



Research paper

Sodium montmorillonite effect on the morphology, thermal, flame retardant and mechanical properties of semi-finished leather

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ABSTRACT

In the present work, the effect of sodium montmorillonite (Na^+Mt) on the resulting properties of semi-finished (crust) leather has been thoroughly studied. Na^+Mt has been added during retanning process of tanned (wet-blue) leather in specific conditions. The morphological analysis by scanning electron microscopy has pointed out that Na^+Mt particles are homogeneously distributed and finely dispersed within the leather structure. The presence of clay mineral has affected the thermal stability of leather in nitrogen and air (assessed by thermogravimetry), as well. According to the sixty second vertical flammability test results Na^+Mt particles have significantly reduced the burning length of the semi-finished leather. A barrier mechanism of the Na^+Mt during combustion process is proposed. Mechanical properties (namely, tensile and tear strength) have proven to be considerably improved by using 1 and 3 mass% of Na^+Mt ; these results have clearly indicated the reinforcing effect of clay mineral platelets that somehow physically interact with leather.

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1. Introduction

There are a wide variety of leather products in the market with flame retardant properties, which accomplish with the standards and demands of different industries such as the automobile and the aircraft ones. The flame retardant properties of such products are generally achieved through a finishing leather process, which consists in applying coating agents containing flame retardant additives (Kozłowski et al., 2006; Ying et al., 2006). In spite of this being an adequate process to impart the leather with flame retardant properties, the final cost of the leather products is strongly increased. One of the strategies that have been explored in the last decades for imparting flame retardant properties to polymeric materials is the preparation of clay polymer nanocomposites (CPN) (Gilman, 1999; Kiliaris and Paspaspyrides, 2010). CPN have proven to greatly reduce the flammability properties of the base polymeric materials, in spite of other advantages such as the lower concentration of the additives that has to be used as compared to traditional methods, the CPN act as non-halogenated flame retardant additives (Sanchez-Olivares et al., 2013a,b).

In the recent years, nanotechnology attention has increased in leather manufacturing processes due to better leather performance and the low cost that represents to use this technology. According to leather nanotechnology research works, important results have been reported on tanning and coating processes, mechanical properties, final properties of leather and effluent treatments (Chen et al., 2011). However, the researches on flame retardant properties of leather by using nanotechnology are still scarce. Xiuli et al. (2010) prepared a waterborne polyurethane CPN to be used as flame retardant leather finishing. They modified sodium montmorillonite (Na^+Mt) to obtain a waterborne polyurethane nanocomposite by *in-situ* polymerization, and this CPN was prepared as a film which was padded on to the leather. The effect of different Na^+Mt contents was evaluated on oxygen index, flammability and thermal stability. Enhanced flame retardant effects were found and attributed to the char layer mechanism of CPN. Huijiao et al. (2012) synthesized a new intumescent flame retardant compound and modified montmorillonite by intercalation method to prepare a flame retardant hide powder. The latter compound was added to pigskin to produce flame retardant leather: as a consequence, its flame retardant properties and thermal stability were improved. The authors concluded that the new CPN has an effective flame retardant performance and a fine retanning property.

In the present work, the effect of Na^+Mt on thermal, flame retardant and mechanical properties of semi-finished leather added during retanning process was investigated in order to develop a new strategy to obtain flame retardant leather for upholstery uses.

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Table 1
Samples description.

Sample Identification	Na ⁺ Mt content [mass%]
Leather	0
Leather-Na ⁺ Mt_1%	1
Leather-Na ⁺ Mt_3%	3
Leather-Na ⁺ Mt_6%	6

2. Experimental part

2.1. Materials

Bovine wet-blue leather, Cr₂O₃ content 4.7%, 2.4% fat and pH of 3.29 from tanning industry of Mexico. Sodium Montmorillonite (Na⁺Mt) PGW from Nanocor Inc, with cation exchange capacity of 145 meq/100 g (\pm 10%) and aspect ratio of 200–400. Anionic fatliquors based on phosphoric esters TRUPON PEM and OLITECH 1620 from Trumpler Mexicana, Mexico as fatliquoring products. Trivalent chromium salt (Cr⁺³) of basicity 33–50%, synthetic naftalenic tanning and vegetal tanning (mimosa) as retanning agents. Acid aniline as dyeing product. Phosphoric acid 85% purity industrial grade for the pH control. Sodium formate and sodium bicarbonate industrial grade were used for neutralization.

