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Study and Use of Organic and Inorganic Nanostructured Consolidants in the Conservation and Treatment of Archaeological Burial Textiles

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Abstract

The archaeological artifact examined in this paper is a rare example of an infant's garment (perhaps from the 16th–17th centuries) unearthed in a subterranean area behind the altar in the Medici Chapels in Florence in the burial chamber of the Grand Duke, Gian Gastone de Medici. Over time, this composite artifact, principally in silk and metal thread, has undergone extensive deterioration (natural degradation of the fibres as well as aging caused by use, the decay of the corpse, and attack from microorganisms and animals) in addition to suffering the effects of the 1966 flood in Florence. The current conditions are characterized by extensive material decay, making the handling of the artifact impossible. The objective of our work was to research and develop an alternative method for cleaning and consolidating the textile. Two different consolidating agents were identified: an organic consolidant (chitosan) and a hybrid inorganic–organic nanostructured consolidant. These were tested separately; they were applied to samples using immersion, an ultrasonic bath, and spray coating. Both consolidants increased fibre stability and mechanical elasticity and resistance without altering the hand and colour of the fabric or creating a visible film on its surface.

Titre et Résumé

Étude et utilisation d'agents de consolidation nanostructurés organiques et inorganiques dans la restauration et le traitement de tissus funéraires archéologiques

L'objet archéologique étudié dans le cadre des travaux faisant l'objet du présent article constitue un exemple rare de vêtement de nourrisson (qui date probablement du XVIe ou du XVIIe siècle) qui a été découvert dans une zone souterraine, derrière l'autel de la chapelle Médicis de Florence, dans la chambre funéraire du Grand-Duc, Gian Gastone de Medici. Au fil du temps, cet objet composite, principalement constitué de soie et de fil métallique, a subi une importante détérioration (la dégradation naturelle des fibres ainsi que le vieillissement causé par l'utilisation, la décomposition du corps et les attaques de microorganismes et de divers animaux), en plus des effets de l'inondation de Florence, en 1966. L'état actuel de l'objet se caractérise par une décomposition considérable des matériaux, ce qui rend sa manipulation impossible. Nos travaux de recherche avaient aussi pour objectif de mettre au point une autre méthode de nettoyage et de consolidation du tissu. Deux agents de consolidation distincts ont d'abord été identifiés, soit un produit organique (le chitosane) et un agent de consolidation nanostructuré hybride inorganique-organique. Ils ont été appliqués sur des échantillons par immersion dans une solution, dans un bain à ultrasons et par revêtement par pulvérisation, et mis à l'essai séparément. Les deux agents de consolidation étudiés permettent d'accroître la

stabilité des fibres ainsi que leur résistance et leur limite d'élasticité mécaniques, et ce, sans entraîner une altération de la couleur ou de la main du tissu et sans former une pellicule visible à sa surface.

Introduction

The discovery of the subterranean chamber containing the remains of the last Medici Grand Duke (1671-1737) and those of eight children (16^{th}-17^{th} centuries) was probably the most unexpected discovery during the first phase of Progetto Medici in 2004 in terms of anatomical pathology and history of medicine (Fornaciari 2008).[1] In 1966, the devastating floods in Florence also affected environmental conditions within the chamber and contributed to the traumatic condition of the artifacts and the remains contained therein (see Figure 1). This chamber was characterized by high relative humidity (RH) and temperatures.

Figure 1. Detail of box n. 29 inside the burial chamber.
The conspicuous deposits of mud can be seen throughout.

Unfortunately, the chamber was opened without adequate preliminary planning. The reduction in humidity due to the sudden opening of the site triggered various chemical and physical processes. After this, the Restoration Laboratories at the Opificio delle Pietre Dure in Florence (OPD) was asked to become involved in the project. OPD carried out preventive conservation and non-invasive and micro-invasive analyses on the remains of Gian Gastone and on one of the children (probably Don Filippino, 1577-1582). The OPD did a controlled and gradual drying of the damp fabric for the garment from box n. 29. This was a critical but inevitable operation, which would permit experimentation with new methods for cleaning and consolidating textiles.

