. However, in the analysis some authors are not related to any other author. The red cluster is the one that brings together the largest number of authors, all of them from India, and currently belongs to the Central Leather Research Institute India. The only author linked to other authors from other clusters (the pink and brown clusters) is Thirumalachari H. Ramasami. At the left, the green cluster is linked to the yellow one. The only line that connects these two clusters is the one that links the authors Bi Shi and Biyu Peng. Both authors are from the same Chinese institution (Sichuan University). Similarly, at the right, in the cluster in salmon pink is linked to the light green one. Both clusters also bring together Chinese authors but, in this case, from different institutions.

Co-citation analysis

The analysis of co-citations consists of knowing the frequency in which two items, whether documents, authors, or journals, are cited together in the list of references of another document. According to H. Small, this type of analysis is one of the best indicators to know the thematic similarity between two documents.[43] In this section, two types of co-citation analysis are presented: by author and by the journal.

For the construction of the co-citation network using VOSviewer software, from the total of 7459 authors cited, those who were cited at least 20 times were selected, obtaining a total of 74 authors cited. Bigger items are linked to a high number of citations made to a cited author,[44] such as Jonnalagadda R. Rao, Palanisamy Thanikaivelan, etc. Five clusters were formed by different researchers, classified by groups of countries. The first cluster is the largest of them all, consisting of 31 authors from different countries (United States, Spain, India, Argentina, Italy, and Great Britain). The second cluster brings together 15 authors mostly from China and Brazil, while the third cluster also contains 15 authors from India. Finally, the last two clusters group 7 and 6 authors, respectively. One cluster contains only Indian authors, while in the other cluster, all authors are from Lithuania except Bi Shi and Yunhang Zeng, who are from China. Countries such as China, Brazil, India, and Lithuania may work more individually since these authors did not appear with links to any cluster.

For the elaboration of the journal co-citation network, a total of 2327 journals were cited, of which 17 were cited at least 15 times. These journals are divided into 4 clusters of different colors, indicating the subject area which is assigned:

1. Technical leather industry journals.
2. Journals related to wastewater treatment.
3. Journals of sustainability and environmental technologies.
4. Journals of microbiology, biochemistry, and molecular biology.

According to the data provided by VOSviewer, the journals with the most co-citation links among other journals are the Journal of the American Leather Chemists Association and the Journal of the Society of Leather Technologists and Chemists, with 572 and 357 citations respectively, followed by the Journal of Cleaner Production, with 316 citations.

Keyword co-occurrence analysis

The concept of co-occurrence in keywords analysis refers to the frequency of appearance and proximity between similar keywords.[45] Of the 291 publications extracted from the query, a total of 2024 keywords were obtained, of which 149 appeared at least 5 times. Before viewing the co-occurrence network, the elimination of some unnecessary keywords such as “article”, “nonhuman”, and

"controlled study" was considered. Special attention was also paid to replacing keywords written almost identically (e.g., animal for animals). Finally, a total of 144 words, distributed according to its thematic area, were found:

1. 40 keywords related to the study and treatment of water and environmental management.
2. 39 keywords referring to the main chemical compounds and other elements present in the tanning process.
3. 35 keywords linked to the biochemistry involved in the tanning process.
4. 30 more generic keywords such as metabolism, temperature, pH, animals, etc.

It could be noted that the word that stands out the most on the map, that is, with a more frequent appearance in publications, is "leather", followed by "tanning" and "enzymes", from different clusters but very close to each other.

Analyzing the keyword "leather", multitude of links with other keywords were seen. The thicker the line that links two words (link strength), the greater the co-occurrence between them. The distance between words also plays a significant role, since the less distance between words, the stronger the relationship between them.[51] So, the word "leather" is strongly linked with the words "tanning", "enzymes", "sulfur compounds", "collagen", "effluent", "leather industry", etc.

Similarly, if the keyword "unhairing" was studied, a strong relationship with the following keywords was found: "leather", "enzymes", "tanning", "sulfur compounds", "leather processing", "protease", "scanning electron microscopy", etc. Therefore, it is likely that those publications where the "unhairing" appears as one of the keywords of the study, more generic keywords could also appear, such as "leather", "enzymes" and "tanning", but also more specific ones, such as "sulfur compounds", "leather processing", "protease", and "scanning electron microscopy", as some publications could be studies on unhairing process either using enzymes such as protease, or applying the scanning electron microscopy, which allows obtaining information from the surface of a sample.[52]

VOSviewer also allows visualizing data in another type of network: overlay visualization. This type of visualization is almost identical to network visualization. The only difference is that the items are colored differently, as they are assigned a score of a certain color. In this case, this score is called "average publication year" (a.p.y), which is the average year of the published documents in which a keyword occurs. An overlay visualization of the different keywords contained in the publications allowed an evaluation of such indicator. Before 2005, the published documents focused mainly on liming, processes such as ultrafiltration and nanofiltration, as well as the effects of pH and skin swelling. From 2006 to 2010, research on unhairing and liming began to increase, causing more variety of keywords to appear, such as "hydrogen peroxide" (a.p.y = 2006), "environmental impact" (a.p.y. = 2007), "proteins" (a.p.y. = 2008), "wastewater" (a.p.y. = 2009), "sodium compounds" (a.p.y. = 2010), and so on. From 2011 to 2016, wastewater treatment of the unhairing process and the use of enzymes were some of the most studied topics in the publications. Some of the most popular keywords were "wastewater treatment", "enzymes" (which a.p.y. = 2011), "effluents", "collagen" (which a.p.y. = 2012), "enzyme activity", "leather processing" (which a.p.y. = 2013), "lime", "pollution" (which a.p.y. = 2014), "leather manufacturing" and "glycoproteins" (which a.p.y. = 2015). Finally, after 2016, chlorine compounds, hydrated lime, together with sustainable development, are some of the new topics used in this period.

Table IV lists some of the keywords added in the publications according to their frequency of occurrence and average year of publication classified into different periods. The fact that a keyword has an associated average year of publication does not mean that it has been appeared only in that period. That is, if 2011 is the average year of publication of the documents for a given keyword, these documents may have been published around 2016 or later, or even before 2005, but in less quantity. Therefore, as seen above, this also means that topics of study such as enzymes and the environment continue to be studied in the publications over these years. For example, the keywords related to the topic of enzymes may be "enzymatic unhairing", "enzymatic treatments", "enzyme synthesis", "proteolytic activities", etc. Regarding the topic of environment, the main keywords related to it may be "environmental impact", "environmental protection", "environmental pollutions", etc. All these keywords have appeared in many documents from 2006 to after 2016.

Conclusions

The big environmental issue generated by the traditional unhairing and liming operations of the leather tanning process has become one of the most important topics for researchers investigating this sector of leather.

The application of Bibliometrics has been a successful methodology to analyze the evolution and current state of this line of research. First, the study has allowed us to observe a notable change between the objectives pursued in the study conducted until the end of the 20th century and in subsequent research. The aim of most articles published until the end of the 20th century falls within the field purely of engineering and production process (quality, productivity, etc.). For some years now, the priority aims of the research conducted have to do with the environment and sustainability. Indeed, in recent years, new alternative and less polluting methods are being investigated that can replace traditional unhairing or somehow reduce the environmental impact and improve the sustainability of the process.

Table IV

Average year of publication of some keywords according to their frequency of occurrence in publications.

Periods	Keywords		
	More than 30 occurrences	**10 – 30 occurrences**	**5 – 10 occurrences**
Before 2005		tannery	swelling
		liming	quality control
		ultrafiltration	physical properties
		pH effects	nanofiltration
			dyes
2006–2010	leather	environmental impact	alkaline protease
	tanning	sodium compounds	hair removal
	unhairing	proteins	waste water management
	wastewater	hydrogen peroxide	peptide hydrolases
	chemical oxygen demand	industrial waste	environmental protection
		bacteria	enzyme synthesis
		etc.	etc.
2011–2016	enzymes	wastewater treatment	metabolism
	leather industry	pollution	waste disposal
	effluents	biochemical oxygen demand	fermentation
	sulfur compounds	enzyme activity	silicates
	lime	alkalinity	glycoprotein
	collagen	biodegradation	tannery wastewater
	sodium sulfide	keratin	ammonia
	etc.	water recycling	*Bacillus subtilis*
		biotechnology	hide unhairing
		enzymatic unhairing	enzymatic treatments
		etc.	etc.
After 2016		mammals	hydrated lime
		fibers	chlorine compounds
		sustainable development	proteolytic activities
			environmental pollutions
			protein degradation
			etc.

The study also highlights a rapid increase in scientific production in this field of research, with an increasing number of countries and institutions around the world involved in the sector. Despite the first document on skin unhairing, found in Scopus, was published in 1927, the trend of publications did not begin to increase until the late 1990s. From this decade, the number of articles published annually increased dramatically. The reason is the incorporation of Indian and Chinese authors, to the point that the institution with the highest number of publications on the subject is from India. Enzymatic unhairing has been one of the most studied alternatives, accounting for 46% of all documents published from the beginning of the century to 2021.

The number of journals published on the subject has also increased. In front of the two specific journals on tanning have been taking on relevant journals related to topics of sustainability and environment.

Regarding the co-authorship relationship, it is shown that the advantage of geographical proximity between countries is not the main factor that influences cooperative relationships. Rather, cooperation is established between countries where there is an important research tradition but with little production at the industrial level (e.g., United Kingdom or the USA), with countries with a big tanning industry, but with a very new research tradition in this field (e.g., China or India).

The results of the bibliometric analysis were conducted to give a reliable portrait of the "State of the art" of research, which is of significant help to the researcher when deciding what the lines of research should be in which to go deeper and which new lines of research are worth exploring. For example, in the case studied seems clear that it is necessary to deepen the search for an enzymatic product that allows eliminating the use of sodium sulfide and related products to increase the sustainability of the process.

Acknowledgments

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A Simple Test to Determine the Propensity of a Fatliquor to Trigger the Formation of Chromium (VI) in Leather

by

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Abstract

Since the entry into force of the EU Commission Regulation regarding hexavalent chromium in leather articles in 2014, it is of paramount importance to follow good manufacturing practices to ensure the production of leather not only free of Cr(VI) but with no tendency to its formation. The equilibrium between Cr(III) and Cr(VI) in leather can be disturbed under stressful environmental conditions such as light or heat exposure. These factors could trigger the lipid peroxidation of unprotected unsaturated fatliquoring agents, thus leading to the oxidation of Cr(III) to Cr(VI).