2.2. Equipment

Semi-finish (wet end) leather process was carried out using tannery test drums Italprogetti CR10/1 model, with dimensions of 100×50 (D×W) cm² at 16–18 rpm velocity. Na⁺Mt dispersion was performed employing a mechanical stirrer Lightnin LabMaster L5U10F model.

2.3. Procedure

1. Na⁺Mt was dispersed in water, the ratio Na⁺Mt/water was 100 g/2 L, at 60 °C under continuous stirring at 550 rpm velocity during 60 min

to render a homogeneous dispersion (clay mineral/water). This dispersion was added during the leather retanning process.

2. Semi-finish leather processes was carried out according to standard retanning, fatliquoring and dyeing processes employed by the tanneries worldwide (Schubert, 1978; Wachsmann, 1999). For each experiment, four wet-blue leather pieces were processed. The main steps of the semi-finish leather process are as follows:

- a) Bovine wet-blue leather was washed to standardize the quality using a surfactant agent. To control pH, phosphoric acid was employed to obtain 3.3–3.8 pH value,
- b) A neutralization process was carried out up to pH of 4.5–5.0,
- c) After neutralization, a retanning process was performed using trivalent chromium salt (Cr⁺³), synthetic naftalenic tanning and mimosa,
- d) Na⁺Mt dispersion from step 1 was added at this stage. Rotate drum time with clay mineral dispersion /leather was of 60 minutes,
- e) Dyeing,
- f) Fatliquoring,
- g) Drying leather was done by vacuum. After the drying step, the humidity of semi-finished leather samples was 15.1 mass%, evaluated by gravimetric drying method.

3. Thickness of semi-finish leather after retanning, dyeing, fatliquoring and drying processes was of 1.4 mm.

2.4. Characterization

2.4.1. Morphology

The surface morphology of the samples was studied using a LEO-1450VP scanning electron microscope (beam voltage: 5 kV); an X-ray probe (INCA Energy Oxford, Cu-K α X-ray source, $k = 1.540562 \text{ \AA}$) was used to perform elemental analysis. Sample pieces (5 × 5 mm²) were cut and fixed to conductive adhesive tapes and gold-metallized.

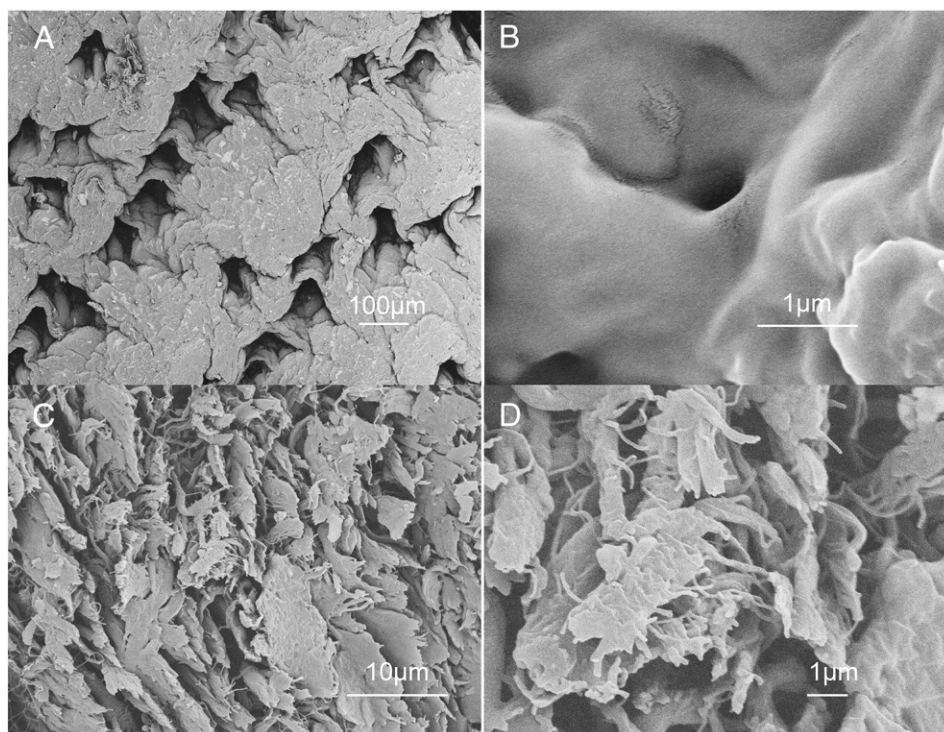


Fig. 1. Leather morphology by SEM. (A) and (B) grain surface micrographs at 100 and 25000X magnification, respectively; (C) and (D) cross section micrographs at 2500 and 10000X magnification, respectively.

