

APPLICATION OF SILANES IN LEATHER TANNING

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Abstract. This work investigates the potentialities and limitations of the use of alkoxysilanes in leather tanning, introducing silica nanoparticles in the hides, aim for process and product innovation in leather industry. The synthesis of silica nanoparticles was carried out by a typical sol-gel Stöber process. From the silica precursor tetraethoxysilane (TEOS), ammonium hydroxide as catalyst, ethanol and water, the formation of nanoparticles dispersion takes place. Vegetable tanning process was explored by introducing the silica nanoparticles in this stage starting from pickled cattle hide. Shrinkage temperature, tensile strength, softness and colour fastness to light were evaluated in the leather samples. The results achieved shown that the tanning experiment with only silica, without other tanning agent, did not reach the minimum shrinkage temperature required to be labelled as tanned leather. Conversely, in the presence of vegetable tannin, the shrinkage temperature reached 80°C. The physical-mechanical properties indicated that the enhanced on the tensile strength of vegetable leathers with nanosilica was about 50% and their softness was not affected by the introduction of silica. A lighter coloured leather was generated with silica but less stable to light. The tanning chemistry involving silica nanoparticles and collagen is complex, therefore, more studies are needed to explore the influence of silanes on hide stabilization.

1 Introduction

The collagen stabilization of the hides with silicon compounds has been investigated for many years with the intention of developing a sustainable and low-cost route for tanning^{1,2}. These compounds are studied as an alternative to wet-blue leather tanning – which is still the predominant method used in tanneries³ – in the context of manufacturing chromium-free wet-white leathers. Usually employed in the form of silicates, these substances can interact with collagen via hydrogen bonding and electrostatic attraction. However, studies have shown that there is no significant effect on the hydrothermal stability of the hides, which indicates that silicates, acting as sole tanning agent, are not effective for tanning^{2,4-6}.

Although the silicon compounds do not stabilize the hide irreversibly, they can act as auxiliaries, being their best application as pre-treatment for vegetable tanning. By occupying reaction sites in collagen structure and, consequently, reducing the reaction rate between polyphenolic plant tannins and collagen, silica facilitates penetration, improving the absorption of tannins in the hide^{3,7}.

However, the synthesis of nanometric silica particles has been exploited for possible application in tanning, due to their small size and ability to combine with polymeric substrates⁸. An in-situ route to produce nanosilica has been established to facilitate the introduction of the nanoparticles into the hide in order to achieve a real tanning effect. In this route, a silane precursor of the nanoparticles is dispersed in the hide. Under a special condition such as pH change, heat, radiation, among others, the nanosilica precursor undergoes hydrolysis and condensation in the organic matrix of the collagen, producing in situ the inorganic silica nanoparticles. Thus, a strong interaction between the organic and inorganic phases is obtained due to the high reactivity of the nanoparticles, favouring the increase of the shrinkage temperature of the leather and conferring

improvement in the mechanical properties^{9–11}. In addition, the surface of silica nanoparticles can be modified by adding reactive groups of various organosilanes in order to control particle size, obtain chemical stability and homogeneous dispersion of nanoparticles in the medium^{12,13}.

Other benefits achieved with the use of silicon compounds in leather process include the use of silicates as lime substitutes in the liming process¹⁴, the improvement in dye and auxiliaries absorption, the decrease in suspended solids, COD, BOD and total N levels, and reduction of chrome content in the effluent, in addition to saving water and chemicals. These hides may also present resistance to fungi and provide a better biodegradability of the organic compounds present in the effluent when compared to the chrome tanning. Further advantages of nano-tanning include studies that omitted the pickle stage and performed the simultaneous tanning and fatliquoring steps, reducing process time^{9,10}. Moreover, silica can also add properties such as increased UV light protection and high-quality gelatine recovery from leather shavings^{8,15}. Table 1 presents some works in the field of silica application in leather tanning.

Table 1. Application of silica products in leather tanning report in the literature.