Due to the relevance that the oxidation of the fatliquoring agents has in the subsequent Cr(VI) formation, the Propensity Test has been developed and verified as an innovative verifying in-house tool for tanners to verify that each of the fatliquoring agents used in the tannery processes are properly protected against oxidation and thus, that Cr(VI) formation is not triggered.

The method has four simple steps and can be easily carried out in the tanneries' pilot plant. It does not require special equipment or specific apparatus because all the necessary instruments are usually available in any tannery and the skills needed to perform the test are the same that leather technicians use in their day-to-day work, so the implementation cost is practically non-existent.

This work leads to the conclusion that there is a higher possibility of Cr(VI) formation among sheep skins rather than among calf hides. The rechroming process also presents risks regarding Cr(VI) content in leather, however, in this study it has been shown that rechroming does not increase Cr(VI) formation risks when the fatliquoring agents are properly protected against autoxidation. Therefore, using a well-protected fatliquoring agent is mandatory for the purpose of producing Cr(VI)-free leather despite the type of leather.

Introduction

In 2014, the EU Commission Regulation Nº301 regarding the limitation of hexavalent chromium in leather was issued. This has led leather manufacturers to revise and improve the tanning and wet-end processes and it states the relevance of the application of good manufacturing practices in order to prevent hexavalent chromium formation. Since the entry into force of the regulation, contact dermatitis studies carried out in Denmark, which was the country that submitted the hexavalent chromium restriction proposal to the European Union, show that the prevalence of chromium allergy is decreasing. The EU Directive that restricts the presence of hexavalent chromium in leather goods is thought to be playing a central role in this change.[1]

Nevertheless, appropriate prevention measures still need to be carried out by tanneries in order to ensure the production of leather without risk of Cr(VI) formation.

Hexavalent chromium in leather can come from the use of Cr(VI)-containing products, although nowadays this is highly unlikely. Currently, it is much more common for hexavalent chromium to be found in leather due to the oxidation of the non-fixed fraction of Cr(III) used for tanning or retanning.

The reduction-oxidation potential of the Cr(III)/Cr(VI) equilibrium might vary depending on certain conditions. The reaction that oxidizes Cr(III) to Cr(VI) is reversible, and some factors can have an impact in the formation or reduction of the most oxidized state. A relevant parameter is the presence of oxidizing conditions. If pH is too high, the equilibrium reaction is displaced towards Cr(VI) formation, so in certain wet-end processes the pH has to be controlled and adjusted. Free radicals also have potential of oxidizing Cr(III) to Cr(VI). They might come from the lipid peroxidation of unprotected unsaturated fatliquoring agents. In presence of air, a free radical can react with oxygen. Peroxides and peroxide free radicals are then formed, and an oxidation environment is created. The autoxidation of unsaturated lipids is promoted by its exposure to light and high temperatures, specifically under radiation in the UV spectrum.[2, 3]

Some companies have developed fatliquoring formulations that include, among other measures, antioxidant substances in order to help preventing free radical chain reaction. Regarding auxiliary products in a tanning formulation, the use of oxidizing bleaching agents such as hypochlorite or hydrogen peroxide can promote Cr(VI) formation. On the other hand, vegetable extracts, antioxidants and reductive agents can help to maintain chromium in its trivalent state.[4–8]

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Besides light exposure and temperature, another factor that can also catalyze Cr(VI) formation is low relative humidity. A tannery cannot control the environmental conditions the leather will be exposed to once it leaves the factory. However, good manufacturing practices can be implemented to ensure that the produced leather is as well-protected against Cr(VI) formation as possible, regardless of the environmental conditions it might be exposed to in its useful life.[6, 9, 10]

Influence of fatliquoring in Cr(VI) formation

Among all the tanning activities, wet-end processes and specifically the fatliquoring process can have the largest incidence in Cr(VI) formation, especially if the leather has been properly degreased during beamhouse and wet-end processes and its natural fats have been eliminated.[2,11] Historically, iodine index, a marker of the degree of unsaturation of an oil, was proposed as a way to predict propensity to Cr(VI) formation.[6] However, chemical manufacturers have developed fatliquoring agents protected against oxidation, thus the level of unsaturation in a fatliquor is no longer an indicator of the propensity of a leather to form Cr(VI). The degree of unsaturation is only relevant when fatliquors are not protected against oxidation. Furthermore, a validated test method for measuring the iodine index in commercial sulphited or sulphated fatliquors is not available, thus the comparison between such products would not be reliable.[10,12]

A protected fatliquor is created by firstly selecting high-purity, strictly controlled raw materials. The second mainstay is to apply up-to-date processing methods (aeration, sulphation and sulphitation among others) to stabilize the natural oils in order to inactivate the multi-conjugated bonds. The last element is to add synthetic antioxidant mixtures that work as radical scavengers. It is very important that these antioxidants are evenly distributed and properly dispersed along the leather matrix. The antioxidant addition is a process widely used by different commercial companies in order to protect fatliquors from oxidation. Among others, synthetic phenolic lipidic antioxidants (SPAs) are widely used when protecting leather fatliquors, being the antioxidant 1135 (CAS number 125643-61-0) one of the most implemented.[8,13,14]

Testing for Cr(VI)-free raw materials

To produce leather that does not contain hexavalent chromium, ensuring that all raw materials used are free from this restricted substance does not provide enough safety to the tanner. Hexavalent chromium may be formed within the leather by oxidation of free Cr(III) originating from chromium products used for the tanning or retanning [6,11,15–18] once exposed to the environmental conditions mentioned above. Tanners should obtain from their suppliers a declaration stating that the acquired fatliquoring agents are properly formulated and protected against Cr(VI) formation. Be that as it may, it is not always feasible to get this kind of statement, and moreover, a reliable declaration. Taking into account the important role that fatliquors play in the origin of hexavalent chromium in leather, and due to the fact that the classic control methods of such products used in the manufacturing of leather (determination of common parameters like Iodine Index, fatty acid composition, active matter, SO_3) do not provide safety regarding Cr(VI) concern, it is highly advantageous to perform a new test that can be carried out in the same tannery, to check the propensity of fatliquors to trigger Cr(VI) formation.[10]

The Propensity Test is presented as an innovative verifying in-house test for tanners: a test to check that each of the fatliquoring agents that are used in the tanning process are properly protected against oxidation and thus, that Cr(VI) formation is not promoted. This test can be carried out in-house and lasts no more than one workday. The method has four steps. The first one is to select a wet-blue leather from a trusted origin. The second step is to perform a simple wet-end process in a laboratory drum / small scale drum, omitting the retanning and dyeing processes. Only the investigated fatliquor is applied to the wet-blue in the fatliquoring step. Then an ageing test at 80 °C is performed to the crust leather, according to ISO 10195. Finally, the aged leather is analyzed for Cr(VI) by one of the available methods. This test can be useful for the manufacturers of fatliquoring agents and also for tanneries that use chromium as a tanning system.

The final goal of the Propensity Test is to easily detect fatliquors that have a tendency to trigger hexavalent chromium formation in leather, as a quality control tool for selecting appropriated fatliquors among the offers that the tannery receives from its suppliers. It is proposed as a control tool for each lot of fatliquoring agents. This tool could also be used to guarantee Cr(VI)-free leather when a modification of formulation arises, or also for changes in the wet-blue provider.

The risk of any hexavalent chromium detection in the leather production due to the instability of the fatliquors employed, which is related with important economic losses, is avoided.

Experimental

Skins and hides

Five different types of wet-blue skins and hides have been evaluated during the development of the test to ensure that it is applicable to all kinds of leathers. The leathers were selected to cover a wide range of species, and they include two bovine full-grain calf hides with

Catalan origins (references CA and CC), one bovine split (SP) from Germany, one sheep skin (SS) from England and one hair sheep skin from Nigeria (HS). Prior to testing, the leathers were cut in a rectangular shape of 30 cm x 20 cm.

Materials and facilities

The studies presented in this work were carried out in laboratory drums, suitable for small scale trials. Simplex 2 from InoxVic (Spain) were the drums used. The diameter of the drums was 30 cm and the width was 15 cm. The rotation speed was fixed at 38 rpm. The drums are capable of achieving proper temperatures to ensure that the fatliquoring agents are well fixed. Other small appliances are needed to perform the test: a balance with a resolution of 0.01 g, a thermometer able to measure temperature in a range between 10-60° C and a pH-meter to measure the pH of the bath. A portable pH-meter is a very useful tool. Otherwise, pH strips in the required ranges can be used as well. A solution of bromocresol green is required to check uniformity through the cross-section of the leather.

Propensity Test recipe

The procedure for testing a fatliquoring agent can be performed in laboratory drums in one working session.

An initial washing and degreasing step is included for the removal of traces of natural fat that might be present in the leather. As a general precaution for lipid peroxidation and hexavalent chromium prevention, it is advisable to always degrease the leather at the beginning of the test. However, in case a tannery worked with wet-blue leather with less than 3.0% of soluble matter in dichloromethane (according to ISO 4048), or had a record of several results over time below this value, the degreasing part could be excluded.

After that, there is the rechroming step. This process might be avoided if the tannery will use the tested fatliquor in an article that does not involve a rechroming step.

The neutralization process is a key aspect in the recipe. The pH of the bath after the neutralization and before draining the bath shall be in a range comprised between 5.4 – 5.8 and all the cross-section of the leather has to be visually uniform when a small cut is made and a solution of bromocresol green is applied to the cross-section. If the pH is lower than 5.4, the drum should run for an extra 30 minutes and then the pH should be checked again. If a pH of 5.4 is still not achieved, 0.2% of sodium bicarbonate should be added, then the drum should run again and finally, the pH should be checked again. The amount of sodium bicarbonate needed to reach the desired range of pH depends on the particular characteristics of the wet blue used as raw material. Once adjusted in the first run of the Propensity Test for the specific wet-blue consumed, it would be practically constant for the next applications.

The fatliquoring agent along with the auxiliaries have to be emulsified in order to ensure that the fatliquoring penetrates through the entire cross-section of the leather. Once the fatliquoring has been incorporated, it is necessary to fix it with formic acid. To do so, two additions of formic acid are incorporated in the drum, previously diluted in a 1:5 rate. The final pH shall be between the range of 3.5 - 4.0. If at this point the pH is higher than that, an additional 0.2% of formic acid has to be added, then the drum shall run for 20 min and the pH must be checked again to ensure it falls within the range.