2.4.2. Thermal stability

Thermogravimetric analysis (TGA) was carried out in a TA-Instruments Q500 analyzer with heating rate of 10 °C/min under nitrogen and air atmosphere (gas flow = 60 ml/min), placing samples (ca. 10 mg) in alumina pans. These tests were duplicated in order to have reproducible data; the experimental error was ± 1 °C and ± 0.5 mass%.

2.4.3. Flame retardant properties

Flame retardant properties were evaluated through sixty seconds vertical flammability test according to Title 14-Aeronautics and Space, Part 25-Airworthiness standard, Appendix F to Part 25, Part I-Test Criteria and Procedures, published by the United State Department of Transportation of the Federal Aviation Administration suitable for testing the flammability of materials in vertical configuration (covered by paragraph (a) (1) (i) of this appendix). Sample dimensions

$30 \times 5 \text{ cm}^2$ and 1.4 mm thickness was used; samples were maintained at 23 °C and 50% relative humidity 24 h prior tests. A Bunsen burner with a 0.95 cm nominal I.D. (internal diameter) generating a methane flame (3.81 cm length) of was used. The flame was applied once to the center line of the lower edge (1.90 cm above the top edge of the burner) of the specimen for 60 s and then removed.

2.4.4. Mechanical properties

Mechanical properties were evaluated using a tensile Instron model machine at 100 mm/min crosshead speed; samples were maintained at 23 °C and 65% relative humidity 48 h before the test.

2.4.5. Humidity

Leather humidity was evaluated using a Sartorius MA35 moisture analyzer balance.

