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Sol-Gel Process for Surface Modification of Leather

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Chapter 14

Sol-Gel Process for Surface Modification of Leather

Franco Ferrero, Monica Periolatto and
Giuseppe Gozzelino

Additional information is available at the end of the chapter

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Abstract

Applications in the textile field of sol-gel processes were widely investigated since coatings of fabrics by materials of nanometric size obtained by sol-gel methods represent a functional surface modification attracting even more attention. However, few experiences of the use of nanostructured coatings are reported for leather finishing. In the experiments reported in the present chapter, a nabuk leather was finished by a sol-gel process to confer hydro and oil-repellency. The silica component could act as a protective coating, improving the rubbing performance of the substrate and conferring a certain grade of hydrorepellency, while the oil repellency was due to a fluorocarbon component. The coatings were applied at low add-on of finishing agent with the aim to keep possibly unvaried the esthetic and hand characteristics of the original leather. Contact angle and sorption time measurements of water and oil drops were carried out on the treated samples and compared with the untreated one. A similar comparison was made by testing color fastness to rubbing and change of esthetic appearance. Finally, chemical surface characterization was carried out by Fourier Transform Infrared in Attenuated Total Reflectance (FTIR-ATR) analysis.

Keywords: leather, sol-gel, TEOS, FOS, Fluorolink S10, hydrorepellency, oil repellency, contact angle, FTIR-ATR

1. Introduction

Applications in the textile field of sol-gel processes were widely investigated [1–28]. In fact, coatings of fabrics by materials of nanometric size obtained by sol-gel methods represent a functional surface modification attracting even more attention. They have exceptional physical properties and resistances: justification to this behavior comes from the huge area of contact generated when the fillers reach the nanometric size, in combination with a polymer layer of interphase with properties much higher than the matrix ones.

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Materials with repellent properties against water or oil-based soils are of high commercial interest for textiles and leather-containing materials with high demand efforts for washings and cleaning. The finishing agents are often perfluorinated compounds [25–28], while sol-gel systems or functional silanes are used as nonfluorinated chemical alternative, but the oil-repellency can be achieved only by fluorine compounds.

Manufacture of water-resistant leather has attracted dramatic attention in recent years as the increasing demand for waterproof upper, upholstery and garment leathers. In general, a water-resistant leather is prepared by using chemicals that enable to form hydrophobic coatings with low surface free energy on leather surface. These coatings can be polymeric thin films containing silicones, fluorinated, or long-chain hydrocarbons. However, the permeability of air and water vapor of treated leather could be compromised, and the development of new methods for the production of waterproof leather maintaining its natural characteristics is still a challenge [29]. As an alternative, plasma treatments [29–31] or hybrid nanostructured coatings [32–34] have been proposed.

Generally, pure laboratory-grade alkoxysilanes are used as sol-gel precursors. A hybrid framework composite can be obtained by mixing alkoxysilanes with organic precursors, and the final properties of the coating can be tailored on purpose by choosing proper precursors. Tetraethoxysilane (TEOS) is the most widely used precursor in the sol-gel technology [13], nevertheless, it can be partially or totally replaced by fluorinated alkoxysilanes to confer together hydro and oil repellency typical of these compounds [7, 9, 10, 17, 19, 35]. Therefore, the finishing of cotton fabrics was satisfactory experimented by TEOS nanosol modified with 1H,1H,2H,2H-fluorooctyl-triethoxy-silane (FOS) [19] or with Fluorolink S10 (Solvay Solexis), cheaper commercial perfluoropolyether already used with TEOS to prepare hybrid coatings on glass [20, 36].

In the case of leather, a silica-based fluorinated hybrid coating can act as surface protection, improving the rubbing performance of the substrate and conferring a certain grade of hydrorepellency, while the oil repellency can be due to the fluorocarbon component. Moreover, nano- or microstructured coatings can be applied by the sol-gel process, reducing the amount of applied finishing agent to keep possibly unvaried the esthetic and hand characteristics of the original leather. Therefore, in the experiments reported in the present chapter, TEOS, FOS, and Fluorolink S10 were experimented as sol-gel precursors for leather finishing by analogy with the process experimented on cotton fabrics.