After finishing the recipe, leathers have to be removed from the drums and left overnight covered in a plastic wrap on a smooth surface, in order to maintain humidity and to allow for the fatliquor agents to set and properly bond to the leather fibers. The next day, the plastic wrap is retired and the leathers are left to dry overnight.

Table I includes the detailed description and proportions of the recipe.

A commercial blend of ethoxylated C_9-C_{14} alcohols was used as a degreasing agent. As a wetting and emulsifier agent, a synthetic emulsifier based on alkyl sulphates was selected.

Formic acid, sodium formate and sodium bicarbonate were purchased from conventional chemical product providers, as well as the chromium salt, with 33% basicity and 25% Cr_2O_3.

It is advisable to refer the calculation basis of the recipe to a wet-blue humidity comprised between 45 - 55 %. In case the humidity of the wet-blue skin or hide was out of this range, recalculate its weight referred to a humidity of 50%. This is the wet-blue weight that should be computed in the recipe of Table I.

Testing for hexavalent chromium

Once the leathers are dry, the amount of Cr(VI) has to be analyzed in an external laboratory according to official standards such as ISO 17075-1:2017 or ISO 17075-2:2017. Both methods have a Quantification Limit of 3 mg/kg of Cr(VI). To check for the propensity of the fatliquoring to Cr(VI) formation, the leathers shall be exposed to specific ageing conditions such as thermal heating for 24 hours at 80°C, as it is described in the ISO 10195:2018. The stress that these conditions involve might trigger Cr(VI) formation if the fatliquoring agent was not adequately protected against the effects of the autoxidation.

Table I

Recipe to test a fatliquoring agent for propensity to the formation of hexavalent chromium

Process	% of wet-blue weight	Products	°C	Time (min)	Remarks
Washing	200	Water	45		
	0.2	Formic Acid 85% (1:6)			
	0.8	Wetting agent			
	0.5	Degreasing agent		40’	Drain float
	200	Water		3’	Drain float
Rechroming	150	Water	35		
	0.2	Formic Acid (1:6)		10’	Control pH 3.3-3.4
	3.0	Chromium salt 33% basicity 25% Cr_2O_3		90’	
	2.0	Sodium formate (solid)		30’	Control pH 3.8-3.9 Drain float
	200	Water		3’	Drain float
Neutralization	120	Water	35		
	1.6	Sodium formate (1:10)		30’	
	1.0	Sodium bicarbonate (1:10) (temperature not higher than 35 °C)		60’	Divide into 3 additions separated by 4 min. pH 5.4-5.8
					Write down pH. Check for uniform cross section. Drain float.
	200	Water		3’	Drain float
Fatliquoring and Fixation	90	Water	50	5’	
	1.0	Emulsifier agent			
	9.0	Fatliquor to be tested (Emulsified 1:5 with water at 50°C)			Emulsify
	20	Water	50	90’	Clean the main container, funnel and pipes of the drum
	0.7	Formic Acid (1:6)		20’	
	0.7	Formic Acid (1:6)		20’	Check pH 3.5-4.0
					If pH= 3.5-4.0, drain float. Write down pH. If not, add 0.2% more formic acid and drum 20’ more until pH=3.5-4.0
Washing	200	Water		3’	Drain float

It is advisable that all the analysis are performed in a laboratory accredited by ISO 17025:2017. For routine testing purposes once the Propensity Test is implemented in a tannery, the analysis could be carried out in its facilities through the application of the LeatherKit_Cr6 testing method.[19] As the recipe for the Propensity Test does not involve a dying step, the colorimetric analysis of the crust leather does not require discoloration of the extract, thus simplifying the LeatherKit_Cr6 test procedure and its costs, as the solid phase extraction cartridges would not be required.

Once the leathers have been processed and tested for Cr(VI), the fatliquoring agent tested passes the Propensity Test and thereby it is accepted for daily use if Cr(VI) is not detected in the sample above 3 mg/kg after an ageing test. Should the value of Cr(VI) detected be superior to 3 mg/kg, the fatliquoring agent would not be suitable for ensuring a Cr(VI)-free leather production and thus it should be considered a failure.

Apparent density of leather

The apparent density of the crust leather was established following the method described in ISO 2420:2017.

Results and Discussion

Performance of the Propensity Test

The usefulness of the Propensity Test as a tool for discerning whether a fatliquor agent could contribute to the Cr(VI) formation was evaluated by testing five types of wet-blue skins and hides. Ten different fatliquoring agents were tested with each type of wet-blue. The method has been further used as a routine control test for other fatliquoring agents, proving its utility as a control tool.

The composition of the tested fatliquors included a wide variety and it is described in Table II.

Fatliquoring agents F1 to F4 are commercial fatliquoring agents produced in a manner that they are protected against lipidic peroxidation, be it due to the origin of the raw material, the good manufacturing practices or the addition of certain amounts of specific and tailored SPAs, or due to a combination of these three factors as it is explained in the introduction section.[8,13] These fatliquors were acquired from international chemical companies and should presumably lead to low Cr(VI) formation, below 3 mg/kg, even after an ageing test was applied to a leather.

On the other hand, three base oils from risky natural unsaturated raw materials that were not ready to be on the market and were not protected against Cr(VI) formation (F5 - F7) would presumably get positive detections in Cr(VI) content.

Confirming these hypotheses would lead to the conclusion that the propensity test is suitable to determine whether a fatliquoring agent can trigger the formation of Cr(VI).

Three more fatliquoring agents (F8 - F10), with unknown degrees of protection, have also been tested, to determine their risk regarding hexavalent chromium formation.

The active matter is the percentage of all components of the fatliquoring agent, water excluded. It serves as a guide for the formulation process.

Validation of the Propensity Test

The main objective of the Propensity Test is to distinguish fatliquoring agents that are protected against Cr(VI) formation from non-protected fatliquoring agents. Table III shows the Cr(VI) present in the 5 types of leathers when treated with the 10 different fatliquoring agents described in Table II.

For fatliquoring agents F1 to F4, no hexavalent chromium was detected in any of the five different wet-blue leathers after an ageing process. They were a "pass" for each type of leather, as expected, leading to the conclusion that the appropriate protection applied to the fatliquoring agents' formulation by the chemical companies is working properly against lipidic peroxidation. For fatliquoring agents F5 to F7, extremely high amounts of Cr(VI) were found. They were "fail" for each kind of leather, as expected according to the characteristics described in Table II. This indicates that the Propensity Test is useful for testing fatliquoring agents as it can accurately distinguish between fatliquoring agents with or without propensity to form hexavalent chromium.

Table II

Fatliquors tested during the development of the Propensity Test.

Code	Percentage of active matter	Features
F1	50	Auxiliary synthetic fatliquor with dispersing properties
F2	60	Fatliquoring agent, "compound" type, natural/synthetic
F3	70	Fatliquoring agent, natural/synthetic, high antioxidant properties
F4	50	Fatliquoring agent, synthetic. Needs a penetration auxiliary
F5	75	Non-protected concentrated sulphated oil base, vegetable origin
F6	90	Non-protected sulphited oil base, vegetable origin.
F7	85	Non-protected concentrated sulphited oil base, fish origin
F8	70	Commercial sulphited fish origin fatliquor. Unknown degree of protection
F9	70	Commercial sulphated triolein intended for vegetable tanned leather. Unknown degree of protection
F10	50	Commercial sulphated triolein. Unknown degree of protection

Table III

Cr(VI) content in mg/kg of the experiments for the developing of the Propensity Test. Results obtained according to ISO 17075-2:2017, after ageing the leather samples according to ISO 10195:2018.

	Cr(VI) content in mg/kg for each type of leather				
Fatliquor	**CA**	**CC**	**SP**	**SS**	**HS**
F1	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F2	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F3	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F4	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F5	14.4	15.8	22.0	43.3	21.4
F6	20.3	27.2	40.6	75.6	41.5
F7	28.6	25.4	37.2	64.2	29.8
F8	21.8	19.8	20.7	20.3	21.0
F9	< 3.0	< 3.0	3.0	3.5	5.9
F10	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0

Products F8 to F10 were three fatliquoring agents with unknown degree of protection. After applying the Propensity Test, F10 has been verified as a protected fatliquoring agent as the Cr(VI) results obtained in the crusts of all type of leather were below 3.0 mg/kg. Fatliquoring agent F9 is intended for vegetable leather, thus implying that it might contain some degree of protection against auto-oxidation and rancidity, but this protection is not effective enough to prevent Cr(VI) formation in leathers with an innate tendency to form Cr(VI). F8 was discovered to be not viable to use for leather tanned with chromium.

Then, in order to validate the propensity test, repeatability and reproducibility were studied. The influence of the substrate (origin and species) and the influence of the rechroming process were studied as well.

Intra-day repeatability was calculated by applying the Propensity Test in a grain bovine leather (CC) six times in the same day. The fatliquoring agent tested was F5 and the average results were 18.6 mg/kg of hexavalent chromium, with a relative standard deviation (%RSD) of 12%. Taking into account the fact that this is a test to be applied in a pilot plant, the %RSD appears to be suitable for the degree of protection needed.

Reproducibility was also calculated following a similar way as the repeatability. A grain bovine leather was also tested with fatliquoring F5 in three different days by two different test operators. This time, %RSD was 21%. Despite of the fact that it may seem a high %RSD, the results of the test show that the process is accurate and precise enough for the main goal of distinguishing between the pass or fail character of a fatliquoring agent, and that it maintains the same qualitative character along all the performed tests.

The test has been implemented in the laboratory of a chemical company that produces fat-liquors and good feedback has been received from the staff.

Cr(VI) content depending on the type of leather

Based on the results shown in Table III, it can be inferred that the result of the analysis of Cr(VI) for fatliquors F5 to F8 follows a certain tendency according to the type of leather. Both bovine grain leather (CA and CC) were the two types of leather where lower amounts of Cr(VI) were obtained, even though the same amount of fatliquoring had been applied to all of the leathers during the Propensity Test, as the recipe states. Split bovine leather (SP) obtains slightly higher concentrations, similar to the hair sheep skins (HS). Finally, sheep skin (SS) is the leather with the highest values of Cr(VI), reaching amounts above 40 mg/kg for all the non-protected tested fatliquoring agents. These findings go in line with more than 500 routine analyses that have been performed at A3 Leather Innovation Center during the 2016-2021 period, where it was observed that split hides and sheep skins tend to have higher

Table IV

Apparent Density of the fatliquored leathers. Results obtained according to ISO 2420:2017.