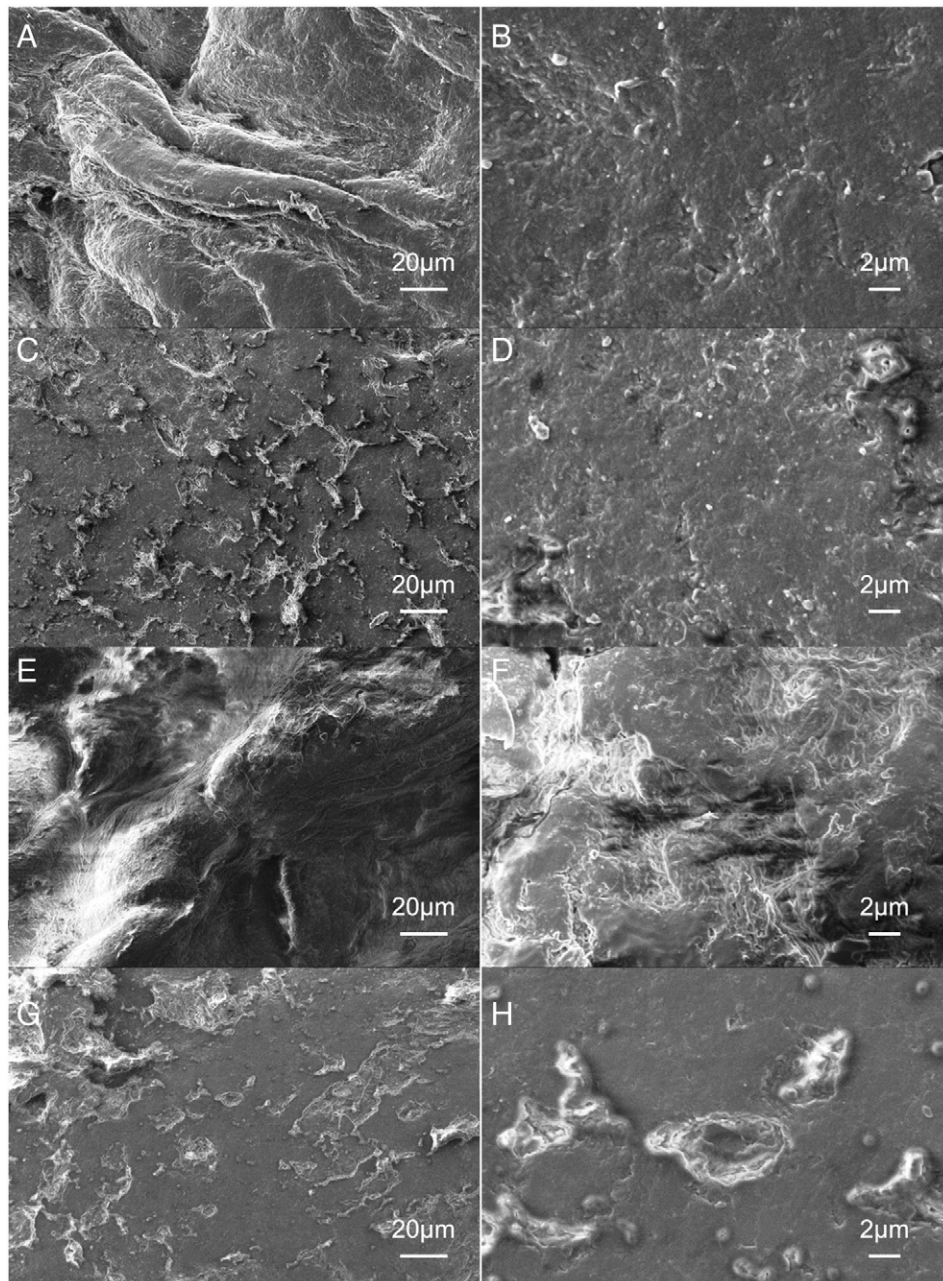


Fig. 2. SEM magnifications of leather (A and B), leather with 1 (C and D), 3 (E and F) and 6 mass% Na⁺Mt (G and H).

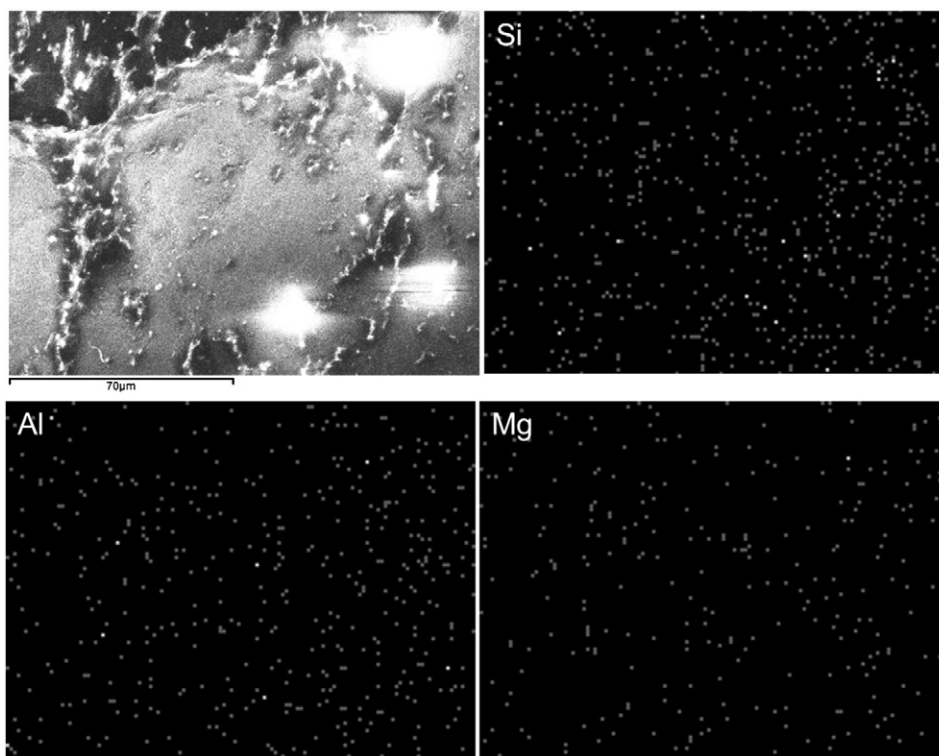


Fig. 3. Elemental analysis of sample: Leather-Na⁺Mt₆%.