Silica precursor	Substrate	Silica synthesis	Tanning agents combined
Tetraethoxysilane - TEOS	Bated pelt	TEOS + modified oil/polymer-based dispersion supporter	Oxazolidine ⁹
TEOS + (3-Glycidyloxypropyl) trimethoxysilane	Goatskin (pickled)	Direct contact with the hide in the drums	Cr ₂ O ₃ 24% B=33% ¹¹
TEOS	Goatskin (squeezed and shaved)	NanoSiO ₂ , 50-150 nm (patented synthesis) + modified animal/vegetal oil	Oxazolidine (as pre-tanning agent) ¹⁶
Sodium silicate (20% SiO ₂ content)	Goatskin (pickled)	Direct contact with the hide as pre-tanning agent	Chromium salts ¹⁷
TEOS (redistilled)	Sheepskin (pickled)	Stöber method + modified oil	Tetrakis(hydroxymethyl) phosphonium chloride ¹⁸
Sodium metasilicate	Goatskin (pickled)	Mixed with the other tanning agents in acidic medium	Sodium dichromate, zinc sulphate ¹⁹
Sodium metasilicate	Goat and sheepskin (delimed)	Direct contact with the hides after the other tanning agents	Aluminium sulphate, tannic acid ²⁰
Sodium metasilicate	Goatskin (pickled/delimed)	Direct contact with the hide (sodium metasilicate previously neutralized)	Aluminium sulphate, Tetrakis(hydroxymethyl) phosphonium sulphate ²¹
TEOS + [3-(Methacryloyloxy) propyl]trimethoxysilane	Sheepskin (pickled)	Modified Stöber method	Methacrylic acid, Diallyl dimethyl ammonium chloride, acrylamide acrylonitrile ²²

The results achieved so far are of great value in exploring chrome-less tanning or future chromium-free tanning technology with the use of silica and help promote the sustainable development of the leather industry. However, the tanning chemistry between nanomaterials and collagen is complex and still not fully understood to date²³.

Then, the objective of this work was to investigate the potentialities and limitations of the use of silanes in leather tanning. It was explored the vegetable tanning step by introducing nanometric silica particles produced by the Stöber method. This study searches for improvements in the properties of the leather or a gain in time, cost of process or less use of chemicals, working on process/product innovation.

2 Materials and methods

The following precursors were used for the synthesis of the silicas: tetraethoxysilane ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$, TEOS, Acros, > 98%), (3-Aminopropyl)triethoxysilane ($\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$, APTES, Sigma-Aldrich, 99%) and octadecylsilane ($\text{CH}_3(\text{CH}_2)_{17}\text{SiH}_3$, ODS, Sigma-Aldrich, 97%). Ammonium hydroxide (NH_4OH , Nuclear, 29%) was used as catalysts in the sol-gel process.

2.1 Synthesis of the silica nanoparticles dispersion

The synthesis of silica nanoparticles was performed based on the Stöber method²⁴ by diluting 5.0 mL of TEOS in 50.0 mL of ethanol, adding to the reaction 1.0 mL of $0.5 \text{ mol L}^{-1} \text{NH}_4\text{OH}$ as the basic catalyst, and 3.0 mL of distillate water. The reaction medium was kept under slow stirring for at least 4 h. This synthesis results in the formation of a dispersion of nanometric silica particles. In another experiment, 1.0 mL of the organosilanes APTES and ODS were added to the synthesis, separately, for the functionalization of the nanoparticles with amino groups and long carbon chains, respectively. Fig. 1 presents a scheme of the synthesis with TEOS.

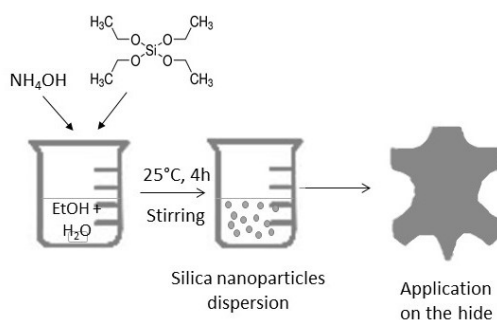


Fig. 1. Scheme of the silica nanoparticles dispersion synthesis and application.

2.2 Tanning process with the silica nanoparticles

The incorporation of the silica nanoparticles to the hides was carried out in the tanning step. Vegetable tannin from *Acacia mearnsii* was used as tanning agent combined with the nanosilicas. The tanning process was started from a pickled bovine hide. The hide weight employed in all experiments was 200 g in each drum. Table 2 shows the formulation used for the three initial tanning experiments with the nanosilica dispersions (nano- SiO_2). The percentage of products used was based on pelt weight. In the Experiment I (E-I) the nanosilica dispersion was employed without the organosilanes and without the fatliquoring step. In the Experiment II (E-II) the organosilane APTES was added in the synthesis of the silica nanoparticles. In the Experiment III (E-III), the organosilane ODS was used to the silica functionalization. Control samples – without nanosilica – were also performed for the experiments. The rotation of the bench drums was set at 25 rpm for the whole process.

Table 2. Tanning process formulation for the three experiments with the silica nanoparticles dispersion.