Type of leather	Apparent density range
Grain bovine leather (CA and CC)	600-720 kg/m^3
Split bovine leather (SP)	530-590 kg/m^3
Hair sheep skins (HS)	400-480 kg/m^3
Sheep skins (SS)	400-480 kg/m^3

Cr(VI) detections and therefore those are the types of leather with higher Cr(VI) risk.

The results obtained with the F9 fatliquoring agent highlight a relevant fact. A fatliquor with a medium-low degree of protection can be used for bovine leather tanning, but only fatliquors with the highest degree of protection can be used for sheep skins and split leather.

These results imply that skin origin and structure have a relevant effect on the final Cr(VI) content. All the leather samples went through a degreasing step, as the Propensity Test recipe describes in Table I. However, differences in Cr(VI) content are still visible, thereby indicating that when performing a uniform degreasing step, the remaining traces of natural fats along with the different features specific for each skin origin might still have some influence in the final concentration.

The compactness of the fiber structure could also play a role. The ISO Standard 2420:2017 for measuring apparent density in leather was applied to the five different types of leather once the Propensity Test was applied and the results are shown in Table IV.

The parameter of apparent density is used to calculate the theoretical mass that one cubic meter of leather weights. Higher values are related with high compacity leathers such as shoe soles, whereas lower apparent densities are linked to more interfibrillar space. Leather samples with lower apparent densities (HS, SS) allow for more air to circulate inside their section. Air contains oxygen, the precursor of lipid peroxidation. The fact of having more interfibrillar space for the air to circulate enables more contact between the oxidizable components of the fatliquoring agents and the oxygen, thereby promoting trivalent chromium oxidation and leading to an increase of Cr(VI) in these samples.

It is also worth noting that when comparing the same breed of animal leather (CA and CC versus SP) there is also a clear tendency for the split bovine leather to obtain higher Cr(VI) values after thermal ageing. The same hypothesis might be applied to this case, as split leather is the part of the bovine leather with less apparent density. Also, split leathers come from the part of bovine hides where it is more likely to find higher amounts of natural grease.

Influence of the rechroming process

The general recipe described for the propensity test involves a rechroming step, as this is a common process to perform when retanning wet-blue leathers for some articles, for example suede splits. However, the rechroming step might not be necessary for other articles and tanners might skip it, thus its effect has been studied.

Rechroming a leather implies the use of more chromium salt, with the risk of increasing the amount of free trivalent chromium present. When there is more trivalent chromium than the collagen can fix, it remains in the interfibrillar space, entailing extra amount of free Cr(III) that is susceptible to oxidation.

The effect of the rechroming step was investigated by performing the Propensity Test with and without rechroming in three types of studied leathers for three protected (F1 to F3) and three non-protected (F5 to F7) fatliquors. According to the results obtained (Table V), Cr(VI) content increases in all the leathers that have been rechromed. It was concluded that the sensibility to detect not well-protected fatliquors is higher for the processes that involve the rechroming, thus confirming the fact that non-fixed Cr(III) can increase Cr(VI) formation when adverse conditions are given.

The study also demonstrates that rechroming has no effect in Cr(VI) formation when protected fatliquoring agents are used in the leather wet-end processes.

Table V

Comparison of the Cr(VI) content in mg/kg of the rechromed and not-rechromed leathers. Results obtained according to ISO 17075-2:2017, after ageing the leather samples according to ISO 10195:2018.

	Influence of the rechroming process. Cr(VI) content in mg/kg.					
Fatliquor	**CC (Bovine)**		**SP (Split)**		**HS (Hair sheep)**	
	Rechromed	**Not rechromed**	**Rechromed**	**Not rechromed**	**Rechromed**	**Not rechromed**
Not protected						
F5	14.4	11.6	22.0	13.0	21.4	14.1
F6	20.3	14.2	40.6	29.4	41.5	30.7
F7	28.6	23.4	37.2	30.3	29.8	28.2
Protected						
F1	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F2	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
F3	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0

Conclusions

The Propensity Test can be used for detecting fatliquoring agents that are not sufficiently protected against the autoxidation, and therefore they have the tendency to promote the formation of hexavalent chromium when applied to chromium-tanned leathers. It is a simple, economic test that is easy to perform. Such testing presents one clear advantage: the improvement of product and consumer safety as unstable and insufficiently protected fatliquoring agents' batches can be detected at the earliest stage, before entering in the production facilities. The risk of Cr(VI) issues, which is related to important economic losses, is drastically reduced.

This test is easy to carry out in the tanneries' pilot plant. It does not require special equipment. All the necessary instruments are usually available in any tannery. The skills needed to perform the test are the same that leather technicians use in their routine work.

For developing the test, four commercially available protected fatliquoring agents and three non-protected fatliquoring agents were used. When applying the developed recipe, the Cr(VI) amount in each of the applied leathers was found to be matching the expected results. For protected fatliquoring agents, no Cr(VI) was detected above 3 mg/kg, and for non-protected fatliquoring agents, there was Cr(VI) detection which was, in some cases, more than 30 mg/kg.

The test validation has been carried out by assessing the repeatability and reproducibility, with results of 12 and 21 %RSD, respectively. These values are aligned with the expected results for this type of test method. The process is accurate and precise enough for distinguishing between the pass or fail character of a fatliquoring agent and maintains the same qualitative character for all the performed tests.

The risk of finding hexavalent chromium is higher among sheep skins than among calf hides. This outcome is in agreement with the data obtained after the analysis of more than 500 routine samples performed at A3 Leather Innovation Center, that showed that split hides and sheep skins are the types of leather with higher Cr(VI) risk. One of the reasons could be because these are skins with more space between the fibers for the air to circulate. At the same time, this type of leather has an elevated probability of containing traces of natural fats despite being degreased thoroughly along the leather tanning process.

The rechroming process has shown to be a risky process regarding Cr(VI) content in the leather, however, in this work it has been shown that rechroming does not involve Cr(VI) formation risks hazards when the fatliquoring agent is properly protected against autoxidation.

This work also demonstrates that using a well manufactured and protected fatliquoring agent is mandatory for the purpose of producing Cr(VI)-free leather.

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Preparation of Polyols and Polyurethane Foams from Olein By-Product of Tanning Industry

by

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Abstract

Olein produced from the solid residues of the tanning industry is already employed as raw material to obtain greasing oil for leather. However, new applications for this product may be advantageous regarding environmental impact and sustainability of this industry. In this work, flexible polyurethane foams (FPUFs) were prepared from polyols obtained from olein. A polyol from olein was prepared through alkaline glycerolysis. The glycerolysis conditions of temperature, glycerol/olein molar ratio, amount of catalyst and reaction time were optimized using a 2^4 factorial design, resulting in an olein polyol containing around 75% of monoacylglycerols, hydroxyl value (388.68±0.40 mg $KOH.g^{-1}$), and hydroxyl functionality of 2.89. FPUFs were prepared at NCO/OH ratios of 1.2:1 and 1.3:1, using an aliphatic hexamethylene diisocyanate trimer and water as foaming agent. The foams were characterized through FTIR, thermogravimetry, morphology, extractable materials, and mechanical properties. Characteristics urethane/urea groups formation were verified by FTIR as well as typical mass loss steps in the thermal decomposition curves. The foams morphology showed a structure composed mainly for polygon-type closed-cells. The obtained FPUFs presented a content of extractable materials lower than 3%. The mechanical properties of the foams were dependent on the NCO/OH ratio, and the foam prepared at the ratio of 1.2:1 stood out as a potential material to be used in the production of mattresses. This study demonstrated the feasibility of transforming olein, a solid residue of the tanning industry, as a precursor to prepare PU foams, which may be a promising material for mattress applications, considering the observed features.

Introduction

The tanning industry is a global manufacturing sector that processes skins and hides of animals (tanning) to produce leather, a finished material used for the fabrication of a variety of articles, such as footwear, clothing, bags, automotive upholstery, fashion accessories, and furniture. The leather manufacturing process occurs basically in three steps: preparation, tanning and finishing. The preparation step begins with the ordering and salting (to prevent putrefaction) of the hide/skin and is followed of the beamhouse operations, which include soaking, liming, removal of extraneous tissues (unhairing and fleshing), deliming, bating, and pickling. The beamhouse process is particularly important when considering environmental aspects because it generates large amounts of solid waste, composed of hairs, epidermis, subcutaneous layer, non-collagenous proteins, salt, fats, blood, and dirt.

Considering specifically the pre-fleshing operation, the solid residues removed from the subcutaneous region of the skin contain about 32% (wt.) of fat content and 20% (wt.) of hide. This residue can be processed through digestion/extraction and winterization techniques in order to produce olein, a lipid matter, yellow and liquid at room temperature. Olein is composed of a mixture of saturated and unsaturated triglycerides (TAG), with oleic acid as the major component, corresponding to about 72%.[1] The olein obtained from pre-fleshing solid residue is used as raw material to produce greasing oil for leather.[2] Nevertheless, the search for new applications for this product is relevant in terms of the environmental impact and sustainability issues related to the tanning industry.

The use of this olein as raw material for the synthesis of polyols to produce polyurethanes appears as an interesting possibility. Polyurethanes (PUs) represent a broad class of polymers usually obtained by a step-growth reaction between a di/polyisocyanate and a di/polyol. A wide variety of products (such as rigid or flexible foams, rubbers, elastomers, coatings, and adhesives) can be produced by varying the proportions and type of isocyanate, polyol, blowing agent, catalyst, and other additives.[3]

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Polyols are hydroxylated compounds used to produce PUs. These polyols add specific characteristics to the final polymer, including mechanical properties such as flexibility, softness, tensile strength, and low-temperature elongation. Conventional polyols are obtained from petroleum derivatives; however, due to growing concerns over environmental pollution, the research on the production of polyols from renewable sources has increased significantly recently.[4] Among the renewable sources considered in the literature to produce polyols, vegetable oils stand out due to the availability, variety and relatively low cost. Castor[5], soybean[6] and andiroba[7] oils are examples of vegetable oils that have already been used in the synthesis of polyols for PUs. Due to its low cost and structural chemical similarity to the vegetable oils, olein has the potential to be used as raw material for polyol synthesis.