3. Results and discussion

3.1. Morphology

The morphology of the investigated leather samples (Table 1) was studied by scanning electron microscopy (SEM). Fig. 1 shows the morphology of grain surface and cross section of leather without clay mineral. In Fig. 1A and B (grain surface) pores of leather are clearly observed; their size varies from 100 μm to 400 nm. Fig. 1C and D report leather cross section, where fibers and many interstitial voids between fibers are observed. This typical morphology of the leather depicts the possibility of clay mineral particles to be penetrated to internal leather structure through the pores.

Fig. 2 reports some magnifications of leather (2A and 2B) and leather with Na⁺Mt (2C–2H). The morphology of the leather is not significantly affected by the presence of the clay mineral, regardless of its content.

Indeed, when the content passes from 1 (Fig. 2C and D) to 3 (Fig. 2E and F) or 6 mass% (Fig. 2G and H), micro-aggregates are not distinguishable; hence, probably the clay mineral nano-platelets turned out to be homogeneously and finely dispersed within the 3D structure of leather. In order to confirm such hypothesis, the elemental analysis has been carried out on all the obtained samples. As an example, Fig. 3 reports the mapping of some elements found in the sample containing 6 mass% of clay mineral. Si, Al and Mg, the main components of Na⁺Mt, are homogeneously dispersed within the network of leather.

3.2. Thermal stability

The thermal stability of leather can be affected by the presence of clay mineral nano-platelets. For this reason, thermogravimetric analyses have been carried out in nitrogen and air. Figs. 4 and 5 plot the TG

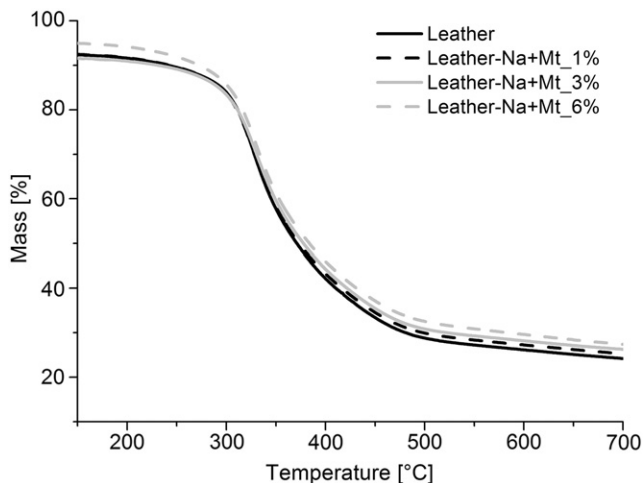


Fig. 4. TG curves of leather samples at different clay mineral content in nitrogen.

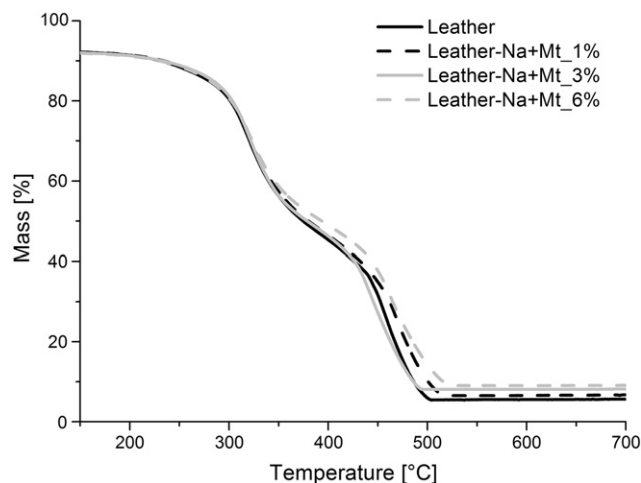


Fig. 5. TG curves of leather samples at different clay mineral content in air.

Table 2
Thermogravimetric data of leather samples in nitrogen and air.

