HALLOYSITE NANOTUBES AS INNOVATIVE CONSOLIDANTS FOR HISTORICAL LEATHER

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Historical leathers, in a huge variety of items as footwear and garments, bookbinding, wall tapestry, upholstery, harnesses, armours, storage vessels, household tools, cases, musical instruments, toys, ritual objects are regarded as important testimonials of our cultural heritage. It is vital therefore that these objects remain well preserved along with all the knowledge involved, from their material aspects and value use to historical, cultural and artistic values. One of the most difficult challenges in leather conservation concerns with consolidation and pH control. To set up a novel green protocol for the long-term protection of historical and archaeological leather we have investigated the filling and stabilization process of vegetable-tanned leathers treated with various mixtures based on halloysite nanotubes (HNTs).

Keywords: vegetable leather, halloysite nanotubes, stabilization

INTRODUCTION

For millennia man has used animal hides in their day by day life for producing footwear, garments, for building their shelters (e.g. tents, yurts), household objects and tools, military accessories (armors, shields, helmets, etc.), boats, musical instruments and even toys. Later, in Middle Ages, the production of artistic objects or components has developed, e.g. travel chests, jewelry boxes, upholstery, wall tapestries, bookbindings, furniture accessories, etc. Nowadays, such artistic, historical and archaeological objects are preserved in museums, libraries or archives, places where history is kept alive and tell us about our ancestors.

Most of the historical leathers are vegetable tanned, alum-tawed or tanned with smoke or fats. Along with the industrial revolution, through the 1850s, the first investigations performed on early and current (industrial) leather showed that the presence of sulphur dioxide in the urban atmosphere strongly affects the performance of the leather: the so-called red rot phenomenon (Haines, 1977) promoted by the atmospheric pollution has proved to be detrimental to collagen structure. Even today museums, libraries, private collections and historical places owing leather artworks are facing this unresolved problem.

The current treatment options, however, are very few, and all commercial products such as Klucel-G and silicone oil showed critical drawbacks (Ludwick, 2012). Recently the use of nanoparticles in conservation has started to be explored, halloysite nanotubes being used as consolidating materials for archeological wood and paper (Cavallaro *et al*., 2015; Cavallaro *et al*., 2014).

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EXPERIMENTAL DETAILS

Chemicals

Halloysite nanotubes (HNTs) from Sigma Aldrich, polyethylene glycol 400 and 1-chlorobutane from Alfa Aesar, glacial acetic acid 99.84% from Chimreactiv, ethanol 96% from Chemical Company, sodium chloride from Salrom, urea from Sigma Life Science, beeswax from EcoNatura and concentrated wool keratin hydrolysate obtained in our laboratory, were used.

Preparation of Nanoparticle Dispersions Applied on Leather Samples

HNTs dispersions were prepared using four different dispersion media: polyethylene glycol 400 (PEG); concentrated keratin hydrolysate (Ke) with neutral pH; sodium chloride (2%) and urea (2%) in ethyl alcohol solution (48%) (Ur) (Badea et al., 2014); 2% beeswax in 1-chlorbutan (Bw). The concentration of HNTs was 0,1% for PEG, Ke and Ur dispersions, while 0,5% HNTs was added to the Bw alcoholic dispersion. All dispersions were ultrasonicated 10 minutes before applying on leather.

Mimosa tanned calf leather obtained in our micro pilot unit was used to test the effect of the various HNTs dispersions.

The samples were immersed for 10 minutes in the HNTs dispersion using a Petri dish placed on a shaker plate (Compact Digital Rocker from Thermos Scientific) at 100 rpm; every two minutes the sample was turned around. Treated samples were hanged and dried at room temperature.

The hydrothermal stability analysis was carried out at both macroscopic and microscopic levels, using the standard method SR EN ISO 3380-2003 and Micro Hot Table (MHT) method, respectively. The MHT system is made of a Linkam-LTS 120 heating plate, a Nikon SMZ745T stereomicroscope equipped with a MDH5 video camera and a computer for the temperature increase control and image acquisition. The shrinkage activity measurements were performed up to 90°C as described earlier (Sendrea *et al*., 2017).

FTIR-ATR analysis was carried out using an Alpha portable spectrometer from Bruker Optics equipped with Platinum diamond ATR at a resolution of 4 cm^{-1} and 32 scans. The spectral rage was 4000-650 cm^{-1}. FTIR-ATR spectra were acquired on both sides of leather samples, corium and grain (Carşote *et al*., 2014).

SEM high magnification images were achieved with a FEI Quanta 200 microscope at an acceleration potential of 10 kV.

Wettability was determined by dynamic contact angle measurements carried out with a Drop Shape Analyzer DSA100 from KRÜSS, the sample being placed horizontally.