Leather is a material resulting from tanning, i.e., the production from animal skin of a chemically and biologically stable material by a process that leaves the original fiber structure more or less intact. A section of the animal skin is reported in **Figure 1** [37].

The most important part of an animal skin is the corium, consisting mainly of collagen, a fibrous protein that is strongly affected by tanning. The basic collagen structure consists of twined triple left-handed helices of peptide chains of different length. The peptide chains within the triple helices are held together by hydrogen bonding as a consequence of the groups belonging to the typical structure of polypeptide, as shown in **Figure 2** [38]. The amino acid composition of collagen is atypical for proteins, particularly with respect to its high hydroxyproline content. The most common motifs in the amino acid sequence of collagen are glycine-proline-X

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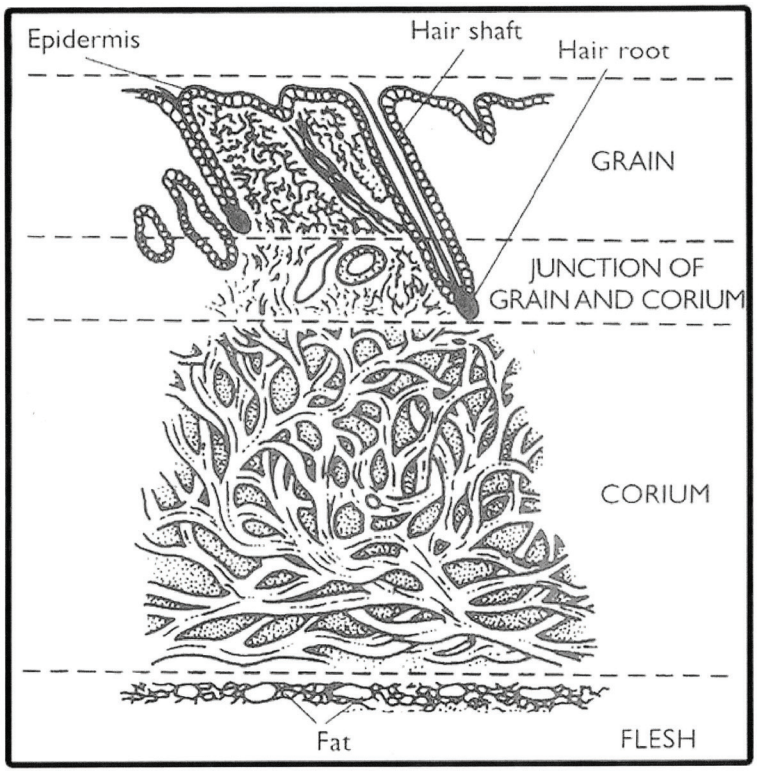

Figure 1. Section of the animal skin.

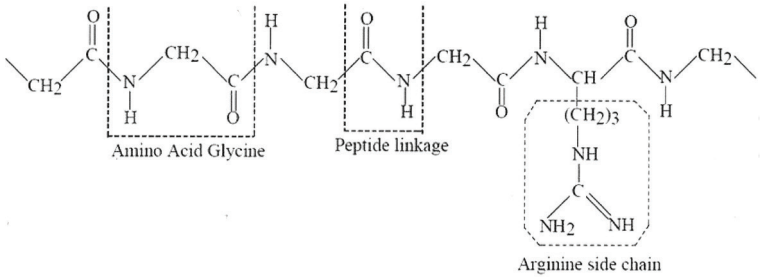

Figure 2. Typical molecular structure of polypeptide.

and glycine-X-hydroxyproline, where X is any amino acid other than glycine, proline, or hydroxyproline. The amino acid composition of a leather collagen is about glycine 26.8% of total nitrogen, alanine 8.0%, arginine 15.3%, proline 9.0%, and hydroxyproline 8.0% [38].

The main chemical processes carried out in sequence to transform animal skin into leather are the following:

- unhairing and liming, by an action of alkali and sodium sulfide to eliminate hair by hydrolysis of the keratin and in the meantime, to induce the modification of collagen yielding hydrolysis of amide groups, arginine residues, and amide linkages, together with swelling and removal of unwanted material;
- deliming and bating, with salts and enzymes to open further the structure;
- pickling, with acids to neutralize alkali;
- tanning with vegetal, synthetic, and chromium(III) salts to impart structure stability;
- neutralizing, dyeing, and fat liquoring with oils to confer desired color and softness;
- drying;
- finishing to improve the quality of the final leather.