Sample	$T_{\max 1}$ [*] [°C]	$T_{\max 2}$ [*] [°C]	Residue at $T_{\max 1}$ [%]	Residue at $T_{\max 2}$ [%]	Residue at 700 °C [%]
<i>Nitrogen</i>					
Leather	327	–	68.7	–	23.5
Leather-Na ⁺ Mt_1%	328	–	68.3	–	24.6
Leather-Na ⁺ Mt_3%	332	–	67.9	–	25.7
Leather-Na ⁺ Mt_6%	329	–	71.8	–	27.1
<i>Air</i>					
Leather	319	459	68.8	24.6	5.5
Leather-Na ⁺ Mt_1%	319	469	69.8	24.8	6.5
Leather-Na ⁺ Mt_3%	321	463	68.8	30.4	7.9
Leather-Na ⁺ Mt_6%	321	463	70.1	30.8	8.9

* From derivative curves.

curves of the samples with clay mineral in comparison with that of leather. The collected data are summarized in Table 2.

In nitrogen, leather degrades through a single step mechanism, whose maximum mass loss occurs in between 300 and 700 °C with a temperature of maximum degradation ($T_{\max 1}$) of 327 °C (Table 2), at which a residue of 68.7% corresponds. Such mass loss can be attributed to the main component of leather, namely collagen (Budrugaec et al., 2003; Kaminska and Sionkowska, 1996). The residue formed at $T_{\max 1}$, evolves towards other carbonaceous species under heating and, at approximately 500 °C, a thermally stable char (up to 700 °C) is generated.

The presence of clay mineral, protects the leather against its thermal degradation, which is evidenced by the shift of TG curves towards higher temperatures. Although the $T_{\max 1}$ values remain almost equal in the presence of clay mineral (Table 2), a residue depending on the clay mineral content is formed in a slight higher amount. At the end of the tests, the final residue turned out to be depending on montmorillonite content: the higher Na⁺Mt content, the higher is the residue at 700 °C.

In air, neat leather degrades through two main steps of degradation (centred at 319 and 459 °C, Table 2); once again, the main mass loss can be attributed to collagen. The residue formed at $T_{\max 1}$ further degrades by an oxidation step giving rise another mass loss ($T_{\max 2}$) and leaving a final residue at 700 °C of 5.5%.

Analogously to what was observed in nitrogen, the presence of clay mineral in air partially protects the leather, more specifically during the second step of degradation (namely, the oxidation of the residue left at

$T_{\max 1}$), shifting the TG curves to higher temperatures ($T_{\max 2}$ values, Table 2). In doing so, a higher residue at 700 °C (depending on the clay mineral content) has been found (8.9, 7.9, 6.5% for leather containing 6, 3 and 1 mass% Na⁺Mt, respectively).

3.3. Flame retardant properties

Flame retardant properties were evaluated according to the Code of Federal Regulations - C.F.R. Although such standard requires the application of a flame for 60 s, this procedure is a too much rigorous test for natural leather-based materials with respect to tests used by many worldwide organizations, especially for upholstery leather where flame time application is only 12 s (ALCA method E50). Fig. 6 reports the length of the burnt area in the tested specimens (namely, burning length, cm) as a function of the clay mineral content (0, 1, 3 and 6 mass%). According to 14 C.F.R. Appendix F to Part 25 Part I (a) (1) (i) standard, the maximum value of burning length is 15.2 cm (6.0 in). Leather (without Na⁺Mt) exhibits 16.4 cm burning length; this means that leather without flame retardant treatment is not suitable to use in aeronautic applications. However, when 1 mass% of Na⁺Mt is added during retanning process, burning length decreases down to 14.3 cm. When 3 and 6 mass% are added to leather, burning length is further reduced to 13.3 and 13.4 cm, respectively (Fig. 6). These results clearly show the effect of Na⁺Mt on flame retardant properties of leather. At low Na⁺Mt contents (1 and 3 mass%), burning length reduction showed to be directly related to Na⁺Mt concentration; probably, clay mineral particles dispersed in the bath penetrate through pores towards the internal leather structure by mechanical forces generated inside the drum; in doing so, they may act as filler between inter-fibrillar spaces. This mechanism can occur at this stage since montmorillonite particles were added, before the finishing of leather, by dyeing and fatliquoring products which fill the inter-fibrillar spaces of the leather. However, at high clay mineral loading (6 mass%) burning length is quite similar to that obtained using 3 mass%: probably, at such content, clay mineral particles are not completely deposited within the leather structure (fiber-network) due to high concentration, and thus a part of the clay mineral probably remains in the exhausted bath, although this phenomenon has not been observed by SEM. Fig. 7 shows some pictures of the specimens after vertical flammability tests, where the burned-out zone is clearly distinguishable. In particular, Fig. 7A refers to the leather (without clay mineral) shows the largest burning length with respect to the samples with different clay mineral contents;

