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Original article

The solution to an unresolved problem: Newly synthesised nanocollagen for the preservation of leather

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ABSTRACT

A widespread problem in libraries is related to the preservation of book covers in leather that are often torn, powdery and abraded. The same problem is encountered in the conservation of leather goods. Until now a satisfactory solution to contrast the leather deterioration had not been found and the applied conservation methods offered only temporary solutions, without guaranteeing a real and durable effectiveness. At the Istituto centrale restauro e conservazione patrimonio archivistico e librario (Icrcpal) it was decided to research more durable results and to apply nanocollagen solutions to the leather. A new synthesis of nanocollagen was performed in collaboration with Università Tor Vergata, and Fondazione INUIT and the newly synthesised nanocollagen was characterised by different spectroscopic and imaging techniques, then applied to laboratory samples and, at the end of the research, it was used in the restoration of the leather cover of a 18th book. All the measurements performed on the tested leathers did not show any colour change after nanocollagen application, an increase of all mechanical characteristics and, of paramount importance, an increase in the shrinkage temperature of the leather with a partial reconstitution of its lost elasticity and flexibility.

1. Introduction

The preservation of torn, powdery, lacunose, worn, abraded, weak and friable book-covers in leather is a real problem for library conservators. These kinds of deterioration are linked to the ageing, the usage and manipulation of the books, the interactions with pollutants, but they are also connected with the products used in the leather manufacture or in the finishing treatments applied for special or decorative purposes.

Moreover, the choice of the materials for the covers was very often more related to their price than to their durability and permanence. Sheep leather, a less durable and stable material in respect to calf or goat leathers, is one of the most widespread materials in the history of bookbinding, especially from 17th century, due to its lower market price.

When a cover book is severely deteriorated, a normal manipulation of the book is almost impossible, without causing the detachment of small fragments or "dust" of leather from the binding, and a restoring treatment is needed.

At present no satisfactory and durable solutions to contrast the leather deterioration have been found, but it is possible to apply environmental control strategies and preventive conservation practices [1]. If environmental control is always advisable, the preventive conservation is rather applicable to museum objects than to artifacts that should be consulted and used, such as books.

Since the 1970s of the last century hydroxypropylcellulose [2] was frequently used for the consolidation of leather. More recently a mixture of waxes and acrylic resin (SC 6000) was proposed and used alone or in mixture with hydroxypropylcellulose [3].

None of these products had the capability to penetrate into the bulk of the leather that after the treatment often showed color changes and increased brittleness.

The challenge has always been the recovery of flexibility and stability of the degraded leather, without altering the appearance and the equilibrium of the internal fats and moisture.

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2. Aim

The Istituto centrale restauro e conservazione patrimonio archivistico e librario (Icrcpal) decided, in collaboration with the Fondazione INUIT, to approach the problem in a different way by using nanomaterials expressly designed for the conservation of leather. Nanomaterials can, in fact, penetrate into the bulk of the treated material, offering a deeper consolidation effect. The idea was to treat the leather with its same principal component, the collagen, synthesised at nanoscale dimension and, after a series of laboratory experiments, to apply it in a real restoration case study.

A promising preliminary investigation was performed in 2014 [4,5], but not implemented. Recently a new electrochemical synthesis was optimised and patented (Patent N. 102016000096336, 2016) obtaining a nanocollagen with enhanced dispersibility in different working media and long-term stability of the colloidal phase dispersion (over 1 year, at ambient temperature, without precipitation of a solid phase).

To assess the final application procedures, the effect on leather of the newly synthesised nanocollagen, soluble both in isopropyl alcohol and in water, was studied by optical measurements, chemical and mechanical tests. Moreover different nanocollagen concentrations and solvents were tested on laboratory samples, to determine the minimal amount of product to be applied to the leather with the best consolidation results.

After a preliminary study, an original book was chosen for the real application.

3. Experimental

3.1. Materials

3.1.1. Reagents for the synthesis of nanocollagen

Bovine Collagen Type I (Sigma-Aldrich) was used as molecular precursor for the synthesis of nanocollagen, performed in acetate buffer aqueous solution 0.1 M, pH 4.7, (Sigma-Aldrich). Alumina/Al_2O_3 tracked etched template membranes (Whatman® Anodisc Inorganic Membranes) were used (membrane diameter 30 mm, pores diameter 200 nm, pores length 100 μm, pores density 1×10^{12} pores/cm^2), as well as HNO_3 and NaOH (Sigma-Aldrich, analytical grade).