Description, Condition, Analysis and Preliminary Treatments

The textile studied for cleaning and consolidation was a small garment, taken from box n. 29 belonging to one of the eight Medici family children (see Figure 2).

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Figure 2. Garment after opening the box n. 29 and removing some bones.

The child in question was about nine months old and the artifact is a rare example of a silk garment with silver trim on the sleeves (see Table 1). The research project was based on the study of the constituent materials and pollutants, investigation into an innovative method of cleaning and consolidation and planning for a method for future controlled-environment storage. The analyses (Bracaloni 2009; Tosini 2009) carried out on the fibres and threads of the artifact established:

1. the garment was made almost entirely from degummed silk (Bombyx mori), characterized by a very low viscosity (0.06 dl/g) indicating a high level of depolymerization (see Table 2);
2. 2. the trim was made from silver strips, which had partially transformed to silver chloride and sulphide, wrapped around a markedly degraded silk core;
3. various organic and inorganic materials were present as deposits, including fats, proteins, amino substances, silicates, oxides and carbonates;
4. the mud consisted principally in a clay matrix, silica, alkaline nitrates and alkaline earths with a prevalence of ammonium nitrate;
5. the presence of lead, iron, aluminium and copper compounds;
6. the presence of sodium nitrate, cellulose derivatives and ethylene glycol, the latter, presumably from refrigerant seeped from cars and refrigerators during the 1966 flood, was found during the cleaning tests in the solubilized materials using water and alcohol extraction.

Table 1. General data on the infant's garment

Type	**Material**	**Weave/ Technique**	**Colour**	**Weft average thread/cm Twist**	**Warp average thread/cm Twist**	**Thread count thread/cm^2**	**Dimensions**
Infant's garment	Silk (Bombyx Mori)	Taffeta	Beige	2 yarns slight "S" twist 72 threads/cm	x-yarns without apparent twist (W.A.T.) 59 warp/cm	4.248	30 x 50 cm
Metal trim (lower sleeve)	Silver strip "S" twist over silk core	Bobbin-lace	Beige core 2 silk yarns	-	-	-	2 cm high and 16 cm long
Ribbons	Silk	Taffeta	Beige	2 yarns slight "S" twist	x-yarns W.A.T.	-	1.5 cm

Table 2. Average values for the intrinsic viscosity of silk.

Type of silk	**Intrinsic Viscosity Value [η] dl/g (average values)**
New silk	$0.7 < [\eta] < 0.5$
Degraded silk	< 0.3
Ancient silk – very highly depolymerized	< 0.1
Silk from fabric n. 29	0.06

The main material in the small garment, the silk, was permeated by a conspicuous presence of mud, which now acts as a support armature. In terms of conservation, the mud constitutes one of the main factors in the degradation with other deterioration phenomena (type of object, its use, the decomposition of the corpse, microorganisms and animals) (see Figure 3).