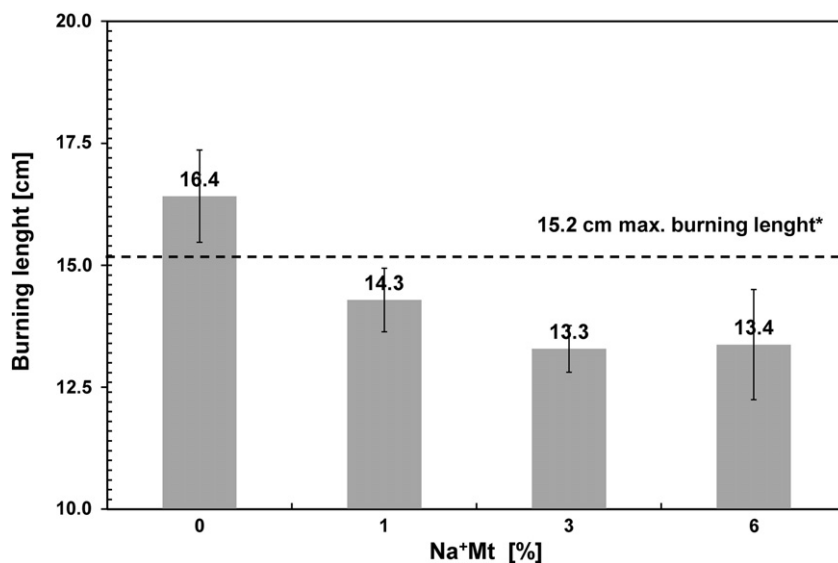


Fig. 6. Burning length of leather with respect to Na⁺Mt content. Leather (±0.9), Leather-Na⁺Mt_1% (±0.7), Leather-Na⁺Mt_3% (±0.5) and Leather-Na⁺Mt_6% (±1.1). *Maximum value of burning length according to 14 C.F.R. Appendix F to Part 25 Part I (a) (1) (i).

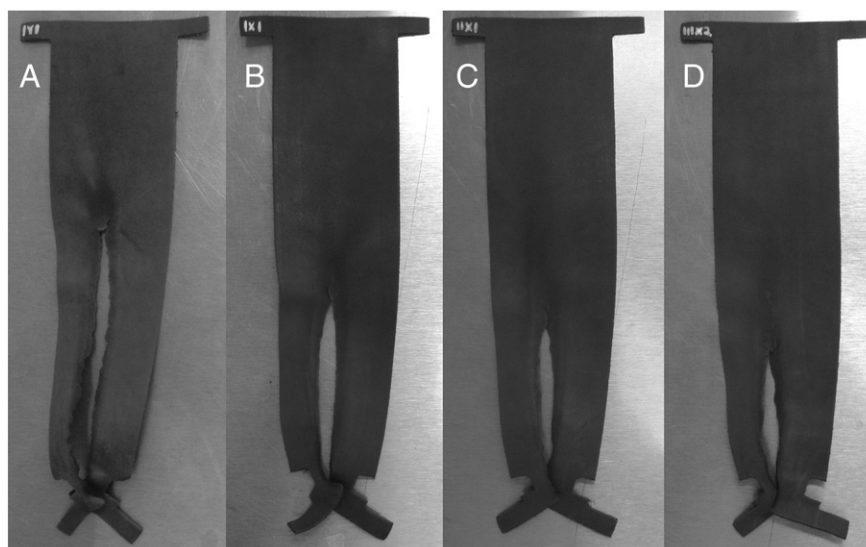


Fig. 7. Samples evaluated by flammability vertical test according to 14 C.F.R. Appendix F to Part 25 Part I (a) (1) (i). (A) Leather, (B) Leather- Na⁺Mt_1%, (C) Leather- Na⁺Mt_3% and (D) Leather- Na⁺Mt_6%.

