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Leather functionalisation by means of MLSE technology

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Abstract

Leather is widely used to make items such as clothing, shoes, car upholstery, boat and airplane seats, and many more items for daily use. Each item requires the use of a leather type with certain properties. Here the use of chemical compounds that are able to change the properties of these raw skins and hides comes into play. In general, traditional finishing treatments that provide leather with the desired functional features involve significant energy consumption as well as large volumes of water (both in finishing liquors and in further rinsing). In addition, in most cases, said treatments involve also the use of chemicals such as halogenated organic compounds, biocides, and organophosphorous compounds, the use of which is currently restricted or under consideration in the European Union (REACH and Biocides legislations).

The main objective of this work is to demonstrate the technical and environmental feasibility of the MLSE technology that combines atmospheric-pressure plasma energy with laser energy for the treatment of leathers as a way of providing them with improved properties for their application in the manufacture of products with functional properties and high added value.

Keywords: functional materials, flame retardancy, water resistance, oleophobicity, antimicrobial properties.

1. INTRODUCTION

Uses of leather date back to prehistory, when the hides and skins of hunted animals were used to protect the human body from adverse weather.

Currently, leather is used for the production of a wide range of products, including clothing, footwear, leather goods, saddlery and upholstery for automobile, boat, airplane and domestic furniture. Depending on the type of product and its intended use, a different type of leather with specific properties is required.

During post-tanning operations, numerous finishing additives are used to improve certain leather properties, such as water resistance, olephobicity, permeability, flame retardancy, antimicrobial properties, abrasion resistance or antistatic properties, among others.

In general, traditional finishing systems employed for obtaining functionalized leather imply high energy and water consumption. Besides, many of these treatments require the use of certain chemicals, such as halogenated compounds, biocides or organophosphorous compounds, the use of which is restricted or under consideration by the EU legislation, as is the case of the REACH Regulation (European Parliament, 2006), the Biocides Regulation (European Parliament, 2012), etc.

For this reason, INESCOP and CCI together with several European companies are working on the LIFE TextiLeather project aiming to obtain leather and textiles with flame retardancy, antimicrobial, hydrophobic and oleophobic properties, by means of a technology that helps reducing the use of hazardous substances for human health and the

Environment.

In spite of the fact that leather is not a flammable material in itself, the use of dyes and other finishing products may affect its fire resistance. However, flame retardancy is more and more demanded for certain applications (European IPPC Bureau, 2013), as in the case of materials for aircraft seats, train seats, boat seats, facilities in public buildings or fire-fighters' footwear.

A combination of certain factors is needed for a fire to initiate and propagate: a combustible material, an ignition source and an oxidant, such as oxygen, have to be present. In general, material treatments are not intended to prevent fire initiation but to prevent or delay fire propagation. In the case of leather, flame retardants are commonly used to increase the quantities of oxygen and/or heat required for combustion (Mohamed y Abdel-Mohdy, 2006). Usually this requires the application of chemical treatments on leather to inhibit flame formation and minimize smoke and fume generation (Donmez y Kallenberger, 1992).

Among the flame retardant substances that have traditionally been employed in the tanning industry, brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PDBEs), stand out. In fact, the consumption of this kind of flame retardants reached 70,000 tons in 2001 (Hale et al, 2003; North, 2004). However, these compounds are being less and less used in Europe due to their associated risks to human health and the Environment. Some of the compounds belonging to the PDBE family were banned for use in 2003 (European Parliament, 2003), which was followed by the restriction on the use of other brominated compounds, such as polybrominated biphenyl (PBB) (European Commission, 2009). For this reason, in recent years alternatives have emerged to improve the flame retardancy of leather, such as ammonium bromide and ammonium polyphosphate. Silicone polymers are another alternative, in that they burn to leave a silica residue that protects the leather beneath (European IPPC Bureau, 2013).

With regard to antimicrobial properties, the use of biocides in tanneries is limited to preserve hides and skins, with the aim of preventing microbial attack and damage. However, the TextiLeather project goes one step further and seeks to confer antimicrobial properties on tanned leather, especially for use in the manufacture of footwear as upper, lining or insock material.

The studies focusing on the development of leather with antimicrobial properties are quite new. Among the agents under consideration, the following stand out: zinc oxide nanoparticles (Nawaz et al., 2011), silver cluster deposition (Pollini et al., 2013), melamine-formaldehyde microcapsules containing tea-tree oil (Sánchez-Navarro et al., 2011), essential oils, such as eucalyptus, lavender or thyme (Sirvaityté et al., 2012; 2011), or polyurethane dispersion coatings containing photoactive antimicrobial agents (Hong et al., 2010).