The chemical transformation of vegetable oils in polyols can be accomplished by functionalization of the double-bonds or by transesterification in order to obtain a product rich in hydroxyl groups. Glycerolysis, a well know transesterification reaction between glycerol and TAG, is one of the main routes for this process, classically used for the preparation of alkyd resins.[4,8] This reaction is carried out under an inert atmosphere and high temperature (200 to 250 ºC) to increase the solubility of glycerol in the oil phase, which is about 4% at room temperature. Besides, glycerol excess is added to shift the reaction equilibrium toward monoglycerides (MAG) and diglycerides (DAG) formation, and alkalis such as NaOH, KOH, and $Ca(OH)_2$ are used as catalysts.[9] The product of this reaction is a polyol that can be used in polymer manufacture.[4]

Therefore, considering the technical viability of the PU production from triglyceride (TAG) from vegetable oils and the great amount olein generated as residue in the tanning industry, this work aims to investigate: (i) the production of polyol by glycerolysis of olein obtained as residue of the pre-fleshing step; and (ii) the preparation of flexible polyurethane foams (FPUF) with the olein polyol (OP) obtained in this way.

Experimental

Materials

Olein produced from pre-fleshing residues was supplied by a tannery (Picada Café City – Brazil) and characterized through acid index (ABNT-NBR-11115:2014), kinematic viscosity (ABNT-NBR-10441:2014), water content (ABNT-NBR-10445:2013), high-performance liquid chromatography (HPLC), and nuclear magnetic resonance (NMR).

Aliphatic hexamethylene diisocyanate trimer (Tolonate® HDT 90) with a content of free isocyanate groups of 16.1±0.1 % (as determined by the ASTM D 2572 – 97 method) was supplied by VencoreX Chemicals © (Guarulhos – Brazil). Silicone-polyether copolymer surfactant (DABCO® DC5986) was supplied by Evonik Industries AG (Essen - Germany) and used as foam structure stabilizer. Deionized water was used as a blowing agent. Dibutyl-tin dilaurate – DBTDL (LIOCAT® 119, Miracema-Nuodex Chemical Industry Ltda., Campinas – Brazil) was used as catalyst. Chromatographic standards of monoolein, 1,3-diolein and triolein were acquired from Accustandard Company (New Haven - USA). Other reagents and solvents were of analytical or HPLC grade.

Synthesis of the olein polyols (OP)

The olein polyol was prepared by glycerolysis of the olein according to a method described by Barrios.[10] A 2^4 full factorial design experiment with four central points was carried out using a fixed amount of olein (10 g) and KOH as catalyst. Catalyst quantity (0.5, 1.0 and 1.5 $\%w_{olein}$), glycerol/olein molar ratio (2.5:1, 3.0:1 and 3.5:1), temperature (180, 200 and 220 °C) and reaction time (2, 4 and 6 h) were used as factors. All experiments were performed under inert atmosphere and magnetic stirring (~800 rpm). After the reaction, OP was neutralized with a 0.01 M HCl solution, at 60°C and under stirring. The water was then removed under reduced pressure (-0.08 MPa) at 80°C in a rotary evaporator.

Preparation of the flexible polyurethane foams (FPUF)

FPUFs were prepared via one-step method, according to the formulations in Table I. The olein polyol was previously heated at 60°C until liquid, then the surfactant, deionized water, catalyst, and HDT were added. The mixture was mechanically stirred at 2,500 rpm for 70 seconds and then transferred to a mold of 150×150×150 mm, previously lined with kraft paper. The FPUFs curing was performed in an oven at 60°C for 24 h and the post-curing by storage at 30°C for 72 h.

Table I

FPUFs formulations

		Parts by weight				
Formulation	NCO/OH*2 Molar ratio	Olein polyol*1	HDT	Deionized water	Surfactant	Catalyst
FPUF1	1.2:1	100	192	6	6	1
FPUF2	1.3:1	100	210	6	6	1

*1Olein Polyol 2 (OP2 - Experiment 2, Table II) was chosen to prepare FPUFs due to its higher MAG and lower DAG, TAG, and FFA contents. For more details, please refer to Section 3.1.

*2Isocyanates (NCO)/Hydroxyl (OH)

Physical and mechanical properties and extractable material of FPUFs

Physical properties (density, tear strength, tensile strength, compression force and resilience) were determined according to standard test methods for flexible cellular materials (ASTM D3574 – 17), with five replicates for each sample. The comfort factor was determined based on Brazilian Standard NBR 9176:2016 method.

Extractable materials in the FPUFs samples were evaluated in hexane, using samples of 20×20×20 mm, according to the following steps: i) the sample was placed in a beaker of 100 mL; ii) 50 mL of hexane was added; iii) static extraction at room temperature for 15 min; and iv) removal of the solvent containing the extracted material to an amber flask. These steps were performed five times for each sample for complete extraction. This experiment was conducted in triplicate. Afterwards, the amber flasks were kept in an oven at 70°C for 24 h to remove the solvent. The percentage of extractable materials was determined through the difference of the weight before and after the extractions. ^{1}H-NMR spectra were performed to identify the composition of the extracted materials.

Analytical methods

The quantification of the glycerolysis products was carried out by high-performance liquid chromatography (HPLC) Agilent© 1260 Infinity (Agilent Technologies, USA), equipped with a column Agilent Zorbax Eclipse Plus C18 (250 × 4.6 mm, 5 µm particle size), according to the methodology proposed by Dupont.[11] Calibration curves of monoolein (R^2 = 0.9957), 1,3-diolein (R^2 = 0.9990) and triolein (R^2 = 0.9976) standards were used to quantify the reaction components. The samples eluted as a group of 3 to 5 peaks in the regions previously identified with these standards: 5–10 min to MAG; 20–28 min to DAG; and 30–37 min to TAG.

The hydroxyl value of the obtained polyols was determined by the ASTM D E222-17 method. Number-average functionality (f) was calculated by Eq. 1.

$$f = \frac{MM_{OP2} \times OH_{val}}{56110} \quad \text{(Eq. 1)}$$

where MM_{OP2} is the average molecular weight determined by HPLC and OH_{val} the hydroxyl value.

Fourier transform infrared (FTIR) spectroscopy measurements were performed on a MIR-FTIR Frontier Perkin Elmer spectrometer in attenuated total reflectance. Spectra were recorded with a resolution of 4 cm^{-1} from 4000 to 650 cm^{-1} with an average of 16 scans.

Thermogravimetric analysis (TGA) of the samples was performed using an SDT Q600 (TA Instruments-Waters, USA) from 0 to 900 °C at 10°C·min^{-1} and nitrogen flow rate of 100 mL·min^{-1}. The morphology of the obtained FPUFs was determined by scanning electron microscopy (SEM) in a JSM 6060 microscope (JEOL, Eching b. München-Germany). Cell area was analyzed using ImageJ software, averaging 100 measured cells of one image per formulation.

The statistical analysis of the data was performed with Statistica® 12.5 (Dell Inc - USA), using t-test (for data of mechanical properties and extractable materials) and analysis of variance – ANOVA (for yield of OP production), considering a significance level of 95% ($p<5\%$).

Results and Discussion

Glycerolysis of olein

The results of MAG, DAG, TAG and FFA yields in the experiments performed with catalyst quantity, glycerol/olein molar ratio, temperature and time as factors are presented in Table II, while Table III shows the significant factors ($p<0.05$) from the ANOVA on these data. Catalyst and temperature had positive effects ($p<0.05$) on MAG yield and negative effects on TAG yield. These effects reflect the fact that higher amount of catalyst and higher temperature (above 200°C) favor the conversion of TAG to MAG, as observed by Echeverri et al.,[12] in the study of biodiesel production through glycerolysis of methyl esters with crude glycerol. Besides, the temperature increase reduces the viscosity of the mixture, enhances the solubility of reactants, and improves their diffusion, reducing mass transfer resistances. Temperature and time had positive effects on DAG yield, which may be related to the reversible nature of the glycerolysis reaction that occurs in three stepwise consecutive reactions.[13] Besides, longer reaction times and higher temperatures can shift the reaction equilibrium toward DAG formation.[14] It is important to note that the factor time was not significant for MAG and TAG, probably because of the relatively long reaction times under consideration.[15,16]

The conditions used to produce the OP2 sample (Table I) were chosen to produce the olein polyol for the FPUFs preparation because this formulation led to the highest MAG yield and the lowest of DAG, TAG, and FFA final contents.

Characterization of olein and Olein Polyol 2 (OP2)

The main characteristics of the crude olein and OP2 are summarized in Table IV. OP2 showed a high content of MAG, as indicated by the hydroxyl value of 348.59±3.40 mg KOH/g. Additionally, OP2 presents functionality greater than two, being adequate to produce thermosetting polyurethane networks. The kinematic viscosity at 40°C increased approximately ten times from olein to OP2 sample, which may be attributed to the higher content of OH groups in the glycerolysis product and, consequently, the expected higher density of hydrogen bonding in OP2. At 60°C, the kinematic viscosity of the OP2 reduces 2.65 times. Since high viscosities can lead to inadequate mixing of the ingredients and imperfections in the cell structure of foams,[17] the use of heated OP2 (60°C) was the selected condition for the FPUFs preparation.

The low acid value of olein (1.18±0.12 mg KOH.g^{-1}, Table IV) can be attributed to its low content of free fatty acids (FFA). The higher value of this parameter for OP2 may be ascribed to FFA formation

Table II

Experiments performed according to a 2^4 factorial design and the respective results of yield.