Step		Product	%	t (min)	Remarks
Conditioning		H ₂ O	200.0	15	25°C
		NaCl	5.0		
		HCOONa	1.5	60	
Washing		H ₂ O	200.0	10	Drain
Tanning		H ₂ O	50.0		35°C
	Experiment I	Nano-SiO ₂	2.3 ^b	30	
	Experiment II	Nano-SiO ₂ + APTES	2.8 ^b		
	Experiment III	Nano-SiO ₂ + ODS	2.8 ^b		
		VT ^a	7.0		
		VT	8.0	60	
		VT	10.0	120	
		VT	10.0	120	
		VT	10.0	overnight	
Fatliquoring ^c		sulphited fatliquor	7.0	30	36°C
		sulphated fatliquor	6.0	30	
Fixing		H ₂ O	100.0	60	Drain
		HCOOH (1:10 v/v diluted)	1.0		

^a VT: vegetable tannin^b percentage of the silica precursors^c step only carried out on the experiments II and III

After that, the following tanning experiment, Experiment IV (E-IV), was carried out with an additional step, the pre-tanning, where phenolic synthetic tannin was employed to facilitate the penetration of the tanning agent. Table 3 shows the formulation for this case.

Table 3. Formulation for the Experiment IV with a pre-tanning stage and the silica nanoparticles dispersion.

Step	Product	%	t (min)	Remarks
Pre-tanning	H ₂ O/NaCl 6°Bé	50.0	120	25°C
	Fungicide	0.1		
	Synthetic tannin	5.0		
	NaHCO ₃	2.0		
Washing	H ₂ O	200.0	10	Drain
Tanning	H ₂ O/NaCl 10°Bé ^a	200.0	120	35°C
	Nano-SiO ₂	2.3 ^b		
	VT	5.0		
	Nano-SiO ₂	2.3 ^b		
	VT	10.0		
	VT	15.0		
	VT	5.0		
	overnight			
Fatliquoring	Sulphited fatliquor	7.0	30	36°C
	Sulphated fatliquor	6.0	30	
Fixing	H ₂ O	100.0	60	Drain
	HCOOH (1:10 v/v diluted)	4.0		

^a for the control sample it was 6°Bé^b percentage of the silica precursor TEOS

2.3 Leather proprieties analyses

The thickness of the samples was measured via an analogue thickness gauge (Wolf). The average thickness was obtained according to IULTCS/IUP 4. The measurement of tensile strength and

percentage extension was carried out according to the IULTCS/IUP 6 in a universal tensile testing machine (AME-5, Oswaldo Fisola).

For the analysis of softness, a softometer (KWS Basic, Wolf-Messtechnik) was employed and leather samples with the dimensions of 7.5 × 5.0 cm was used for the measurements²⁵. The outcome of this measure is the surface tension of the sample. The leather shrinkage temperature was measured according to the IULTCS/IUP 16, where a sample of leather with the dimensions of 10.0 × 2.0 cm was used to evaluate the hydrothermal stability of the samples.

The colour fastness to UV light of the leather samples was analysed, where the samples had 50% of their surface exposed to an UV lamp with 300 W for 24h. After that, the colour change of the leather samples was evaluated with the use of a colorimeter (Colorium, Delta Color) and the Lab7[®] software. The measured values were distributed into three-dimensionally colorimetric coordinates that describes the psychometric colour space of CIELab lightness (L*), coordinate a* (red content (+), green (-)) and coordinate b* (yellow content (+), blue (-)). The obtained coordinates of each sample were converted into numerical values, providing relative values to the colour differences between the materials:

ΔL^* = represents the difference in lighter and darker (positive = lighter, negative = darker)

Δa^* = represents the difference in red and green axis

Δb^* = represents the difference in yellow and blue axis

The total colour difference (ΔE) is defined by the equation:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \quad (1)$$

The water contact angle (WCA) analysis was performed on the drop shape analyser (DAS 100, Krüss GmbH) equipped with a video camera. Using the sessile drop method, where a drop (3-6 µL) of deionized water at room temperature was deposited on the surface of the leather by means of a micro syringe. The image of the drop on the leather was captured and the angle formed between the drop and the surface was measured.

The 3D Optical Profiler (Contour GT-K, Bruker) was used to measure roughness in nanometric scale (1 nm of vertical resolution) and fast obtaining 2D and 3D surface images of the leather samples.

3 Results and discussion

Preliminary experiments were carried out to generate silica *in situ* in the leather tanning process as a tanning agent. Silica nanoparticles from the Stöber process were added to the hides and the drums were run for extended time in order to ensure the silica formation for all routes. Initially a large amount of silica precursor (TEOS) was used in relation to the hide weight, which results in rigid hides. Although the experiment was kept running for a long time, the shrinkage temperature reached by the hides was 55°C, concluding that the hide was not tanned. This indicated that the silica produced cannot be considered as a single tanning agent. For this reason, it was investigated in the following experiments if the silicon compounds could act as auxiliaries in the process, in order to aggregate properties of strength, colour, and filler, among others.