The chemical modifications induced by these treatments on collagen make many polar groups, such as –OH, –NH–, =CO, available for adsorption through hydrogen bonding, in the case of sol-gel finishing, with the silanol groups yielded by acid-catalyzed hydrolysis of silane groups of the precursors. Moreover, the condensation reactions occurring in the following thermal step can promote grafting of silanols with polar groups of collagen, improving the adhesion of silica nanoparticles on leather. When TEOS is introduced as a coprecursor, $–O–Si(OH)_3$ groups can be bonded on the leather surface and are able to condense with other ≡Si–OH or $≡Si–O–CH_2–CH_3$ groups of the fluorinated alkoxysilane precursor.

Fluorolink has a fairly high molecular weight compared with FOS and two silane grafting end groups. These characteristics have been recognized to increase the hydrophobic/oleophobic character of coatings and resistance to mechanical removal from the matrix [39].

2. Experimental

In the experiments, a nabuk leather provided by Foglizzo Leather, Torino, Italy, was finished by a sol-gel process to confer hydro and oil-repellency. Besides the standard preparation, it was dyed with anionic dyes in the presence of auxiliaries to improve dye penetration. Samples of 15 × 4 cm^2 were subjected to the treatment.

Tetraethoxysilane (TEOS) and 1H,1H,2H,2H-Fluorooctyltriethoxysilane (FOS), both pure laboratory-grade reagent purchased from Sigma-Aldrich (Italy), and Fluorolink® S10, commercial product from Solvay Solexis (Italy), were used as precursors. In **Figure 3**, the molecular structures are reported; in particular that of Fluorolink was taken from the literature [39], and the molecular weight of the reagent used was in the range of 1750–1950 g/mol.

Finishing nanosols were synthesized via sol-gel method with acid catalysts in ethanol/water solution. TEOS and FOS, TEOS and Fluorolink S10, or the three products alone were used as

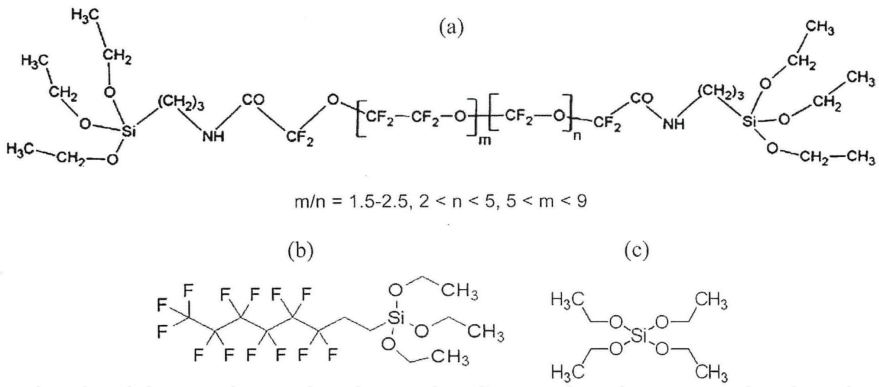

Figure 3. Molecular structure of (a) Fluorolink S10, (b) FOS, (c) TEOS.

precursors obtaining different nanosols by magnetic stirring at 25°C for 24 h. Five nanosols were prepared as detailed in **Table 1**.

The nanosol solutions were applied with the spraying technique, widely used at industrial level in dry finishing, which enables an uniform product distribution, but cannot be utilized in the presence of sediments or precipitates. Hence, before the application, the homogeneity of the solutions was tested by a visual check.

The solution amount to be sprayed on each sample was calculated on the basis of the content of dry resin in each solution providing 2, 5, or 10% add-ons. Higher add-ons were not applied to avoid the overhead of the substrate and maintain the nabuk properties unvaried. Since small solution volumes were needed, these were diluted with ethanol to assure a more homogeneous deposition.

In **Table 2**, the composition of the various samples is reported.

After spraying on both the leather surfaces, an impregnation time of 24 h was adopted, and the samples were maintained in sealed test tubes at room temperature. The following step was a thermal treatment in an oven at 120°C for 1 h to promote the solvent evaporation and at the same time the xerogel formation and the grafting reactions on leather.