Furthermore, the polar groups of the amino acid residues of collagen fibers promote the interaction of leather with water molecules, conferring a hydrophilic nature on leather. However, this property is not desirable in certain applications where water-resistant leather is required. In this case, it is necessary to apply water-proofing treatments that, generally, imply a costly process, which dramatically increases the price of the end product. Besides, the effectiveness of the water-proofing treatments depends on the surface structure of leather. Generally, coatings based on waxes, fatty acids, silicones, silanes, etc. (Luo et al., 2008; Serenko et al., 2014) are used. Their main drawback is that, despite the creation of a hydrophobic film on the leather surface, they may not be sufficient if the film is damaged or deformed upon flexing, which is quite usual when leather is employed for footwear manufacture.

Alternative treatments exist, such as the application of low-pressure plasma. Depending on the nature of the atmosphere in which the treatment is applied, materials can be provided with different properties. Thus, plasma treatment in a He and O_2 atmosphere confers hydrophillicity, while the presence of CF_4 can confer hydrophobic properties. Nevertheless, the use of greenhouse gases, as is the case of CF_4, is restricted by the European Union (European Parliament, 2014).

As an alternative to the above-described treatments and drawbacks, the LIFE TextiLeather project proposes the use of Multiple Laser Surface Enhancement (MLSE) technology for the functionalization of textiles in a sustainable way, avoiding the use of toxic or hazardous substances. MLSE technology combines plasma and laser treatments and in the presence of non-toxic gases, such as N_2 y O_2, allows the surface modification of materials (Mistry and Turchan, 2013). This treatment produces nanometric scale modifications, which enables the functionalization of the material without noticeably affecting its appearance. In addition, the MLSE technology consists of a dry, continuous process; therefore, its application in the tanning process will lead to a significant reduction in the environmental impacts of traditional leather finishing operations, especially in the case of flame retardant and water proofing treatments, in terms of greenhouse gas emissions and water and energy consumption.

The research presented in this paper focuses on the preliminary studies carried out in the framework of the LIFE TextiLeather project to improve the hydrophobicity of leather by means of the new MLSE technology. The results obtained in this study lay the basis for further testing for process optimization.

2. EXPERIMENTAL

2.1 Materials

Bovine and lamb leathers were used as raw materials, supplied in wet blue state by Incusa. These were processed by conventional processes at INESCOP facilities to produce non-functionalized leathers and leathers with a conventional waterproof finish. Table 1 shows the different references prepared at INESCOP.

Table 1. Leathers obtained by conventional processes

Leather	**Ref**	**Properties**
Bovine	**B**	Non-functionalised
	BWR-0	Conventional waterproof
Lamb	**S**	Non-functionalised
	SWR-0	Conventional waterproof

Non-functionalized leathers (references B and S) were cut into A4-size test-pieces and delivered to the MLSE technology supplier (MTiX Ltd) for functionalization.

Conventionally functionalized leathers (references BWR-0, and SWR-0) were used as standard materials to assess the effectiveness of the treatment by MLSE.

2.2 Leather treatment by MLSE

Non-functionalized leathers (references B and S) were treated by MLSE. The equipment had been conceived and optimized for the treatment of textile materials, which are continuously fed into the system, and had never been used to treat leather.

For this reason, discrete pieces of leather were stuck using adhesive tape on a continuous textile material that served as a conveyor belt (see Figure 1).