Therefore, in Experiment I (E-I) the nanosilica dispersion was incorporated in the hides at the tanning step of the leather process with vegetable tannin as tanning agent. The results (Table 4) demonstrate that the control sample and the sample with the nanosilica achieved the same shrinkage temperature, indicating that the presence of the nanosilica did not compromise the hydrothermal stability of the leather.

The tensile strength at the breaking point for the leather with the nanosilica dispersion was 52% higher than the control sample. The results of elongation at break for the sample with the nanosilica were also greater than the control sample (without silica), demonstrating that the nanosilica added resistance properties to the leather. From the softness analysis it was found similar values of surface tension, revealing that the quantity of the nanosilica provided in this experiment did not affect the

softness of the leather. Regarding the increase in the thickness between the initial hide and the final leather, it was higher for the leather with silica compared to the control, suggesting greater filling provided by the silica.

In the Experiment II (E-II) and III (E-III), the presence of the organosilanes APTES and ODS, respectively, and the addition of the fatliquoring step in the tanning formulation result in significant variations in the physical-mechanical properties analysed (Table 4).

The main function of the fatliquoring step is to ensure softness to the leather, an important quality requirement, especially in the case of upholstery leathers. In relation to the softness, the experiment with the presence of the organosilane APTES (E-II) resulted in the most rigid sample, with the highest surface tension. In the literature, the values found for leather without fatliquoring step were 5.27 N/mm and ranged between 2.36 and 3.11 N/mm in leather with fatliquor²⁶. These values are in line with that found in this work, when compared the E-I (without fatliquoring) with the experiments E-II and E-III (with fatliquoring).

A satisfactory shrinkage temperature was achieved for all the samples, but the one with APTES (E-II) was lower than the others because the vegetable tannin diffusion was not complete in this experiment. For vegetable tannin, the shrinkage temperature achieved after tanning ranges between 70 and 85°C²⁷.

The tensile strength was higher for the control sample and the lowest for the sample with APTES, possibly for the incomplete diffusion of the vegetable tannin. Conversely, the percentage extension revealed that the samples with the organosilanes (E-II and E-III) elongated more than the control sample before the breaking point. The thickness increase after the tanning process was similar for the control sample and the sample with APTES (E-II) and lower for the E-III.

Table 4. Results for the leathers from Experiment I, II and III.

Parameter	Experiment I		Experiments II and III		
	Control sample	E-I	Control sample	E-II	E-III
Shrinkage temperature (°C)	76	76	80	74	80
Tensile strength – breaking point (MPa)	17.9	27.2	42.7	27.6	36.6
Elongation at break (%)	45.8	58.5	48.8	51.8	54.5
Surface tension (N/mm)	4.86	5.01	1.3	2.2	1.4
Thickness increase (%)	-	25	46	40	22

Contact angle and optical profile analysis were performed for the leathers resulting from the experiments II and III in order to verify the influence of the organosilanes on the hides. For contact angle analysis, the leather without nanosilica (control sample) absorbed the water very fast and it was not possible to capture the image of the drop. Instead, the leather samples with the organosilanes took more time to absorb the drop of water, being possible to capture the image. The results were for the E-II with APTES, an angle of 84.8° in the left side, and 82.4° in the right side (Fig. 2a). For the E-III with ODS, the angles were 69.2° for the left side and 70.5° for the right side (Fig. 2b). This suggests that the leather surfaces with the organosilanes are more hydrophobic than the surface of the control sample. However, as the measured contact angle was less than 90°, all the samples presented hydrophilic surface.

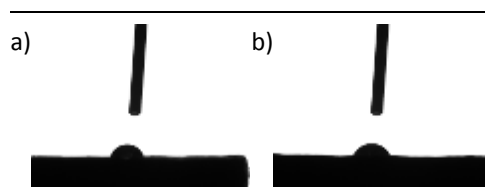


Fig. 2. Contact angle images of a drop of water on leathers with organosilanes. Sample (a) E-II with APTES and (b) E-III with ODS.

From the optical profile analysis (Fig. 3), which shows the roughness of the surface, we can see the red regions, which indicate peaks and the blue ones, which indicate valleys. The leather sample with the organosilane ODS (Fig. 3b) presented the red region more homogeneous than the control sample (Fig. 3a), as can be better observed in the 2-D image. This analysis is useful to compare the roughness of treated leather with silica and leathers without silica, looking for more uniform surfaces, since smooth leathers are of great value for the consumer market.