Component	Nanosol-1	Nanosol-2	Nanosol-3	Nanosol-4	Nanosol-5
TEOS	0.17	0.21	0.17	–	–
FOS	0.19	–	–	–	0.49
Fluorolink S10	–	–	0.19	0.50	–
Ethanol 96% v/v	0.58	0.74	0.58	0.46	0.46
0.01 M HCl	0.06	0.05	0.06	0.04	0.05

Table 1. Composition, in percent weight, of the prepared nanosols.

Sample	Nanosol type	Add-on (% weight)	
		F	R
1	Untreated	–	–
2	Nanosol-1	10	10
3	Nanosol-1	0.5	0.5
4	Nanosol-2	10	10
5	Nanosol-2	0.5	0.5
6	Nanosol-2	0.2	0.2
7	Nanosol-3	10	10
8	Nanosol-3	0.5	0.5
9	Nanosol-4	10	–
10	Nanosol-4	0.5	–
11	Nanosol-5	10	10
12	Nanosol-5	0.5	0.5

Table 2. Composition of the samples (F: front; R: reverse).

Contact angle and sorption time measurements were carried out on the treated samples and compared with the untreated leather, as well as the color fastness to rubbing, esthetic, and hand properties. The color fastness to rubbing was tested by a Taber crockmeter mod. 418 according to ISO 11640.

Water and oil repellency were tested by static contact angle and sorption time measurements using HPLC-grade water and paraffin oil (Sigma–Aldrich) with a surface tension of 72 and 31.5 mN/m, respectively. The instrument was a DSA20E Easydrop standard tensiometer (Krüss, Germany) equipped with DSA software. Measuring liquid drops were deposited from a glass syringe on the sample surface by means of the software controlled dosing. The contact angles were the average of three measurements for each sample with a standard deviation of about 2%.

Finally, chemical surface characterization was carried out by FTIR-ATR analysis performed on a Nicolet 5700 instrument equipped with a Smart Orbit ATR single bounce accessory mounting a diamond crystal. A 128 scans at 4 cm^{-1} resolution in the 4000–500 cm^{-1} wavelength range were averaged.

3. Results and discussion

3.1. Contact angles and absorption time measurements

The results of static contact angles with water and paraffin oil as well as the absorption time measurements are reported and compared in **Table 3**.

Sample	Contact angle (°)		Absorption time (min)	
	Water	Paraffin oil	Water	Paraffin oil
1F	133	0	30	0
2F	154	99	70	10
3F	151	0	70	> 60
4F	160	0	65	0
5F	155	0	60	0
6F	150	0	50	0
7F	152	103	60	60
8F	138	111	63	> 60
9F	136	0	60	0
10F	146	0	63	0
11F	160	128	58	2
12F	148	126	65	10
1R	125	0	7	0
2R	138	70	> 60	>180
3R	127	71	> 60	>180
4R	133	0	60	0
5R	126	0	60	0
6R	125	0	30	0
7R	137	0	50	0
8R	154	0	60	0
11R	149	131	56	16
12R	150	107	60	5

Table 3. Contact angles and absorption times (F: front; R: reverse).

The untreated sample shows intrinsic water repellency (133° and 125° contact angles) due to the reagents used in the wet finishing, in particular in the greasing step. The absorption times of water drop are 30 and 7 min on front and reverse side, respectively, since the more relaxed structure of the latter justifies the faster absorption.

Instead, the untreated leather does not show oil repellency, as it can be deduced from the measurements with paraffin oil. The oil drop is immediately absorbed on both the sides with a persistent and hard to remove halo.

All the treatments on the front side improve the contact angle with water. Except the sample 8F, with the lowest amount of nanosol containing TEOS and Fluorolink, and 9F, with 10% Fluorolink alone, all the others show contact angles around 150°, threshold beyond which they can be defined superhydrophobic. The best results were obtained with the Nanosol-2,

based on TEOS alone, and with the Nanosol-5, containing FOS alone; in fact, the samples 4F and 11F showed a contact angle of 160°.

The treatments on the reverse side generally yielded lower contact angles. This is ascribable to the less compact structure of the collagen fibers, which absorb the lyogel, preventing the formation of a homogeneous film. Nevertheless, the treatment with TEOS and Fluorolink and that based on FOS alone enabled to achieve superhydrophobicity in the case of samples 8R, 11R, and 12R.

