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Inhalt

Comparative study between four consolidation systems suitable for archaeological bone artefacts

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Abstract

This study started with the restoration of a 14th century Italian crosier during the final Master year project at the *Institute National du Patrimone* in Paris (Palazzo 2014). The characterization and consolidation of the bone materials constituting the crosier was needed due to its poor state of conservation.

Several products, both organic polymers and inorganic consolidants applied on artificially altered bone material underwent scientific investigations consisting of several analyses and mechanical tests in order to choose the most suitable for the restoration intervention.

The results thus obtained showed that both nanolime and a mix of Paraloid® and calcium phosphate seem to be adequate for treating such objects.

1 Introduction

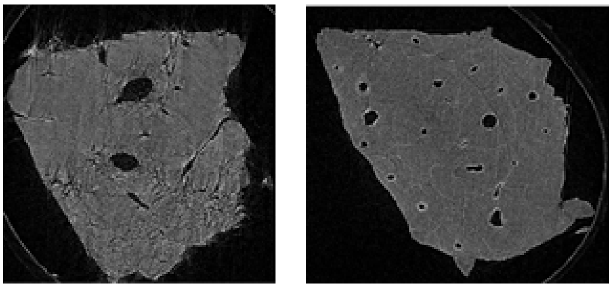
This study begins with the necessary restoration of the crosier of Hardouin de Bueil (fig. 1), bishop of Angers (Pays de la Loire) from 1374 until his death on 1439. The object was discovered as several fragments in his tomb at the end of the 19th century (De Farcy 1899).

The crosier is typical of 14th century Italian production. The carved fragments represent the Lamb fighting a snake, a scene originating in Arabo-Sicilian tradition (Cott 1939, Antoine 2012). About twenty similar examples of this type of crosier were found in Italy, notably Perugia, Siena and Bologna (Palazzo 2014).

These crosiers are "characterised by an exhuberant decoration and they are in the logical filiation of Arabo-Sicilian crosiers of the 12th and 13th centuries, having kept the colour highlights and gilding" (Gaborit-Chopin 1978).

In 2010 several non-invasive analyses were performed on the crosier. The chemical composition was studied using the external micro-PIXE set-up of the AGLAE accelerator at the Centre de recherche et de restauration des musées de France (C2RMF) and the micro-morphology by micro-tomography at the BAM*line* of the synchrotron BESSY II (Helmholtz-Zentrum für Materialien und Energie Berlin). This allowed identifying the nature of the osseous material, the state of conservation of the crosier, and traces of polychromy. MicroCT showed by the characteristic micro-morphological features that the crosier is made of bone and not as previously postulated of ivory (fig. 2). The Hardouin de Bueil's crosier also showed a severe decay condition as can be seen on the virtual microCT sections. The bone material was fragile, quite cracked and altered in colour (fig. 3). According to the shapes and dimensions of the crosier elements, the bones were then identified as bovine metatarsi.

Figure 1: "Crosier of the tomb of Hardouin de Bueil" kept in the St. Anne's chapel of the St. Maurice cathedral of Angers dating from the 15th c. (inv. no. 58, 36.5 x 15.7 x 3 cm^3). © C2RMF, D. Bagault.



Figures 2: Virtual cross-sections of two fragments of the crosier obtained by microCT. The size of the Haversian canals is comprised between 20 and 100 microns.

Bone is classified as biological nanocomposite consisting of poorly crystalline hydroxyapatite bonded by a collagen matrix (Lowenstam & Weiner 1989, Currey 2002).

Some samples collected from erratic fragments underwent FTIR analysis. The spectra highlighted the low concentration of collagen identified by a weak 1634 cm^{-1} peak. The intensity of the IR absorption band allowed the evaluation of the collagen content in the crosier ranging from 4 to 6%, much lower than in fresh bovine bone, which is around 20%.

Depending on environmental conditions the main alteration phenomena occurring on bone materials are related to the loss of collagen. Moreover a part of the original poorly carbonated hydroxyapatite crystals can be converted into calcite and well crystalline apatite, leading to tensions within the material creating to micro or macro cracks (Reiche 2000).