Fig. 7B, C and D report pictures of 1, 3 and 6 mass% Na⁺Mt, respectively. According to the previous reports for flame retardant CPN, the mechanism to reduce flammability can be ascribed to the formation of a char layer (acting as a thermal barrier) able to reduce heat, oxygen and mass transfer during the combustion process (Gilman et al., 2000; Schartel et al., 2006). In the case of leather, it is possible that the presence of clay mineral nano-platelets in the inter-fibrillar spaces of the leather contributes to the formation of a protective char layer acting as a barrier to the combustion process. In particular, the presence of a ceramic material (clay), within the char formed during combustion, can contribute to improve the flame retardant properties of the final material due to its intrinsic thermal insulation property.

In addition, a reaction of the clay mineral with phosphate compounds that stabilizes the char formed during the combustion process has been reported by Bourbigot et al. (2000) and Ma et al. (2008). In this work, two fatliquor agents (based on phosphate esters) and phosphoric acid were added to the leather in order to take advantage of this effect, although no confirmation of a reaction between the clay mineral and the phosphorous was confirmed. Clay mineral reaction with the retanning and finishing products was not evaluated here, although these reactions are not probable since the clay mineral used here was not organically modified. Reactions of clay mineral and tanning products has been reported for organically modified clay in combination with chrome (Bao and Ma, 2010; Ma et al., 2005). Moreover, in the present work, these products are added at a later stage after the clay mineral has penetrated the leather inter-fibrillar spaces.

3.4. Mechanical properties

Table 3 discloses the mechanical properties of 0, 1, 3 and 6 mass% Na⁺Mt content samples in terms of tensile strength, strain at break and tear strength. In general, Na⁺Mt particles have been proved to

improve the tensile and tear strength of the leather sample with respect to the sample with no clay mineral added. Tensile strength has been increased from 165 to 225 and 228 kg/cm² for the sample with 1 and 3 mass% clay mineral, respectively; at high Na⁺Mt content (6 mass%), tensile strength is not considerably improved (170 kg/cm²) with respect to leather without clay mineral (160 kg/cm²). Tear strength has been increased from 7.9 to 9.4 kg with only 1 mass% of clay mineral; on the other hand, 3 and 6 mass% Na⁺Mt has induced the same effect (8.5 kg). As far as strain at break is considered, no change has been observed at the lowest clay mineral content. However, when Na⁺Mt content has been increased to 3 or 6 mass-%, the strain at break has been drastically reduced down to 41 and 34%, respectively. These results suggest that the Na⁺Mt particles located in the internal leather structure may be acting not only as filling agent between inter-fibrillar spaces, but also as reinforced agent, producing a stiffer leather.

4. Conclusions

In the present work, the effect of sodium montmorillonite (Na⁺Mt) content on the morphology, thermal stability, flame retardant and mechanical properties of semi-finished leather was investigated. Such clay mineral has proven to be homogeneously dispersed into the internal structure of leather, regardless its content. The presence of clay mineral improved thermal stability of leather depending on the concentration as well as the flame retardant properties of leather. The latter were assessed by a rigorous vertical flammability test (60 s of methane flame application). Indeed, the length of burnt area has been notably decreased with the addition of 1 and 3% Na⁺Mt. Mechanical properties, tensile and tear strength, were enhanced by the use of Na⁺Mt. According to the collected results, it is reasonable to suppose that Na⁺Mt nano-platelets are able to penetrate through leather pores towards the internal leather structure by mechanical forces developed inside of drum; in doing so, they may act as a barrier under combustion process as well as reinforcing particles. Finally, the observed efficiency of such clay mineral as flame retardant for leather makes the proposed system suitable for preparing upholstery materials in the aeronautic industry.

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Table 3
Mechanical properties of leather samples.

Sample	Tensile strength [kg/cm ²]	Tear strength [kg]	Strain at break [%]
Leather	165 (±7)	7.9 (±0.3)	51 (±1)
Leather-Na ⁺ Mt_1%	225 (±4)	9.4 (±0.1)	51 (±2)
Leather-Na ⁺ Mt_3%	228 (±8)	8.5 (±0.5)	41 (±1)
Leather-Na ⁺ Mt_6%	170 (±8)	8.5 (±0.5)	34 (±1)

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