The tests of oil repellency generally showed the same trend as those with water, but with the same treatment on the same side, the contact angles are obviously lower, due to the difference of surface tension of both test liquids. The Nanosol-1 and Nanosol-2, based on TEOS added by FOS and TEOS alone did not confer oil repellency. This was expectable with the latter nanosol that was lacking in oil repellent component, while with the former, the concentration of fluorocarbon resin added was not enough to give such property. The contact angles of oil on the samples 2R and 3R treated with Nanosol-1, based on TEOS added with FOS, did not attain the threshold of 90°, hence, these samples cannot be defined as oil repellent. The treatment with the Nanosol-5, based on FOS alone, was the most powerful, above all on the front side.

The results are confirmed by the images of drop shapes of water and oil on the Samples 11F and 11R reported in **Figures 4** and **5**.

3.2. Color fastness to rubbing

The resistance test to rubbing is fundamental to evaluate the property of a leather of not giving color release on textiles and at the same time, the color degradation of the leather itself. It is important for any use to simulate contact and friction between the leather and other fabrics, such as a bag on a shirt, an upper on trousers, and a shoe lining on a stocking. It is carried out by a continuous rubbing of wool felts loaded with 500 g, in the case of suede or nabuck, followed by a visual comparison with standard gray scales of the possible color release on the felts together with the color degradation of the leather. The number of cycles is varied according to the intended purpose, usually 100 cycles in dry conditions or 20 in wet.

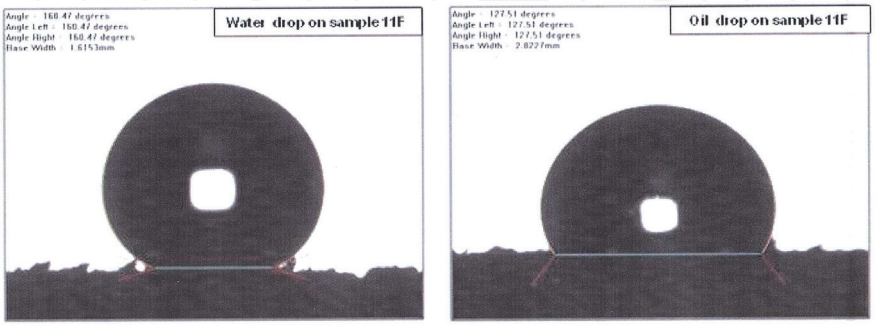

Figure 4. Images of water and oil drops on the Sample 11F.

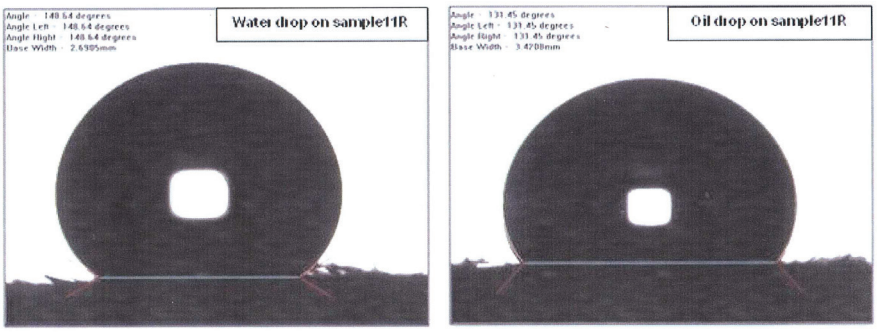

Figure 5. Images of water and oil drops on the Sample 11R.

The values of the standard gray scale for color release range from degree 1 for the maximum release to degree 5 for the minimum. The results of such evaluation on the all samples, in front and reverse sides, after rubbing tests in wet conditions are plotted in **Figure 6**. The color fastness to abrasion was generally improved by the finishing presence with respect to untreated leather (Sample 1), on which just a 1.5 value on gray scale was measured. The best results were obtained with Fluorolink alone (Samples 9 and 10); however, even FOS yielded a good fastness increase (Samples 2 and 11).

3.3. Esthetic aspect

The esthetic aspect should be critical in order to choose an optimal finish treatment for leather articles. In fact, for these products, the functional property, in this case water and oil repellency, is not the only aspect to consider.