Using microPIXE, the following polychromy was referred from the elemental composition of the surface of the crosier: vermilion (HgS), gold (Au) and carbon black (C, confirmed by its colour and the absence of other characteristic chemical elements as Mn). On the Lamb's wool were found in the mordant traces of green with high contents of Cu (0,25%), Pb (2–3%) and S (6–9,5%). Presence of Cu was also detected on a similar crosier kept at the Louvre (Inv. no. OA12319) (Antoine 2012, Le Hô 2011). This Cu component could be characteristic of gilding materials found on other medieval Italian bone crosiers.

The state of conservation of the crosier was so poor that a restoration was needed. Particular attention was payed to the consolidation of bone materials, as these fragments are the essential part of the artefact, and to the preservation of the traces of polychromy. According to our best knowledge there is no systematic consolidation procedure of such fragile bone objects. Therefore the aim of this work was to study consolidating materials suitable for archaeological bone materials. This was particularly challenging as the object was brittle and finely carved. There was a need to use an agent able to re-establish hardness and mechanical properties to the bones without introducing any colour modification neither new tension. In order to obtain such results the material has to penetrate easily and deeply within the bone porosity and has to be stable with respect to all environmental factors, i.e. temperature, humidity, biological decay factors, UV radiation. Moreover the solvent to be used for the consolidant has to be compatible with the original material. In this study several available solutions ranging from organic synthetic polymers to nanolime were compared. Then, the best proven material tested on bone model samples was used for the consolidation of the crosier. These model samples were also artificially aged.

2 Materials and Methods

2.1 Material

According to the previous considerations and to a literature review some widely used consolidants were selected for our tests:

- **PARALOID B72®** is a copolymer of ethyl-metacrilate and methyl acrilate. It is one of the most common restoration products and it can be used in Solvanol® (40% isopropanol, 60% ethanol). This solution is neither dangerous for the hydroxyapatite nor the restorer. In this work Paraloid® was used in a 10% concentration by weight. This concentration is a good compromise between consolidating action and viscosity.
- The same 10% **PARALOID B72®** solution in Solvanol® was used with an addition of a chemically pure **calcium phosphate** ground at 20 µm, with a twofold purpose: on one hand the presence of a mineral aggregate reduces the shrinkage due to solvent evaporation; on the other hand the hardness of the composite is higher than that of simple Paraloid B72®.
- **MOWITAL B60HH®** is a Polyvinyl butyral (PVB) traditionally used for archaeoloegical bone and ceramic consolidation. It offers quite good flexibility and resistance. Unfortunately it often leads to colour modification, which is not acceptable in such a case. Nevertheless it was included in our tests due to its widespread use. It was used in a 10% isopropanol solution.
- **NANORESTORE®** is a commercial nanolime 5% by weight dispersion in ethanol, recently proposed for consolidation of archaeological bone materials (Dei et.al 2014). As shown in a recent study, even if

Figure 3: Details of the degradation of Hardouin de Bueil's crosier

Figure 4: Samples of cow metatarsi boiled, cut and heated at high temperature

brittleness of archaeological bone is strictly related to the loss of collagen, the loss of mechanical properties is related to mineral loss also, as elasticity of bone depends on calcium content and porosity (Currey 1990). According to such studies it is possible to use the nanolime for its good compatibility with hydroxyapatite. Particularly in the case of this crosier, the very low content of collagen suggests that high pH associated with nanolime will not cause severe problems to the object.

– **CALOSIL**® is another commercial nanolime 1.5% dispersion in ethanol.

2.2 Bone test sample preparation

Bovine metatarsi were used in order to realize model samples as close as possible to the original object. Samples underwent several treatments. At first they were boiled in water for two hours and all flesh remains have been cleaned off. Boiled and cleaned bovine metatarsi were then cut in 3×3×2 cm^3 samples. These samples were heated at high temperature in order to reduce the collagen content (Reiche et al. 2000, Reiche 2010). All the samples were then heated in a muffle oven at 580 °C for 5 hours in order to significantly reduce the collagen content without affecting the colour. Heating time and temperature were chosen after several preliminary tests. Aged samples became brittle and white, consisting of hydroxyapatite with a very low collagen content, as revealed by FTIR analysis (fig. 5).

Under the microscope it is possible to observe the presence of a network of shrinkage cracks and a dusty surface (fig. 6).