Polyol sample designation*1	Factor				Yield (%)			
	Glycerol/olein (mol mol^{-1})	Catalyst (%w_{olein})	Temperature (°C)	Time (h)	MAG	DAG	TAG	FFA*3
OP1	3.5:1	1.5	220	6	68.41	29.57	0.21	1.81
OP2	3.5:1	1.5	220	2	72.49	25.39	0.51	1.61
OP3	3.5:1	1.5	180	6	68.82	29.12	0.21	1.85
OP4	3.5:1	1.5	180	2	60.85	25.45	11.52	2.18
OP5	3.5:1	0.5	220	6	68.98	28.59	0.78	1.65
OP6	3.5:1	0.5	220	2	10.57	7.95	79.65	1.83
OP7	3.5:1	0.5	180	6	23.56	24.44	50.36	1.64
OP8	3.5:1	0.5	180	2	3.34	1.2	94.58	0.89
OP9	2.5:1	1.5	220	6	62.18	33.32	2.46	2.04
OP10	2.5:1	1.5	220	2	69.8	26.01	0.51	3.68
OP11	2.5:1	1.5	180	6	65.61	30.81	0.86	2.72
OP12	2.5:1	1.5	180	2	12.99	2.50	82.66	1.85
OP13	2.5:1	0.5	220	6	65.24	31.64	1.09	2.03
OP14	2.5:1	0.5	220	2	62.13	35.07	0.84	1.96
OP15	2.5:1	0.5	180	6	16.52	9.95	70.90	2.62
OP16	2.5:1	0.5	180	2	21.6	16.25	60.59	1.56
OP17*2	3.0:1	1.0	200	4	64.36	26.51	6.03	3.09
OP18*2	3.0:1	1.0	200	4	62.61	34.22	1.34	1.83
OP19*2	3.0:1	1.0	200	4	63.57	30.37	3.38	2.68
OP20*2	3.0:1	1.0	200	4	63.59	27.78	3.28	5.35
Yield at the central point [%]					63.53±0.72	29.72±3.40	3.51±1.93	3.24±1.50

*1Sample designation scheme: i) OP stands for olein polyol; ii) the number indicates the specific treatment in the factorial design, according to the standard order.
*2Central point replicates.
*3Free fatty acid

Table III

MAG, DAG, and TAG yields: effects of the significant factors ($p<0.05$) from the ANOVA on data of Table I

Components	Factor*1	Effects	Std.Err.	t(5)	p	-95.%	+95.%	R^2
MAG	Mean/Interc.	50.361	2.983	16.884	0.00001	42.694	58.028	0.9213
	(2)Catalyst (%w_{olein})	13.076	3.335	3.921	0.011	4.503	21.648	
	(3)Temperature (°C)	12.907	3.335	3.870	0.012	4.335	21.479	
DAG	Mean/Interc.	23.807	1.597	14.907	0.00002	19.702	27.912	0.8764
	(3)Temperature (°C)	4.864	1.786	2.724	0.042	0.274	9.454	
	(4)Time (h)	4.851	1.786	2.717	0.042	0.261	9.441	
TAG	Mean/Interc.	23.588	4.661	5.061	0.004	11.607	35.569	0.9032
	(2)Catalyst (%w_{olein})	-16.241	5.211	-3.117	0.026	-29.635	-2.846	
	(3)Temperature (°C)	-17.852	5.211	-3.426	0.019	-31.247	-4.457	

*1Factors are coded by numbers: (1) glycerol/olein (mol.mol^{-1}), (2) catalyst (%w_{olein}), (3) temperature (°C) and (4) time (h)

Table IV
Properties of olein and OP2

Properties	Olein	OP2
MAG (%)	1.08±0.10[b]	74.68±0.14[a]
DAG (%)	2.18±0.11[b]	22.10±0.08[a]
TAG (%)	96.14±0.16[a]	0.75±0.11[b]
FFA (%)	0.59±0.05[b]	2.47±0.02[a]
Hydroxyl value (mg KOH.g^{-1})	-	348.59±3.40
MM (g.mol^{-1})[*1]	-	417.15
Relative functionality	-	2.6
Kinematic viscosity at 40 °C (cSt)	58.11±0.15[b]	548.56±2.81[a]
Kinematic viscosity at 60 °C (cSt)	-	206.85±0.59
Acid value (mg KOH.g^{-1})	1.18±0.12[b]	4.90±0.03[a]
Water content (%)	0.41±0.15[b]	7.39±0.20[a]

[*1]Molecular weight determined using HPLC analysis (supplementary information);

(a-b) Different letters within the same line indicate significant difference between the respective mean values ($p < 0.05$).

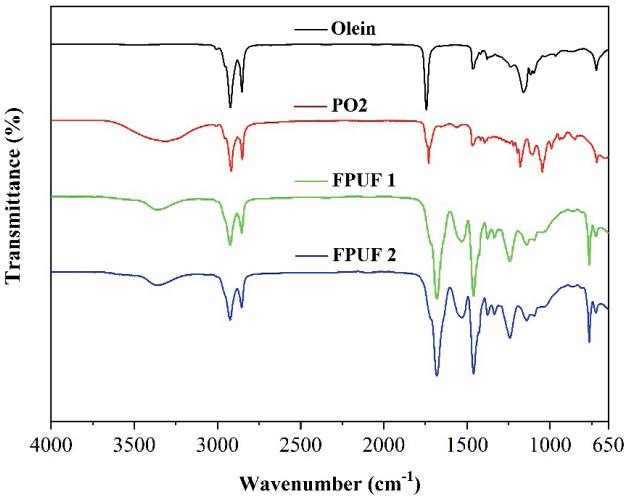

Figure 1. FTIR spectra of the FPUFs.

during the glycerolysis reaction due to the presence of water in glycerol and olein.[10] The water content of OP2 was higher than that of olein, indicating low efficiency of the drying process performed after the neutralization step; however, this residual water may act as a blowing agent during the FPUF preparation.

Characterization of the produced flexible polyurethane foams (FPUFs)

Structural characterization

Figure 1 shows the FTIR spectra of olein, OP2 and the two polyurethane foams prepared (FPUF1 and FPUF2). The OP2 spectrum presents a broad band at ~3600-3100 cm^{-1}, which is absent in the olein spectrum and is related to the stretching of OH groups that arose after the glycerolysis reaction. The peak appearing in the same region in FPUF1 and FPU2 spectra is attributed to the overlap of -NH from the urethane group and OH stretching of the unreacted polyol. The intensity of this peak is lower for FPUF1 than FPUF2 due to the consumption of OH groups in the polymerization reaction. The peaks at 1686 cm^{-1} and 1562 cm^{-1} are related to the stretching vibrations of carbonyl of urethane and urea groups, and urethane N-H bending vibrations associated with C-N stretching vibrations (amide II), respectively.[18,19] The peaks at 1464 cm^{-1} and 1249 cm^{-1} correspond to the C-N bond of the urethane groups and to –C-O-C ester stretching vibration,[20] respectively. So, these bands suggest the formation of a polyurethane matrix. Besides, the absence of bands in the range from 2274 to 2100 cm^{-1} indicates complete reaction of the isocyanate groups.

Figure 2 shows the weight loss (TGA, 2a) curves and their first derivate (DTG, Figure 2b) for the olein, glycerol (for reference), OP2 sample, FPUF 1 and FPUF 2. Olein exhibited only one step of weight loss in the range of ~290 – 500 °C, which corresponds to the ester linkages decomposition. OP2 presented two steps of weight loss, being the first one (~150 – 230 °C) attributed to the thermal decomposition of the residual glycerol, and the second one (~330 – 500 °C) related to the thermal degradation of the ester bonds.[21,22] The FPUFs present four steps of weight loss. The first one was attributed to non-reacted

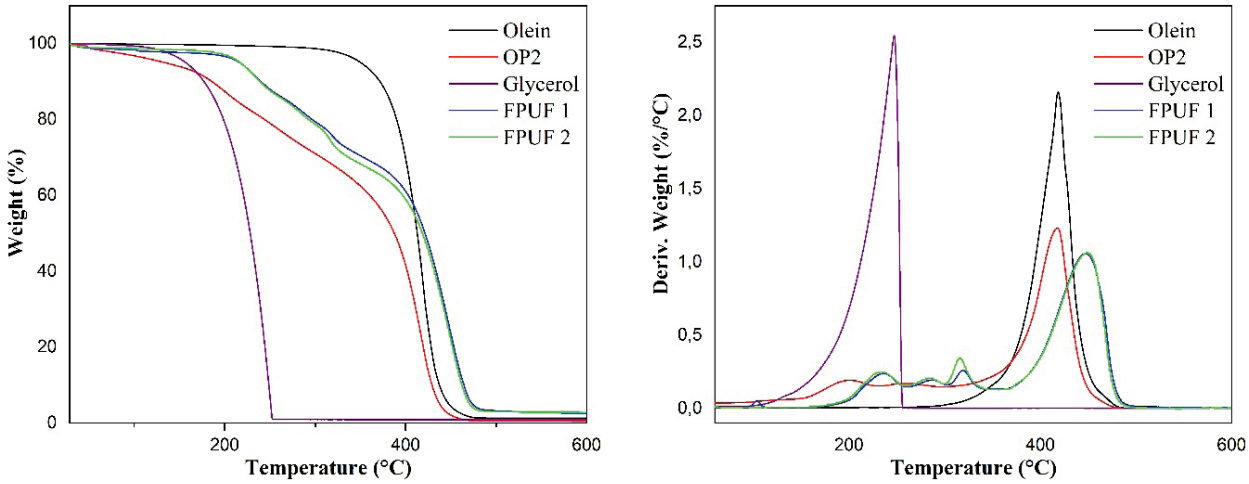

Figure 2. TGA **(a)** and DTG **(b)** curves for O, OP2, FPUF1, and FPUF2.