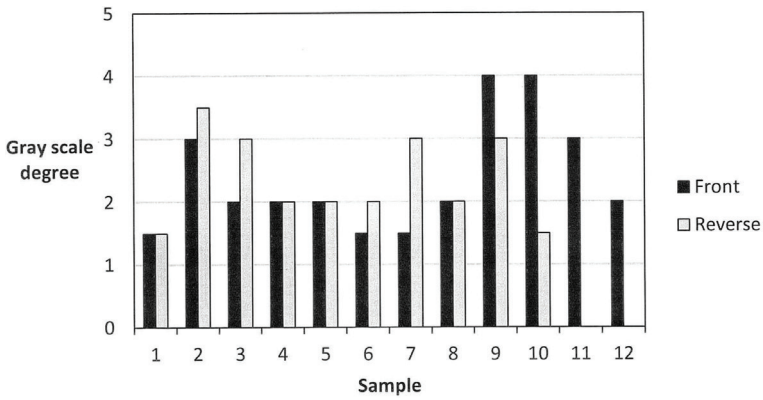

Figure 6. Color fastness evaluation after wet rubbing.

By comparison between treated samples and reference, four parameters were visually, or to the touch, evaluated by assigning a number decreasing as the difference with respect to the original sample is increasing:

- shade change of color: by analogy with the gray scale for fastness evaluation, the value 5 was assumed corresponding to the visual shade of the reference, while 1 was attributed to the maximum change toward darker shades;
- structural stiffness: the value 5 was assumed for the original texture, while 1 was attributed to the maximum stiffness;
- surface structure or "grain": the value 3 was assigned to the original sample, while 1 was attributed to maximum compaction of the fibers;
- writing effect, characteristic for nabuk: it was evaluated 3 if unvaried, 1 if absent.

The results are plotted in **Figures 7–10** for each aspect. With all the treatments, a worsening of the esthetic characteristics was generally observed, but not all can be considered equally important. An uniform darkening of color, if not excessive, is preferable to other changes, since in the previous dyeing a clearer shade can be conferred in order to obtain, after the sol-gel process, the desired shade. This is the case, for example, of the Sample 12F, treated with the lowest add-on of FOS alone, which showed only a color shade change of one degree lower with respect to 11F, one of the best samples, treated with the same nanosol, but with a higher add-on (10%).

Some treatments caused a compaction of surface fibers, with consequent worsening of hand properties and comfort; hence, they should be avoided.

The writing effect is considered a marginal aspect, and its change is not critical for a sample evaluation.

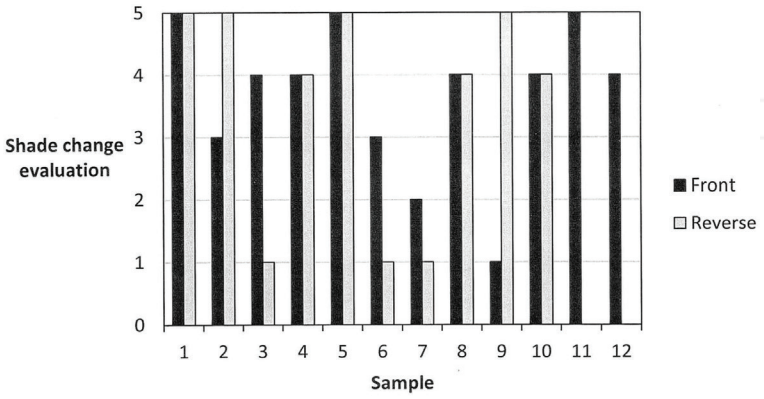

Figure 7. Shade change evaluation.

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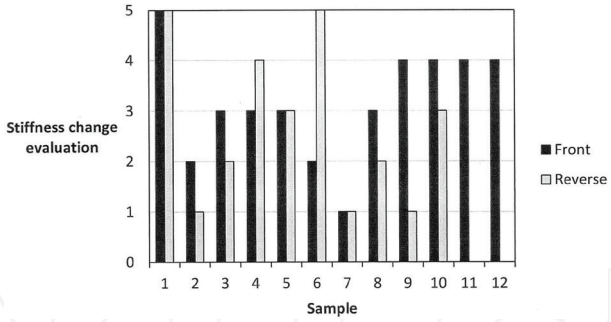

Figure 8. Stiffness change evaluation.