Non-Invasive Single-Sided ^{1}H NMR measurements were performed at room temperature using a Magritek GmbH NMR MOUSE PM2 controlled by a Kea 2 spectrometer operating at 27 MHz ^{1}H resonance frequency as described earlier (Badea *et al*., 2016). The Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used to measure the spin-spin relaxation time T_{2eff}. The CPMG curves were best analyzed by a combination of two exponential functions. The spin-lattice relaxation times, T_1, were measured with a saturation-recovery pulse sequence.

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RESULTS AND DISCUSSION

Hydrothermal Stability Measurement

The values of shrinkage temperature reported in Table 1 indicate a stabilizing effect for all treated samples, Bw_HNT treatment being the most effective treatment. It should however be mentioned that, even though T_s increases, there is a net decrease of the first shrinkage temperature (Figure 1) which could be attributed to the destabilization of collagen populations with lowest thermal stability due to the solutions used to disperse the HNTs.

Table 1. Thermal stability measured by both the standard method SR EN ISO 3380-2003 and MHT method

Sample/ Treatment	Shrinkage temperature (standard method), °C	Shrinkage activity determined by MHT method		
		T_f, °C	T_s, °C	T_l, °C
CM_Ref	66	41.6	58.2	79
CM_Ke	67	24.2	60.6	83.4
CM_Ke_HNT	68	24.7	61.1	80.1
CM_Ur	70	33	61.1	79.3
CM_Ur_HNT	70	34.4	59.7	85
CM_PEG	68	34.3	64.4	80.2
CM_PEG_HNT	70	35	63.1	81.6
CM_Bw	69	24.4	63.1	81.6
CM_Bw_HNT	71	26.2	65.3	79.3

T_f-first shrinkage temperature, T_s-shrinkage temperature and T_l-last shrinkage temperature [6]

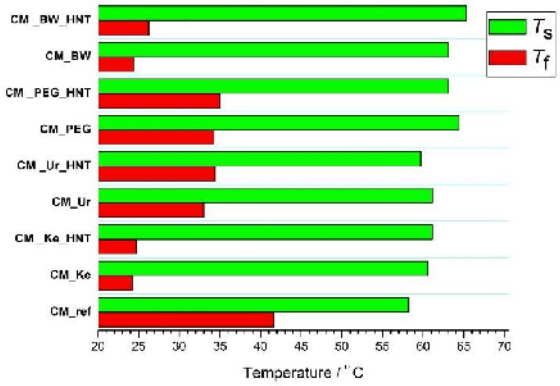

Figure 1. Values of main shrinkage temperature T_s and first shrinkage temperature T_f before and after the consolidation treatment

ATR-FTIR Measurements

The ATR-FTIR spectra of the treated and untreated samples are shown in Figures 2 and 3, for corium side and gran side, respectively. The HNTs characteristic bands at 3695 cm^{-1}, 3624 cm^{-1}, 1027 cm^{-1}, 908 cm^{-1}, 529 cm^{-1} and 463 cm^{-1} are evident for the CM_Bw_HNT_c and CM_Ur_HNT_f spectra suggesting the presence of the nanotubes on the corium and grain surface of these samples, as demonstrated by SEM observations (Figure 5). On the other part the Ur_HNT dispersion shown a much better penetrability

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on the leather corium side. The much lower intensity or the absence of these bands for the samples treated with Ke_HNT and PEG_HNT dispersions indicate a more effective penetration of the nanotubes into the structure of the leather.

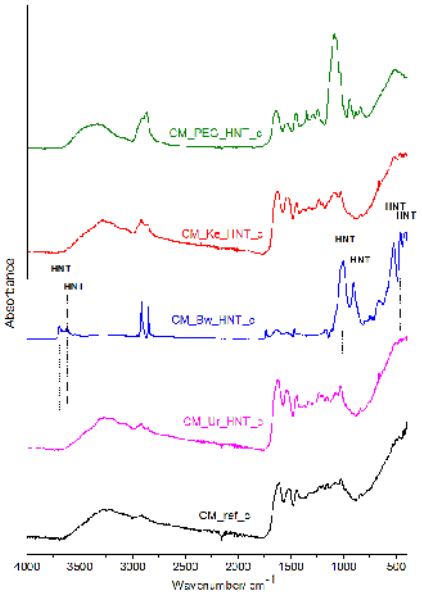

Figure 2. ATR-FTIR spectra of untreated and treated leather samples - corium side

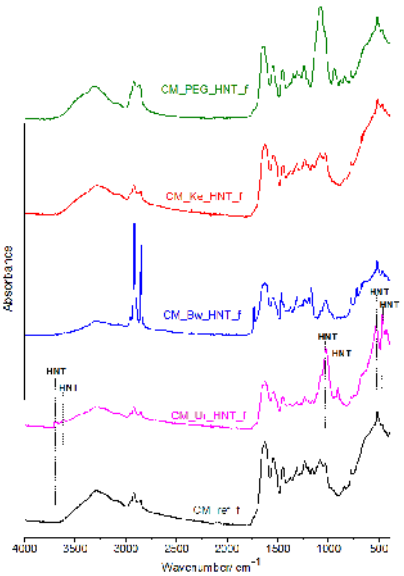

Figure 3. ATR-FTIR spectra of untreated and treated leather samples - grain side

SEM Observations

SEM high-resolution images of the network of collagen fibres on the surface of parchment were used to assess their state and follow their deterioration (Della Gatta *et al*., 2005). SEM furnished a collection of local images that show a network of integral collagen fibres with clear contours and sharp edges (Figure 4). No shape changes resulted after the treatments using various HNTs dispersions, only a slight coating effect was observed in the case of leather treated with the Bw_HNT dispersion (Figure 5).