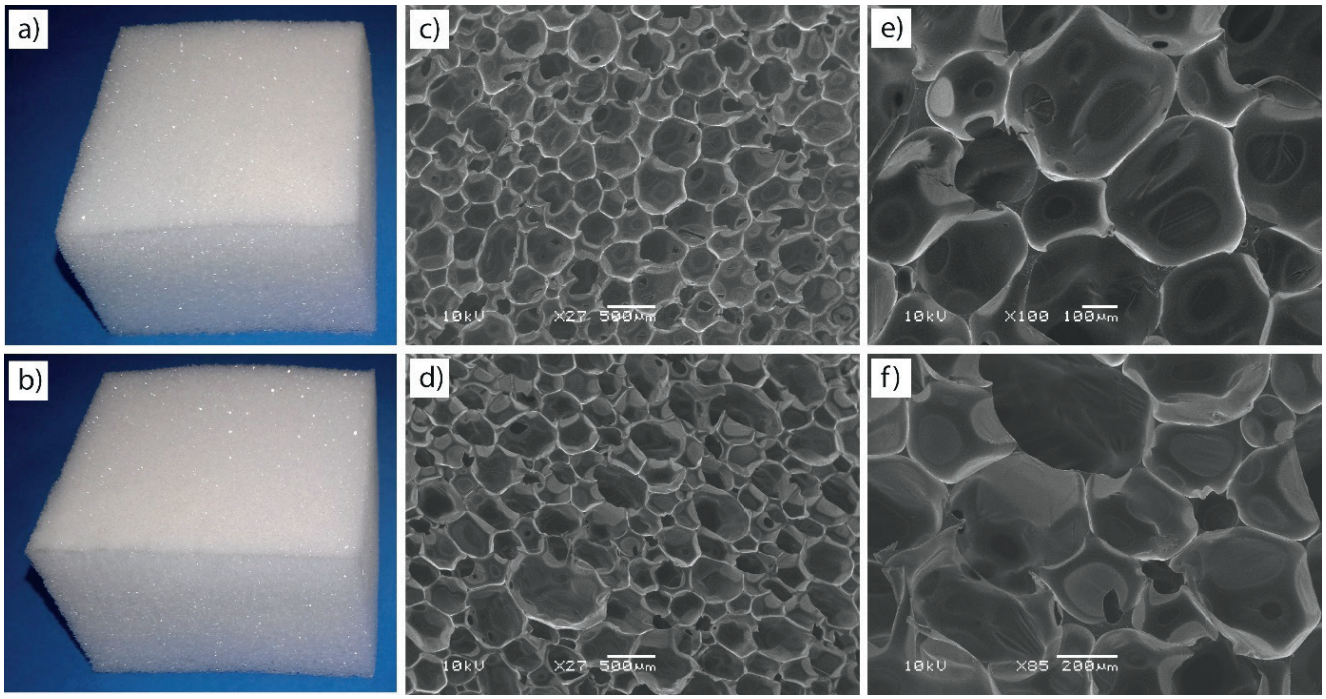

Figure 3. The visual aspect of FPUF1 **(a)**, FPUF2 **(b)** and SEM morphologies of FPUF1 **(c, e)**, FPUF2 **(d, f)**.

glycerol, the second and third ones (~250 – 350 °C) to the degradation of urethane/urea bonds and hydrocarbon chains,[21,22] and the last one (~350-490°C) to the degradation of the polyol ester bonds.[21,22] The third stage of weight loss was higher for FPUF 2, which is in agreement with the higher amount of isocyanate in its production.

Figure 3 shows the visual aspect (Figure 3a, b) and the SEM morphologies (Figures 3c-f) of the produced FPUFs. Both FPUF1 and FPUF2 were glossy white and dimensionally stable in the absence of applied stress (Figure 3a, b). Polygon shaped closed cells were predominant, but structures with openings (probably caused by the passage of CO_2) and many wrinkled walls were also observed, mainly in FPUF2 (3d, f).

Figure 4 shows the histograms of cell area distribution obtained for FPUF1 and FPUF2 from the analysis of the images of Figures 4c, d. Both histograms are quite similar and the frequency of cells with the measured area between 25 and $174\times10^3\mu m^2$ represents about 60% for both FPUFs. This indicates the efficacy of the type and amount of surfactant used in the formulation in promoting cell size uniformity. This is attributed to fact that the surfactant acts controlling the process of foaming and regulates the ratio of open/closed cells, producing fewer cells with smaller size.[23,24]

Extractable material

Both samples presented low contents of extractable materials, 2.83±0.69% for FPUF1, and 0.93±0.33% for FPUF2, indicating that both samples presented a crosslinked structure. Nevertheless, the

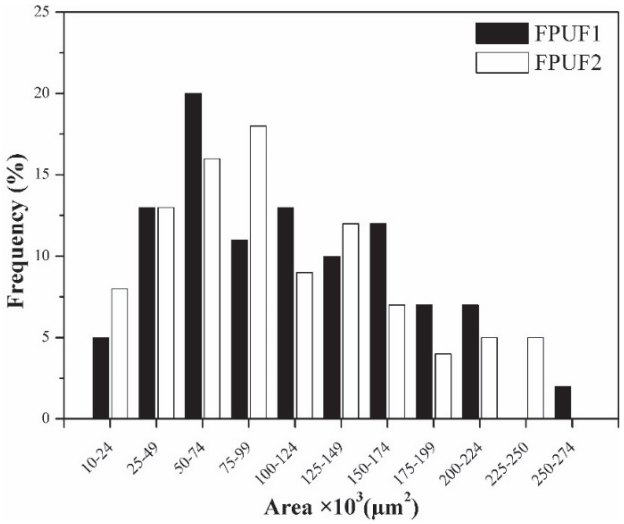

Figure 4. Distribution of the measured cell area of FPUF1 and FPUF2.

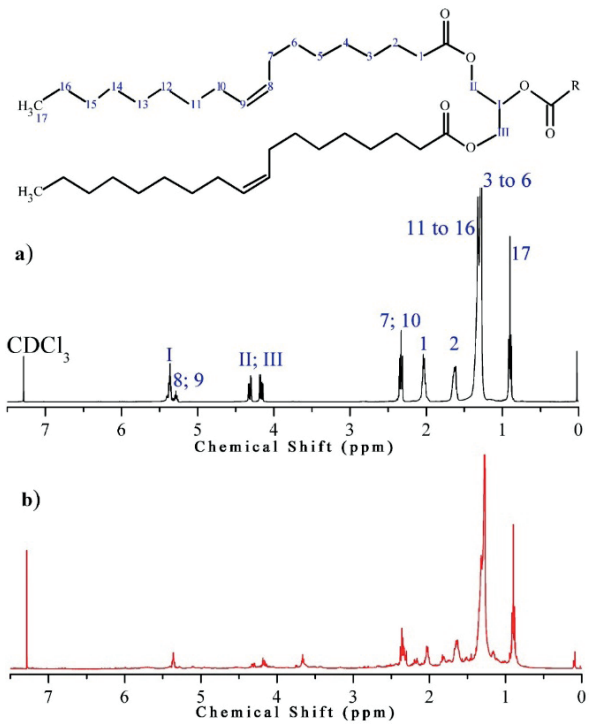

Figure 5. ^{1}H NMR spectra of olein **(a)** and extractable material of FPUFs **(b)**.

difference of extractable material content between the two samples was statistically significant ($p < 0.05$) and in qualitative agreement with their relative NCO/OH ratios. The extractable fraction of the produced FPUFs was composed mainly of TAG (about 0.75±0.11 %, Table V), since the signals of H_I, H_{II} and H_{III} were observed in the ^{1}H NMR spectrum of Figure 5b.[25] Additionally, the presence of unreacted components in the samples is confirmed by the signals in the 3.7 ppm region (Figure 5b). These signals are attributed to unreacted MAG, DAG or FFA, since the region from 3.3 to 4.2 ppm is characteristic of methylenic protons next to an oxygen atom ($-CH_2-O-$).[26]

Physical and mechanical properties

Table V presents the physical and mechanical properties of the FPUFs. Considering the evaluated properties, FPUF1 and FPUF2 were statistically different only in terms of density, comfort factor, rebound, compression force and elongation at break. Such differences can be explained based on the values NCO/OH ratios used in the formulations. The higher the NCO/OH ratio, the greater the number of rigid segments formed. Consequently, FPUF1 is expected to present higher concentration of rigid segments than FPUF1, which would explain its higher density and lower elongation at break. The fact that FPUF2 presented the higher rebound value and compression force is also in agreement with this analysis, since the capacity of recovering of the foam is expected to increase with the increase of rigid domains in the system.

These results, more specifically for density and compression force, are supported for those found in the other works of the literature for similar systems. For example, Kattiyaboot and Thongpin[27] prepared FPUFs from blends of petroleum-based and vegetable-based polyols (NCO/OH fixed at 1) and blown by distilled water, observing a directly proportional correlation between the foam density and the compression force. Hoong Yeoh et al.,[28] studying FPUFs prepared with palm oil-based polyester polyol, have also attributed the variations in the mechanical properties to the content of hard segments, although they have not found a significant correlation between the compressive properties and density.

The fact that some parameters (maximum strength, tear strength, breaking load, and modulus of rupture) were not statistically different between the produced FPUFs, indicates that these properties are less sensitive to the NCO/OH ratio than those discussed in the last paragraph. Similar results were reported by Hoong Yeoh et al.,[28] who reported that FPUFs prepared at an NCO/OH ratio of 1.1:1 and 1.2:1 presented a small variation in the tensile strength (from 85.27±8.5

Table V

Extractable materials, physical and mechanical properties of the prepared FPUFs.

Tests	Parameters	FPUF1	FPUF2
Extractable materials	Weight of extractable materials (%w)	2.83±0.69[a]	0.93±0.33[b]
Density	Density (kg.m^{-3})	48.42±4.34[a]	36.42±2.15[b]
Tear strength	Maximum strength (N)	4.30±0.48[a]	4.47±0.42[a]
	Tear strength (N.mm^{-1})	172.03±18.72[a]	179.17±13.46[a]
Tensile strength	Breaking load (N)	11.42±3.20[a]	9.22±2.07[a]
	Modulus of Rupture (MPa)	0.07±0.01[a]	0.06±0.01[a]
	Elongation at break (%)	182.88±33.63[a]	157.61±14.36[b]
Compression Force	Compression Force (N)	10.69±2.22[a]	15.75±2.66[b]
Resilience	Rebound value (%)	10.77±1.32[b]	16.03±3.03[a]
Comfort Factor	C.F	4.38±0.88[a]	2.74±0.39[b]

(a-b) Means values within a same line are significantly different ($p < 0.05$).

to 70.85±13.4 kPa) compared to the elongation at break (from 45.86±3.6 to 32.12±1.6%) and compression stress (from 49.19±7.6 to 115.09±18.2kPa).

Regarding potential applications of the FPUFs produced from olein obtained as byproduct of the tanning industry, it is worthwhile to mention that, according to NBR 13579-1:2011, density greater than 30 $kg{\cdot}m^{-3}$, resilience up to 15% and comfort factor above 1.8 are some of the basic requirements for viscoelastic foams. Considering that FPUF1 exhibited those features, it may be a potential material to be used in mattresses. Besides, FPUF1 is favorable in an economic sense, since it uses nearly 10% less isocyanate, which has a significant impact on the production cost.