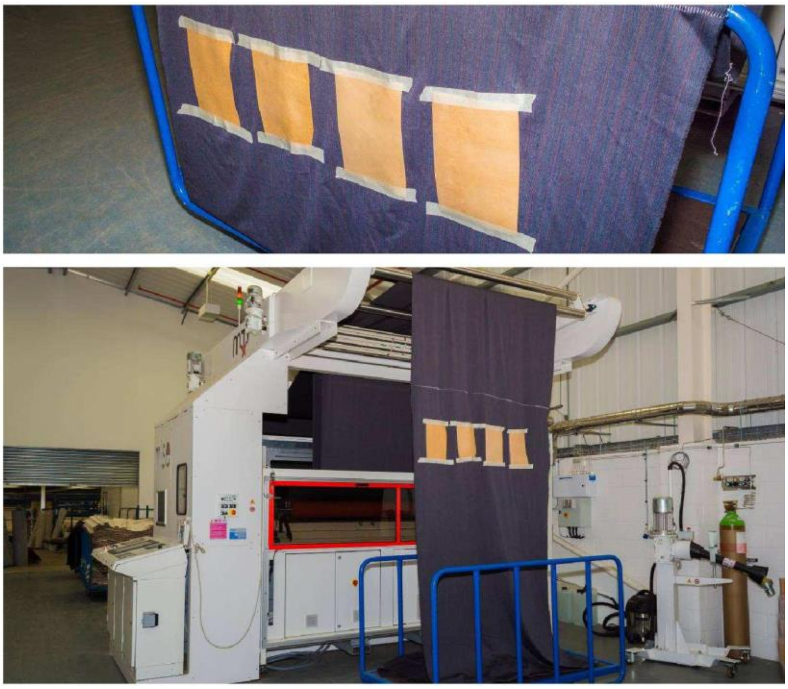

Figure 1. Leather samples stuck on a textile material for functionalization in the MLSE system.

In the first tests to check the feasibility of the application of the treatment on leather, the reference working conditions for textile waterproofing by this technique (not available) were used. Table 2 shows the sample references prepared by means of this technology.

Table 2. Leather samples prepared by the MLSE waterproofing treatment

Leather	**Reference**	**Treated side**
Bovine	BWR-MLSE-1	grain
	BWR-MLSE-2	grain + flesh
Lamb	SWR-MLSE-1	grain
	SWR-MLSE-2	grain + flesh

Once treated, the materials were delivered to INESCOP to be subsequently assessed.

2.2. Leather characterization

Water repellency of non-functionalized and waterproofed leather samples was assessed in static conditions, according to ISO 23232.

Table 3 shows the standard test liquids employed.

In addition, water penetration and water absorption after 60 min were measured in dynamic conditions by means of repeated linear compression according to EN ISO 5403-1 (see Figure 2).

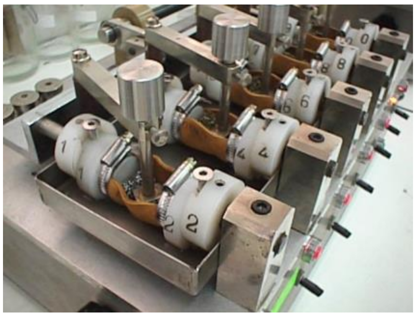

Figure 2. Water resistance test for footwear upper materials according to EN ISO 5403-1.

Finally, the effect of these treatments on water vapor permeability (WVP) properties was checked according to EN ISO 14268.

Tabla 3. Standard test liquids for the assessment of water repellency according to ISO 23232

Aqueous solution/ Repellency grade	Composition
0	None: Test liquid No 1 is absorbed by the substrate
1	98:2/Water:isopropyl alcohol (by volume)
2	95:5/Water:isopropyl alcohol (by volume)
3	90:10/Water:isopropyl alcohol (by volume)
4	80:20/Water:isopropyl alcohol (by volume)
5	70:30/Water:isopropyl alcohol (by volume)
6	60:40/Water:isopropyl alcohol (by volume)
7	50:50/Water:isopropyl alcohol (by volume)
8	40:60/Water:isopropyl alcohol (by volume)
9*	30:70/Water:isopropyl alcohol (by volume)
10*	20:80/Water:isopropyl alcohol (by volume)
11*	10:90/Water:isopropyl alcohol (by volume)
12*	isopropyl alcohol

* Additional standard liquids not included in the test method.

3. RESULTS AND DISCUSSION

First of all, the effectiveness of the MLSE treatment was assessed in static conditions, according to ISO 23232. Treated leathers were checked against the materials functionalized at INESCOP. Figure 3 shows, by way of example, the results obtained on lamb leathers. Table 4 lists the results obtained on all materials studied.

It was observed that, under the working conditions applied in this preliminary study, the MLSE treatment produced an irregular functionalization effect on some spots of the leather surface. However, MLSE treated leathers generally achieved a water repellency grade up to 12, which is much higher than the grade achieved with conventional treatments currently applied in the tanning sector.

With the aim of assessing the suitability of these materials for use as footwear uppers, water resistance in dynamic conditions was determined according to EN ISO 5403-1. Also, tests were conducted according to EN ISO 14268 in order to check if the hydrophobic treatment compromised water vapour permeability (WVP) properties. Table 5 shows the results obtained on the different references.

In spite of the fact that the MLSE treatment slightly improved water resistance properties in dynamic conditions with respect to non-functionalized materials (references B and S), for the time being it has not possible to achieve the requirements established by EN ISO/TR 20879 for use as upper material in water-resistant footwear. This result could be attributed to the treatment irregularities detected during the assessment of water repellency in static conditions.