Helium picnometry, performed by means of a Pycnomatic ATC della Thermo Electron Corporation, reveals that the density of aged samples is very close to that of pure hydroxyapatite, confirming a very low content, or absence, of collagen. A similar result has been obtained on a sample taken from the crosier.

According to such results the use of nanolime can be considered for use since its high pH cannot remove more collagen.

2.3 Experimental consolidation tests and artificially aging procedure

All consolidants were applied with a brush. The number of applications and preliminary observations are reported in table 1. Optical and electron microscopy observation were also made to observe the effects of the treatments applied.

Then, the samples were treated following an ageing procedure consisting of two steps: the first one was a three week exposure to a 765W/m^2 illumination power at 50 °C in ATLAS SUNTEST XLS equipment; in the second step the samples were kept for three weeks alternatively at 20 °C and 50% R.H. or 45 °C and 85% R.H. for 24 hours in a BLINDER KBF 240 apparatus.

2.4 Evaluation of the treatment efficiency

A mechanical test was is required to verify the effectiveness of consolidation. A standard compression test appeared to be inadequate. In this test, the whole section is stressed, whereas the principle purpose of such a consolidation is to increase the surface hardness. According to these considerations, an ad hoc penetrometer was realized, designed in order to allow a hardness test similar to that of Vickers. As shown in figure 7, the penetrometer

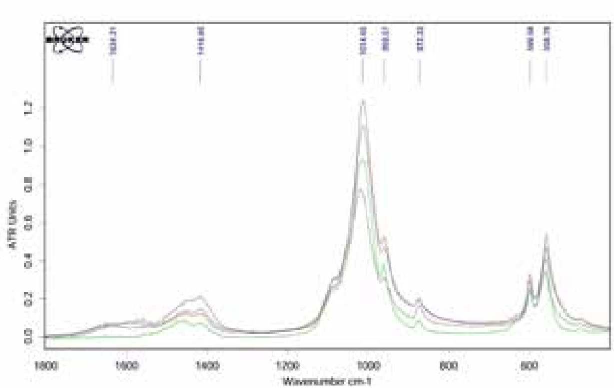


Figure 5: The spectra highlights the presence of collagen identified by the 1634 cm^{-1} peak in very low concentration

Figure 6: Shrinkage cracks and dusty surface of one of the heated bone samples

Table 1: Consolidant, number of applications and preliminary observations

Consolidant	Solvant	Concentration		Number of applications		Preliminary observations
PARALOÏD B72®	Solvanol	5%	10%	2		penetrate easily
PARALOÏD B72® + 2% PHOSPHATE DE CALCIUM	Solvanol	5%	10%	2		penetrate easily
MOWITAL B60HH®	Isopropanol	5%	10%	3		viscous, penetrate hardly
NANORESTORE®	Isopropanol	0,5%		10	20	penetrate easily, application long
CALOSIL®	Éthanol	1,5%	3%	2		penetrate easily, milky aspect, whitening of the surface

consists of a pyramidal brass pin moving in a rail at the centre of a table-like structure.

The load was applied on the samples by means of a ZWICK ROELL Z005 universal testing machine equipped with a 5 kN load cell. All the samples underwent the test with a pre-fixed maximum load of 40 N.

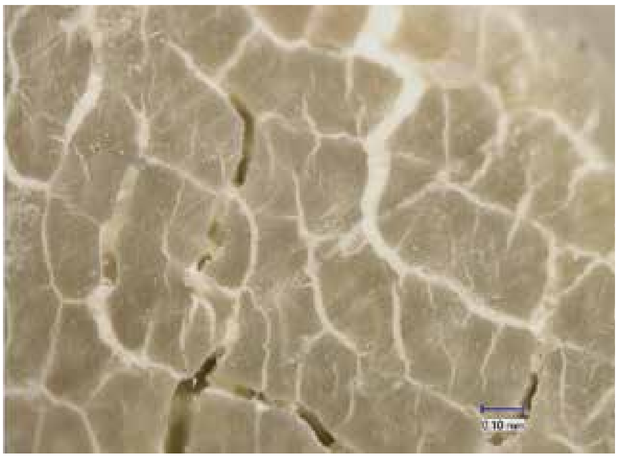
Digital optical (Keyence microscope) and environmental scanning electron microscopy (ESEM Quanta 200, Fei) were used at the Rathgen-Forschungslabor to observe the penetration of the consolidants into the test samples.