Wettability Measurements

The hydrophobic effect is generated only by the BW treatment, the presence of HNT causing an increase in the contact angle by up to 10-15° (Figure 6). For all other treatments the presence of HNT caused a slight hydrophilic effect.

NMR MOUSE Measurements

The overall model of water hydration in collagenous tissues/materials involves the monomolecular layer in which the water molecules are H-bonded to the helical structures and several outer polymolecular layers which are considerably more mobile (Bella *et al*., 1995). The specific interaction between water and such structures has an important

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contribution to the stabilization of the investigated materials. The values of spin-spin (T2eff) and spin-lattice (T1) relaxation times obtained for the investigated leathers and listed in Table 2 show a significant difference between untreated and treated samples.

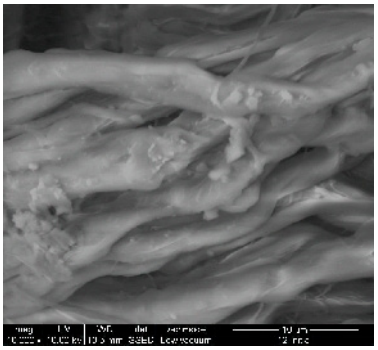

Figure 4. High magnification SEM showing the typical morphology of intact fibre network - untreated leather sample

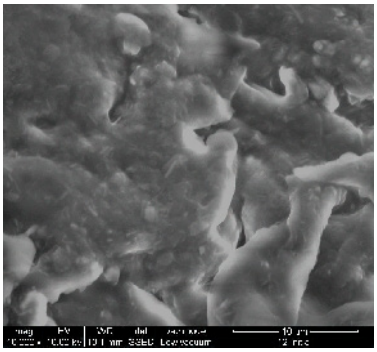

Figure 5. High magnification SEM showing the presence of HNTs on the grain surface of CM_Bw_HNT sample

T_1 values increase suggesting that the degree of ordering of water in all treated samples decreases. On the other part, $T_{2\text{eff-long}}$ clearly differentiates between the samples treated with urea (CM_Ur_HNT) and keratin hydrolysate (CM_Ke_HNT) and that treated with PEG (CM_PEG_HNT), suggesting a destabilising effect of the latter.

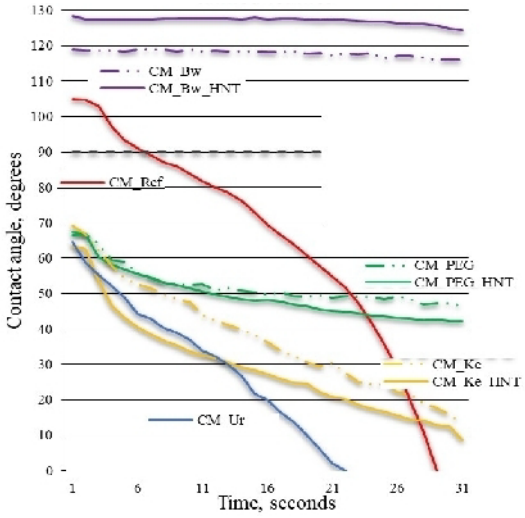

Figure 6. The variation of contact angle value on time depending for all types of treatments

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Table 2. Values of spin-lattice relaxation time T_1, and spin-spin relaxation times T_{2eff_long} and T_{2eff_short} in untreated and treated leathers

Sample/ Treatment	Spin-lattice relaxation time, T_1	Spin-spin relaxation time, T_{2eff}	
	T_1 (ms)	T_{2long} (ms)	T_{2short} (ms)
CM_Ref	34.5	2.71	0.01
CM_Ur_HNT	37.9	2.27	0.01
CM_PEG_HNT	37.2	4.56	0.01
CM_Ke_HNT	37.3	2.45	0.01

CONCLUSIONS

The main conclusions can be summarized as follows:

- All treatments result in an increase in thermal stability at the macroscopic level, while at the microscopic level there is an increase in the degree of heterogeneity.
- The rehydrating effect increases in the order of PEG_HNT <Ke_HNT <Ur_HNT
- The hydrophobic effect is generated only by BW_HNT treatment.

Acknowledgments

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