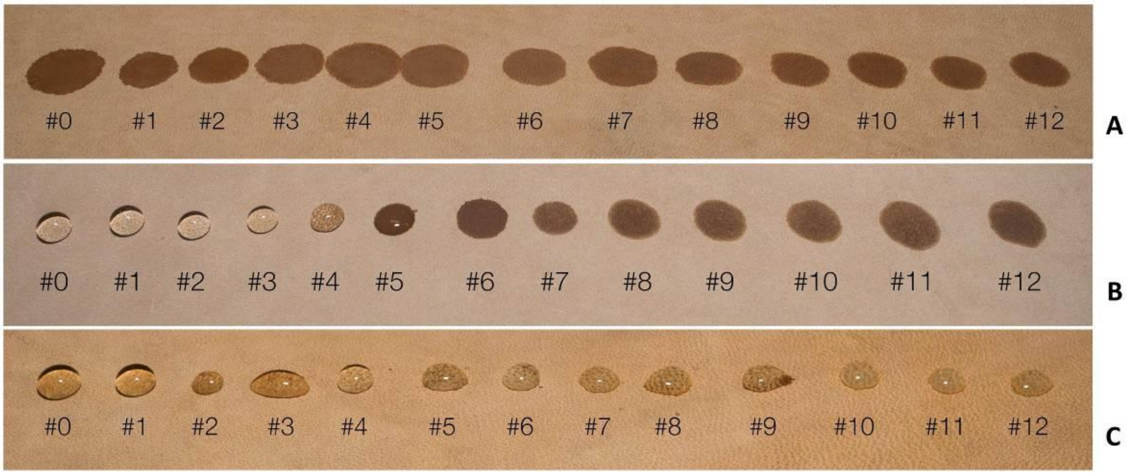

Figure 3. Water repellency assessment according to ISO 23232. **A:** Non-functionalized lamb leather (Reference S); **B:** Lamb leather with conventional waterproofing treatment (Reference SWR-0); **C:** Lamb leather with MLSE waterproofing treatment (Reference SWR-MLSE-1).

Table 4. Water repellency of materials assessed according to ISO 23232

Leather	Reference	Repellency grade number
Bovine	B	0
	BWR-0	4
	BWR-MLSE-1	Irregular results, grade 12 was achieved
Lamb	S	0
	SWR-0	3
	SWR-MLSE-1	Irregular results, grade 12 was achieved

Table 5. Water resistance of materials assessed according to EN ISO 5403-1

Reference	Hydrophpbicity Penetration time (min)	 Water absorption after 60 min (%)	WVP (mg/cm^2 h)
B	1	84	9,8
BWR0	>360	6	9,7
BWR-MLSE-1	2	75*	7,7
BWR-MLSE-2	19	25	9,7
S	1	140*	16,3
SWR0	> 120	11	20,4
SWR-MLSE-1	11	75	14,5
SWR-MLSE-2	8	65	15,2
Requisitos para calzado	≥ 60**	≤ 20**	≥ 0,8

* Measured after 10 min ** Requirements for water-resistant footwear

On comparing the materials treated by MLSE on their grain side (references BWR-MLSE-1 and SWR-MLSE-1) with those treated on both their grain and flesh sides (references BWR-MLSE-2 and SWR-MLSE-2), no noticeable differences were observed in the case of lamb leathers. However, the improvement in water resistance was significantly greater when bovine leathers were treated on both sides.

Furthermore, none of the materials studied lost its water vapor permeability properties.

4. CONCLUSIONS

For both types of leather, the surface treatment by MLSE technology provided promising results with regards to water repellency in static conditions, which could indicate the suitability of this treatment for leathers intended for upholstery or clothing. Besides, it was checked that the MLSE treatment could even yield water repellency properties, in static conditions, much higher than those obtained by conventional processes.

When these materials were subjected to continuous linear compression simulating the wearing conditions of footwear, their water resistance properties slightly improved after MLSE treatment. However, neither the levels achieved with conventional waterproofing processes nor the minimum requirements for water-resistant footwear were attained.

It should be highlighted that both the equipment employed in this study and the treatment conditions applied had been optimized for treating textile materials. Treatment parameters, laser and plasma power, ambient gas concentration, residence time of the material in the treatment zone, etc. are currently being revised. In addition, the substrate feeding system is being modified to allow the treatment of discrete materials, such as leathers. As a result of this work, the MLSE technology is being adapted to treat new materials: leather.

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