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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.

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 (Kozlowski 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 Papaspyrides, 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, Cr_2O_3 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 (±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 Italprogectti CR10/1 model, with dimensions of 100×50 (DxW) cm^2 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-Kα X-ray source, k = 1.540562 Å) was used to perform elemental analysis. Sample pieces (5 × 5 mm^2) were cut and fixed to conductive adhesive tapes and gold-metallized.

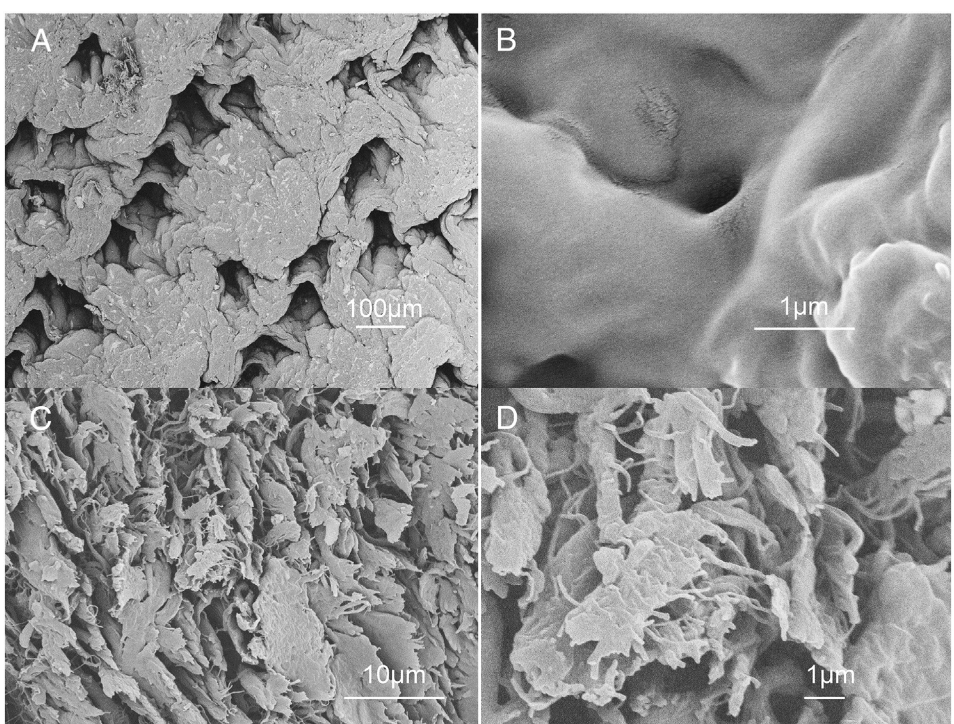

Fig. 1. Leather morphology by SEM. (A) and (B) grain surface micrographs at 100 and 25000X magnification, respectively; (C) and (D) cross section micrographs at 2500 and 10000X magnification, respectively.

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