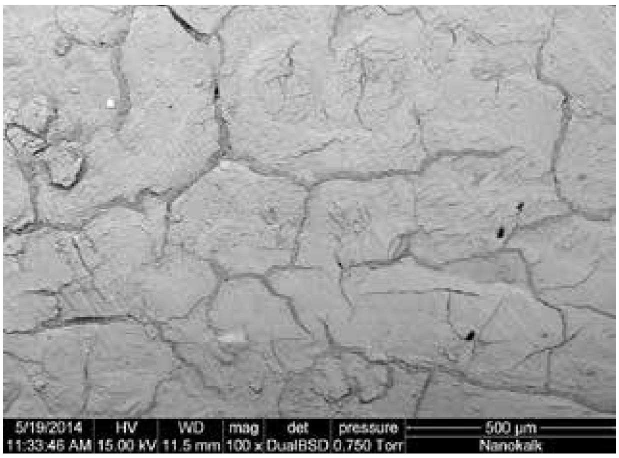
3 Results and Discussion

According to preliminary observation Calosil® causes a slight but evident whitening of the surface. Nevertheless it was not excluded by further tests.

Optical and electron microscopy observation confirm that nanolime is able to penetrate in the small cracks on the surface, filling them with calcite. Nanorestore® was very effective in filling all the cracks as shown in figures 8–9. Moreover high magnification ESEM image shows that nanolime has penetrated even into the smaller cracks (fig. 10).

Figure 7: Mechanical test by ZWICK ROELL Z005 and penetrometer





Figures 8–9: Optical (left) and electron microscopy (right) observation: nanolime has penetrated in the small cracks filling them with calcite

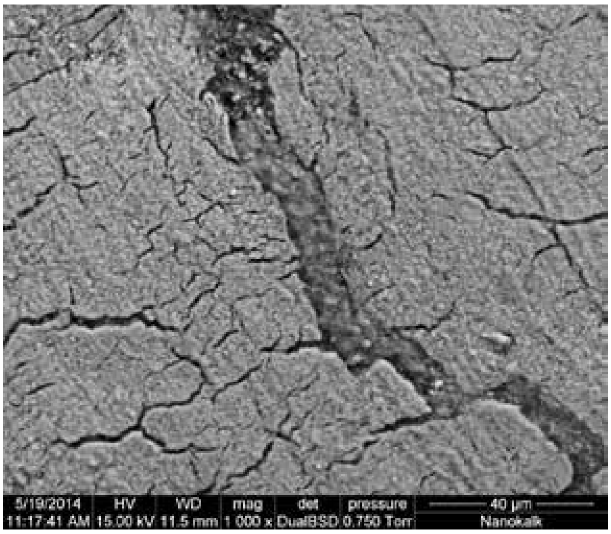


Figure 10: High magnification SEM image shows that nanolime has penetrated even in the smaller cracks

Figure 11: Bone samples treated with Mowital B60HH® show a clear yellowing

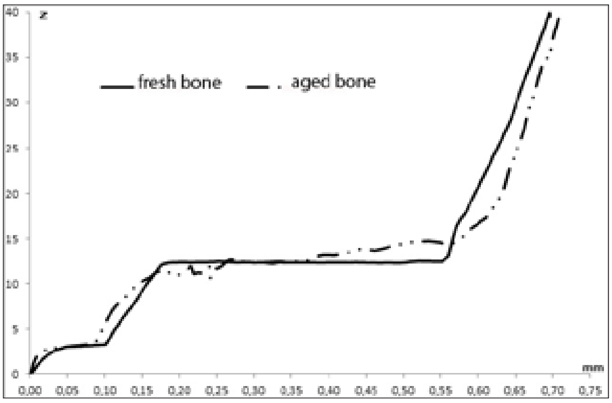
On the contrary, Paraloïd B72® with or without calcium phosphate and Mowital B60HH do not fill the cracks.