Conclusions

This work demonstrated the feasibility of using olein, a byproduct of the tanning industry, as a raw material for preparing polyols for flexible polyurethane foams. The olein polyol was prepared through glycerolysis of the olein. The content of monoglycerides in the final product was experimentally maximized by using a full factorial design with catalyst quantity, glycerol/olein molar ratio, temperature, and reaction time as factors. The highest MAG content was of 74.68±0.14%, obtained at the following conditions: molar ratio between glycerol and olein of 3.5:1, 1.5% of catalyst (KOH), 220°C, and reaction time of 2 h. The flexible PU foams prepared with olein polyol and HDT isocyanate had a low content of extractable materials (below 3%), indicating that the polymerization reaction was successful. Density, compression force, elongation at break and resilience of the produced FPUFs were dependent on the NCO/OH ratio. The obtained FPUFs showed a structure composed mainly of polygon closed cells, with some wrinkled walls. The mechanical properties observed are like that of viscoelastic foams, and it is suggested that that PU foams from olein are potential materials to be used in mattresses. In this way, the use of olein to prepare polyol and produce PU foams can add value to this byproduct and contribute to the productive chain of the tanning industry.

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Francina Izquierdo, see JALCA 112, 81 2017

Anna Bacardit, see JALCA 101, 284, 2006

Rosa Cuadros, see JALCA 108, 420, 2013

Felip Combalia, see JALCA 105, 353, 2010

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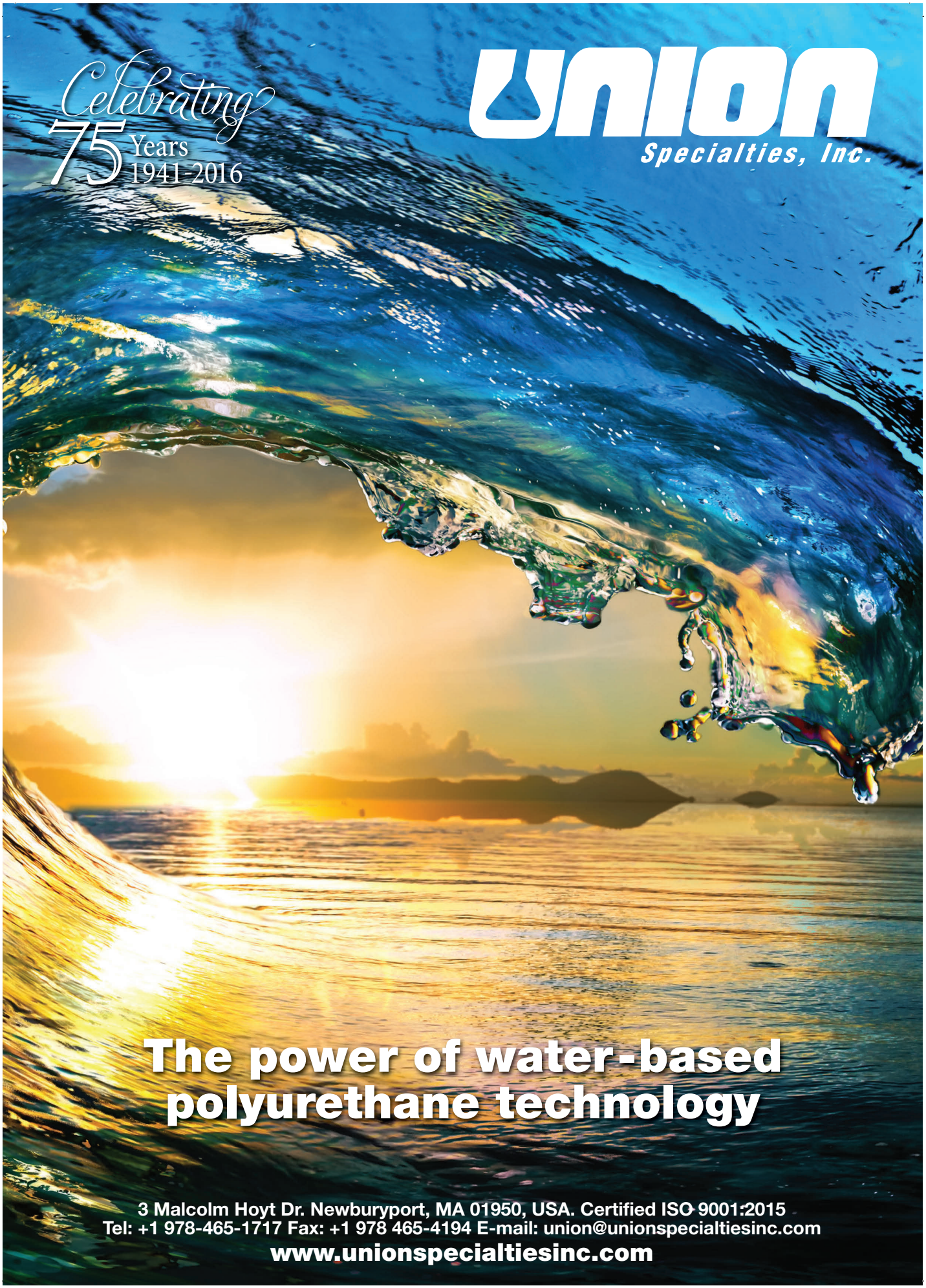
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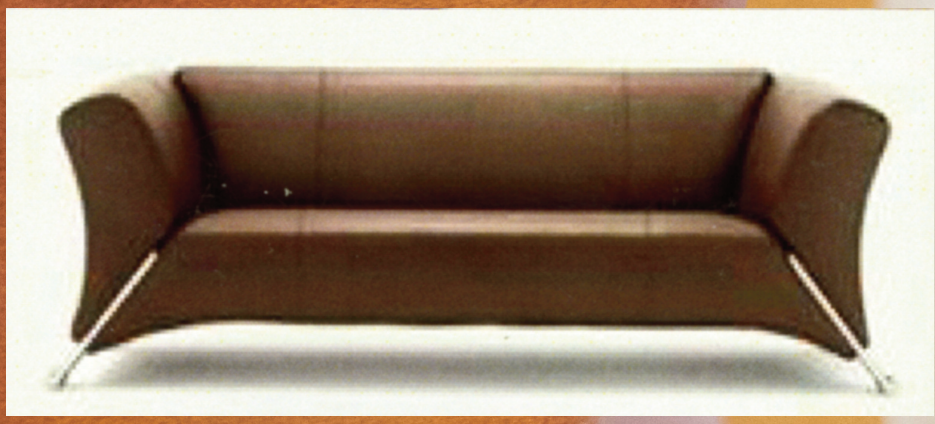

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Obituary, Jean J. Tancous

Jean Jacobs Tancous, former President of the American Leather Chemists Association (ALCA), passed away on October 6th, 2022 at the age of 96. Jean graduated from the University of Cincinnati (U.C.) holding a B.A. degree in Chemistry (1945) and an M.S. degree in Chemistry (1949). While in college she worked as a Research Assistant for the Tanners' Council Research Laboratory (located on the U.C. campus) which conducted research for the tanning industry. Upon graduation, she continued working for the Tanners' Lab as a Research Associate for 37 years (1949-1986). While at U.C., Jean also taught graduate level courses in microscopy, histology and leather chemistry.

Throughout her career, Jean was involved in basic and applied research studying the causes of hide and leather defects. This included studies of the effects of diseases and injuries to the living animal, defects occurring during processing, curing and storage of hides. She recommended solutions for eliminating these serious economic losses to the livestock, meat packing, tanning and leather industries.

Jean published over 54 articles in professional journals concerning research on skin, hide and leather and presented over 40 lectures/papers to her colleagues at the ALCA. In 1974 Mrs. Tancous was elected President-Elect of the ALCA and subsequently served as President from 1976-1978 and again from 1983-1984.

A major undertaking was the compiling of the subject matter for a book entitled *Skin, Hide, and Leather Defects* published in 1959. Jean co-authored this book with Dr. Fred O'Flaherty and William T. Roddy. Jean subsequently updated this book and published a second edition in 1986.

Jean joined the ALCA on March 2, 1960 and was bestowed life membership in 1978. She served the ALCA as a Councilor from 1965-1967, President-Elect from 1974-1975, and President from 1976-1977 and 1983. In 1962 she was the first woman recipient of the Alsop Award for her creative research. In 1965 she won the ALCA Prize Paper Award for her paper "Occurrence and Nature of Pulpiness in side Upper Leather" which she presented at the 9th IULTCS Congress in Lyon, France. For many years she was a member of the Raw Stock Committee and chaired the committee from 1972 to 1974. She was on the 1974 Alsop Selection Committee and chaired the same committee in 1980 plus being a member of the committee in 1995. In 1975 she presented the John Arthur Wilson Memorial Lecture entitled "Rawstock" at the 71st ALCA Annual Convention at Lake Placid, New York. She chaired the John Arthur Wilson Lecture Selection Committee in 1983. She was the recipient of the 1996 ALCA Fred O'Flaherty Service Award recognizing individual active ALCA members who have made significant contributions to the Association and the leather and leather products industries through the ALCA. Finally, in 1997 Jean was the recipient of Hall of Fame award from the United States Hide, Skin and Leather Association. Because of her accomplishments, she was listed in "Who's Who in Science and Engineering".

After retirement from the Tanner's lab (in 1986), Jean built a small testing lab in the basement of her Cincinnati home where she provided consulting services for the U.S Hide, Skin & Leather Association. Jean worked part time in this lab until she was 93, giving 32 more years of service to the leather industry. Jean passed away 3 years later.

Jean loved researching everything, recoding statistics (football), bird watching, growing plants, playing the piano, puzzles, cryptograms, sewing and reading to her grandchildren.

She was preceded in death by her husband of 56 years, Ernest Tancous. She is survived by son, John W. (Betsy) Tancous of Akron, OH; daughter, Judy A. (William) Thompson of Columbus, OH; grandchildren: Emily (Collin) Ferguson, Catherine (Justin) Miller, Stephanie Tancous, Laura (Adam) Gossett and Natalie (Scott) Shellhorn; great grandchildren: Adelyn, McKenna and Brynlee Ferguson, William Gossett, Bodie and Callie Miller, and Emery Shellhorn.

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