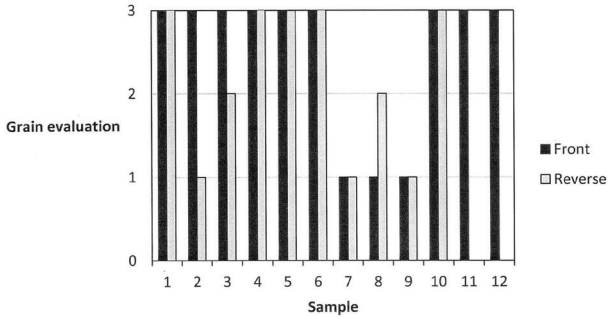

Figure 9. Grain evaluation.

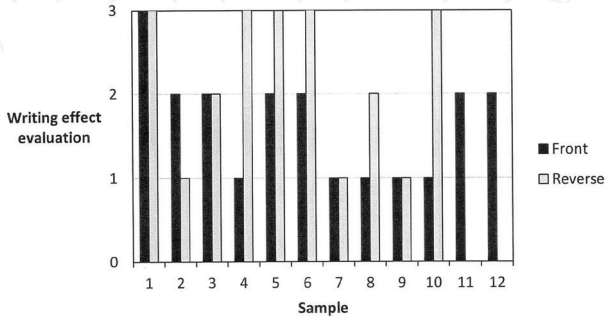

Figure 10. Writing effect evaluation.

3.4. FTIR-ATR analysis

All the samples were subjected to FTIR-ATR analysis to investigate the chemical composition of the leather substrate, highlighting the presence of characteristic groups of leather tanned and dyed as well as of finishing agents. In **Figure 11**, the spectra of the Sample 2F, treated with TEOS and FOS, are compared with that of untreated leather, and the peaks assignable to the characteristic groups according to literature data are evidenced.

The wavelength interval useful to reveal the presence of various finishing agents ranges from 1400 to 700 cm^{-1}. In particular, the peaks between 1250 and 1150 cm^{-1} shown by the finished leather are due to stretching of C-F bond in CF_2 e CF_3 groups and indicate the presence of fluorinated compounds on the leather surface. The peak at 1088 cm^{-1}, ascribable to Si-O-Si group, shows the presence of silicone nanoparticles on the surface. Such peak is present also with lower absorbance on the untreated sample since it is due to collagen component of the leather.

The spectrum of the Sample 9F, treated with the Nanosol-4, based on Fluorolink alone, shows a strong presence of fluorine and silicon compounds on the surface, as it can be observed in **Figure 12**. In the spectrum of the Sample 11F, treated with the Nanosol-5, based on FOS alone, a peak at about 900 cm^{-1}, ascribable to Si-C bond, also appears, as evidenced in **Figure 13**. Coupling it with the lowering, in comparison with the reference, of peaks related to OH and CH groups, at 3300 and 1600 cm^{-1}, it can be concluded that a grafting of the finishing agent on the leather surface could occur during the thermal treatment. The comparison between the spectra of the samples treated with nanosols containing TEOS and those with nanosols based on FOS or Fluorolink alone shows a decrease of surface concentration of fluorine groups confirming a dilution effect due to TEOS.

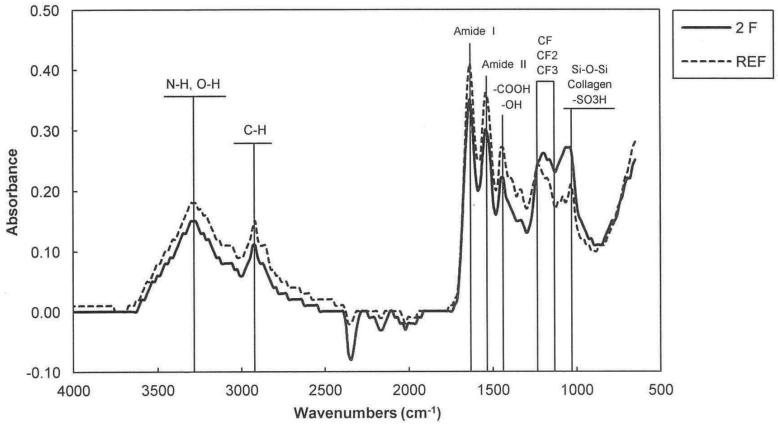

Figure 11. FTIR-ATR spectra of Sample 2F, treated with TEOS + FOS, and untreated reference (REF).