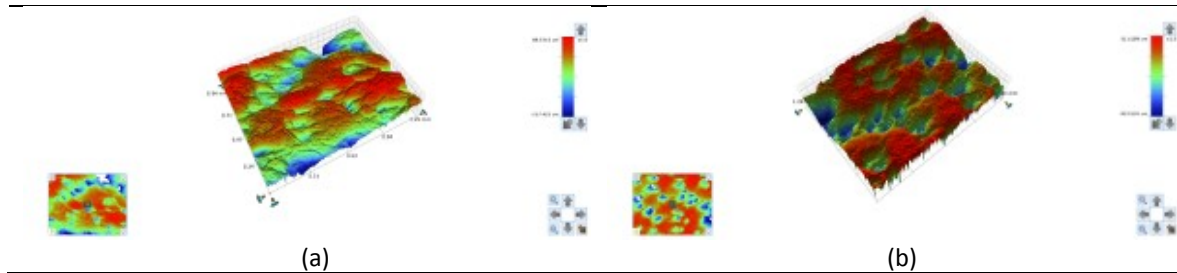


Fig. 3. Optical profiler images from (a) control sample and (b) E-III with ODS.

In the Experiment IV (E-IV), a pre-tanning formulation was used to facilitate the diffusion of the vegetable tannin. In this experiment there were two additions of the nanosilica dispersion in order to maximize the effect of silica on the properties of leather. The leathers resulting from this experiment were tested for their physical-mechanical properties and the results are presented in Table 5.

Table 5. Results from the Experiment IV.

Parameter	Control sample	E-IV
Shrinkage temperature (°C)	78	78
Tensile strength – breaking point (MPa)	19	23
Elongation at break (%)	47	54
Surface tension (N/mm)	1.33	1.54
Thickness increase (%)	85	115
Total colour difference (ΔE) – lightening	-	3.25
Total colour difference (ΔE) – UV-light exposition	-	3.87

According to Table 5, the presence of silica did not impair the stabilization of the hide, since the shrinkage temperature was the same for the control sample and the leather with silica. From the tensile and percentage extension test, leather with silica showed 22% higher tensile strength when compared to the control. The percentage of extension was also higher for the leather with silica. From the softness analysis it was found that the introduction of silica did not compromise the softness of the leather. The thickness increase revealed the greatest filling for the leather sample with silica.

The total colour difference (ΔE) indicated that the Experiment IV produced lighter coloured leather than the control, which can also be observed visually in Fig. 4. Light hides are interesting for the industry once which facilitate dyeing with lighter colours.

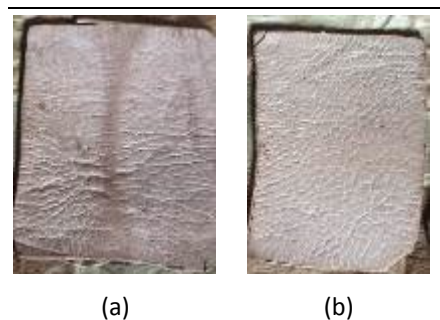


Fig. 4. Leather samples from experiment IV: (a) control sample (b) E-IV.

The stability of the leather - with and without nanosilica - to ultraviolet light was also evaluated. The colour variation before and after exposure to UV light was higher for the silica samples, indicating that the leather obtained in this experiment was less stable to UV light.

From the Experiment IV, it was also concluded that there was an increase in the amount of salt required for the vegetable tanning due to the alcohol existent in the synthesis of the nanosilica dispersion that reduces the density of the tanning liquour. On the other hand, in the same experiment, the addition of 5% of pre-tanning agent reduced in 10% the vegetable tannin amount needed to complete the tanning process.

4 Conclusions

This work investigated the use of silanes in leather tanning, where variations in the nanosilica synthesis from the precursors TEOS, APTES and ODS were tested. The shrinkage temperature to consider the hide tanned was only achieved in the presence of vegetable tannin as tanning agent. The physical-mechanical properties varied according to the formulations used. There was improvement in the tensile strength in the most cases and the softness was not altered by the introduction of the silica. Lighter coloured leather was produced with the introduction of the nanosilica dispersion. However, it was less stable to UV light and demanded more salt in the process. On the other hand, the vegetable tannin amount required to complete diffusion decrease representing considerable savings of product. Therefore, to explore the influence of organosilanes on hide stabilization, further studies are needed because the tanning chemistry between nanomaterials and collagen is complex even so promising.

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