3.1.2. Laboratory leathers

In the preliminary tests, the vegetable tanned calfskin leather (mean thickness 1.6 mm) of a 18th century cover, contemporary with the original volume, was used. For further tests a calfskin grain split leather (chrome tanned, coloured with soluble aniline dyes, mean thickness 0.66 mm) was employed, because it showed mechanical characteristics similar to those of the original cover.

3.1.3. Original cover

The Estro Poetico Armonico by Benedetto Marcello (Mus. 243, 18th century, Biblioteca Casanatense, Roma) was a perfect case study, presenting all the damages described in the introduction. It belongs to a series of five books with the same binding (first edition in folio, Venezia, 1724–26), thus allowing for a comparison with other original specimens, after the treatment. The cover of Mus. 243 (mean thickness 0.60 mm), a vegetable sheepskin leather, tanned with hydrolysable tannins, after the manufacture was mottled with an acidic solution.

3.1.4. Tanning detection

The tanning was detected by specific spot tests: ferric chloride for vegetable tannins, rhodanine for hydrolysable tannins, acid butanol for condensed tannins, alizarin sulphonate for aluminium detection [6–8].

3.2. Methods

3.2.1. Electrochemical synthesis of nanocollagen

ChronoAmperometry was the electrochemical techniques applied for the synthesis of nanocollagen. The optimised parameters were patented in 2016 (Patent N. 102016000096336, 2016) and are briefly discussed below.

The tropocollagen precursor was used at concentration 1 mM in 0.1 M acetate buffer solution at pH 4.7. To assemble the Alumina Template Working Electrodes (ATWEs), it was necessary to make the Al_2O_3 membrane conductive. An Ag layer (20 nm thickness) was then deposited by sputtering for 2 min at 2 mA. During the electrochemical synthesis, a constant and controlled working potential value of −1.0 V/versus Ag/AgCl/Cl–reference electrode was applied by ChronoAmperometry with deposition time 3600s under N_2 at flow rate of 0.3 cm^3/min. During the ChronoAmperometry deposition, the electrolysis solution was magnetically stirred, at ambient temperature. After the electrochemical synthesis of nanocollagen, the silver conductive layer was dissolved in concentrated HNO3 and the alumina template membrane was removed with concentrated NaOH solution unable to dissolve the nanocollagen that was rinsed in water until neutrality.

3.2.2. TEM (Transmission electron Microscopy)

TEM Philips Electron Optics 301 was employed for the morphological study of nanocollagen samples prepared by coating Cu grids (φ = 3 mm), by deep coating in 0.7 mg/ml of nanocollagen dispersion. After immersion, the coated Cu grids were dried under Wood lamp.

3.2.3. SEM (Scanning Electron Microscopy)

For the morphological characterisation of nanocollagen a FE-SEM/EDX, LEO 1550 equipped with a sputter coater (Edwards Scan Coat K550X) was used. A volume of 5 μL of the nanocollagen dispersion was deposited on Si (111), allowing the solvent to evaporate at room temperature, and then fixed on aluminium stub with carbon tape. The samples were then coated with Au layer (thickness 10–20 nm), deposited by sputtering for 2 min at 25 mA.

For the studies on the application of nanocollagen to leather, the SEM analyses were performed with a Carl-Zeiss EVO 50 instrument equipped with both a detector for electron-backscattered diffraction (BSD) and for Secondary Electron scanning in Variable Pressure mode (VPSE). SEM observations were performed at 20 kV accelerating voltage with a tungsten filament. All the samples were mounted on Al stubs and observed at different magnification ranging from 500× to 3000×, following a fixed measurement grid, before and after the treatment with nanocollagen, which was applied on the sample directly in the SEM chamber, in order to repeat the observations after the consolidation, exactly at the same point observed before the treatment. It was possible to perform the analyses also on some original fragments spontaneously detached from the binding and no more repositionable.

3.2.4. FT-IR (Fourier Transform-Infrared Spectroscopy)

IR spectra for the nanocollagen structural characterisation were recorded by a Perkin-Elmer Spectrum One FT-IR spectrometer from KBr pellets in N2 environment.

3.2.5. Colour coordinates

A Minolta Chroma Meter CR22 colorimeter was used in the CIE L* a* b* space, averaging 3 measurement for each analysed point.

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