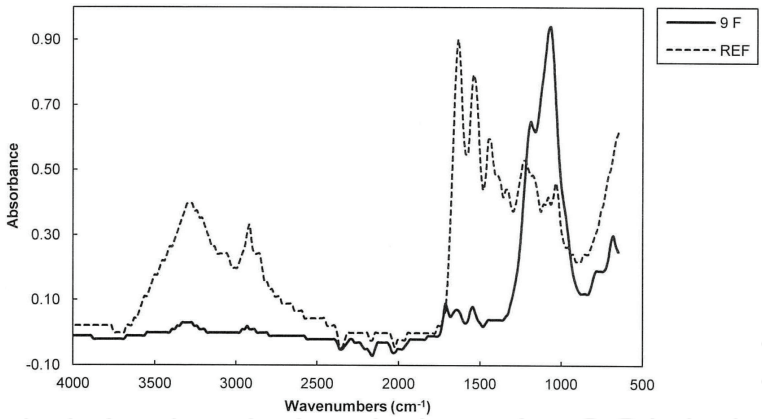

Figure 12. FTIR-ATR spectra of Sample 9F, treated with Fluorolink alone, and untreated reference (REF).

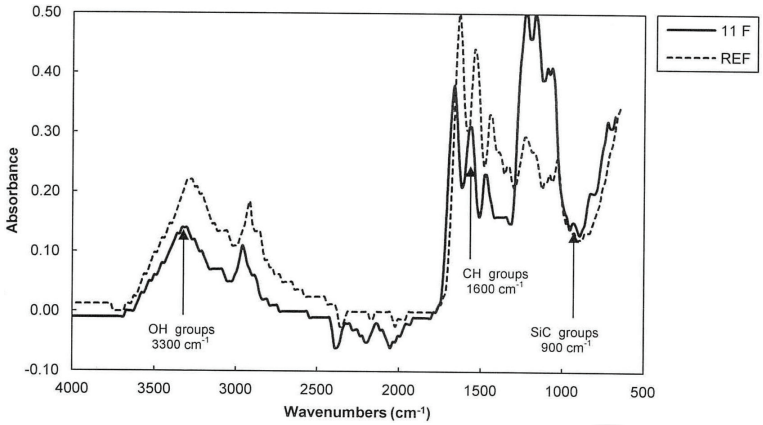

Figure 13. FTIR-ATR spectra of Sample 11F, treated with TEOS alone, and untreated reference (REF).

4. Conclusions

The research work on the leather was aimed to confer water and oil repellency and increase the color fastness to abrasion through a coating able to give the desired properties without unduly damaging the esthetic characteristics of the final product.

The application of a functional finishing on the leather by sol-gel conferred the desired properties, keeping the peculiar properties of the substrate unvaried. In particular for water and oil repellency, FOS-based nanosol at 10% add-on can be considered the best solution.

However, the nanosol based on Fluorolink alone enabled to obtain the best increase of color fastness to abrasion, but satisfactory results of this property were observed also with FOS-based nanosol at 10%, which can be considered as the optimal solution able to couple the two objectives. Moreover, the evaluation of the esthetic properties did not evidence a significant worsening of these with respect to the untreated leather.

Nanosols obtained by TEOS + FOS and TEOS + Fluorolink mixtures showed results generally worse both in terms of performance and esthetic appearance. This was attributed to the dilution effect due to TEOS.

The surface analysis carried out by FTIR-ATR has validated some previous knowledge in the textile field confirming the possibility to successfully apply the sol-gel treatment on a different substrate.

Thanks to the simple involved reactions and process, and the good obtained results, sol-gel can, in conclusion, be indicated as a valid finishing process for leather, opening the way for a future industrial scale up.

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Author details

Franco Ferrero*, Monica Periolatto and Giuseppe Gozzelino

*Address all correspondence to: franco.ferrero@polito.it

Department of Applied Science and Technology, Polytechnic of Torino, Torino, Italy

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