At the end of the ageing treatment, the samples treated with Mowital B60HH® showed a clear yellowing (fig. 11), which is not acceptable for the treatment of real bone artefacts. According to this observation Mowital samples were excluded for further tests.

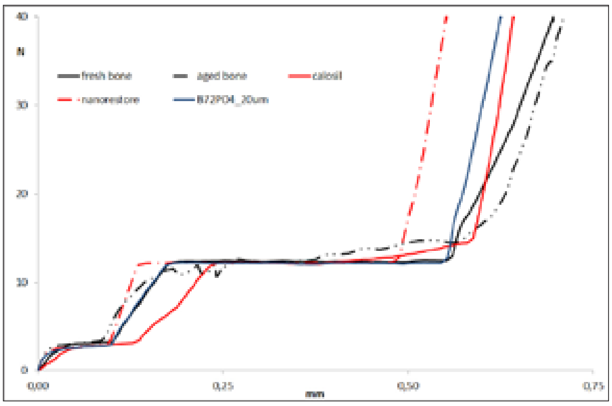
Regarding the mechanical test, the preliminary test had shown a fragile collapse of all samples at around 60N. Fresh bone can resist at quite higher loads.

As a first point, the test was performed on both a fresh bovine bone and an aged one (fig. 12). It can be observed that load grows with displacement in several steps. This pattern is explained as at the first point the pin penetrates in the tissue moving the hydroxyapatite crystals, going deeper the crystals become more compact and load increases quickly. The only notable difference at this low load level is that the aged samples have an irregular pattern, probably due to the lack of collagen, leading to small failure of single hydroxyapatite crystals until a good compactness is achieved.

Comparing the behaviour of fresh and aged bone with the consolidated samples (fig. 13), it can be easily noted that Paraloid® with calcium phosphate filler brings the aged sample back to the behaviour of fresh bone reference. Nanolime consolidation offers very good results also, as the samples show very similar patterns to fresh one, with regular linear variation of load with displacement. Calosil treatment increases the hardness of samples, but the pattern is still irregular indicating a non-uniform consolidation.



Figures 12: Mechanical test of fresh bovine bone compared with an aged one



Figures 13: Mechanical test comparing the behavior of fresh and aged bone with the consolidated samples

As a final consideration, both nanolime and Paraloid® filled with calcium phosphate offer acceptable results in terms of consolidation. The first leads to a higher stiffness, the latter to fresh bone-like properties.

In both cases the treatment stays only near the surface, as indicated by the fact that all samples failed at very low loads, around 60N, whereas fresh bone can resist to quite higher loads.

4 Conclusions

In this study several products proposed as consolidants for archeological bone artefacts were tested on altered model bone samples. The treated bone samples were artificially aged analysed and submitted to mechanical tests in order to choose the best suitable restoration method for the consolidation of the 14th century Hardouin de Bueil's crosier.

The non-invasive characterisation of the artefact revealed the nature of the crosier, the poor conservation state of all the bone fragments and traces of polychromy. The poor conservation state made a restoration intervention necessary, particularly a consolidation. As there is no systematic consolidation procedure for fragile carved archaeological bone objects to our best knowledge, this restoration and the choice of the consolidation agents were very challenging.

Mowital is a polymer of widespread use in archaeological field but it was excluded in our study as it showed a severe yellowing after weathering procedures. Paraloid®

B72 showed better results in terms of stability against weathering processes and offered a very good consolidation of aged bone samples.

Two different commercial nanolimes ethanol dispersion have also been tested. Nanorestore® offered better results than Calosil®, particularly less whitening and slightly better mechanical results according to our established test.

According to these results the restoration intervention of the 14th century crosier was performed using both Nanorestore© and Paraloid® B72 filled with calcium phosphate. The first one was used in the powdery parts as Nanorestore© can effectively fill microscopic cracks bonding the smaller fragments together. Paraloid® B72, which shows a higher flexibility than nanolime, was used in the most decayed parts, where the cracks were larger or where pieces had fallen.

The main inconvenience of the use of nanolimes is the number of applications required, which implies a long intervention. In spite of this, our consolidation experiments using nanolimes ethanol dispersion showed its efficiency on the fragments of the crosier. This could represent a potential procedure for the treatment of archeological bones with low collagen level.

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