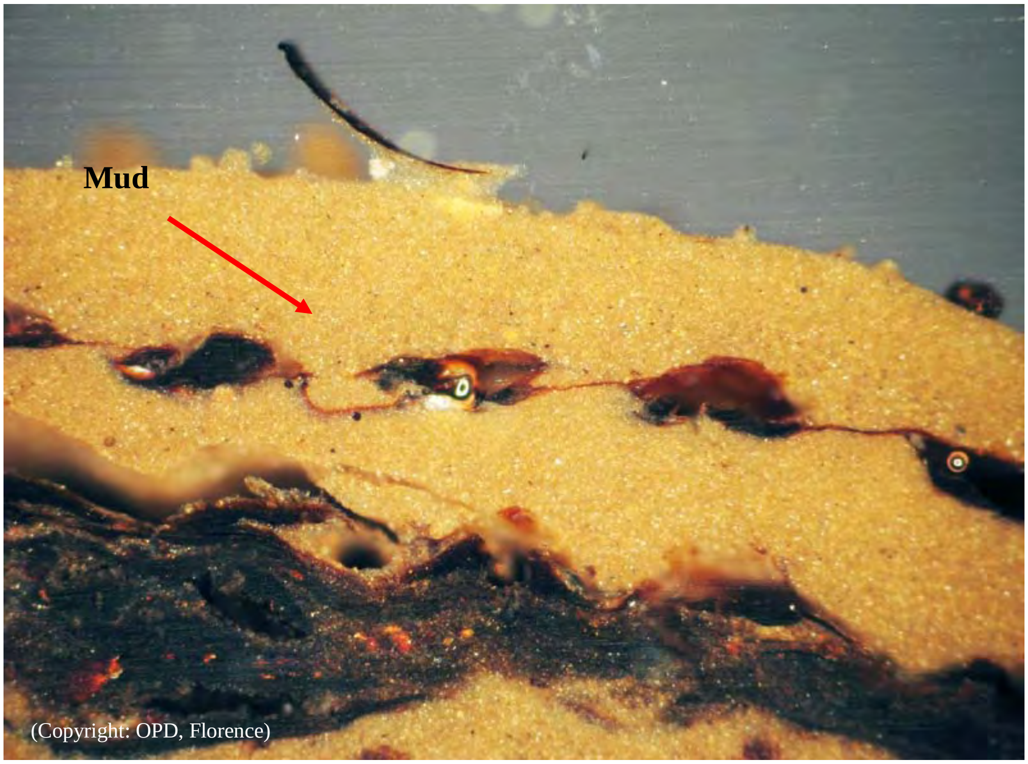

Figure 3. Cross section of a textile fragment taken from the Gian Gastone's burial garment; the mud deposited in the structure of the fabric is clearly visible.

After the preliminary cleaning tests carried out on tiny fragments of the garment that could no longer be reattached, we decided to gradually bring the working environment RH to 55-60% at room temperature in order to carry out an initial removal of the surface mud using a micro-suction apparatus (Conti 1996) and, where the conditions of the silk allowed, an ultrasonic dry ablation (see Figure 4).

As a result of these cleaning tests, we subsequently found that:

- it would be necessary to perform a series of successive humidification phases in order to gradually increase the RH, and to prepare the textile fragments for the subsequent cleaning phase;
- later, it would be necessary to immerse the fragments in an ultrasonic bath with a solution made up of 80% distilled water; 10% ethyl alcohol; 10% acetone at a pH c.5 in order to remove and eliminate the mud and diminish application time of bath;
- the rinsing phase would be done in an ultrasonic bath with continuously recycled distilled water to remove as many foreign materials as possible from the textile along with the residues of the water-alcohol-acetone solution;

- these steps would need to be carried out in succession without moving the artifact while keeping it in the same container equipped with a duct system allowing for the inflow and outflow of various liquids and dirt. This system would ensure that the textile would be constantly immersed, thus avoiding any alterations as the liquids are drained;
- consolidation must follow the rinsing without a drying phase in order to minimize mechanical tensions associated with wet-dry-wet treatments. The fragment would stay immersed in distilled water between these two phases, and the water would gradually substituted with the consolidating solution until the required concentration is reached.
- based on the type of textile fabric and its condition, in general, consolidation could take place before or after the cleaning phase and it could be structural (fabric) and/or material (fibres). In our case, it was unthinkable to carry out a structural consolidation without first consolidating the materials.

Bibliographic research found that artificial and synthetic consolidants such as acrylic resins, fluorides, amides and cellulose ethers have been used in almost all cases to date dealing with consolidation of archaeological textile material. These categories of consolidants are highly invasive, are difficult to apply using the methods described above and, in some cases, lead to changes in mechanical and aesthetic properties of the fabric (Stauffer 2005).

Figure 4. Full view of the work during treatment.
The result after the physical cleaning phase (micro-suction and ultrasonic dry ablation).

Selection of consolidant

For years our Laboratory has worked under the treatment criteria of "compatibility", "durability","retreatability" and minimally invasive as possible (Conti 2010). Minimal intervention in conservation is always a question of choice. An "under treated" approach would result in an ineffective treatment, just as "over treatment" would be excessive (Ciatti 2009). Consequently, in choosing the consolidants we were constantly guided by the principle of minimal invasiveness, the nature of the consolidant, the molecular size, the minimal concentration and the effectiveness of the treatment.

In collaboration with Istituto di Fisica Applicata (IFAC-CNR) of Florence and Stazione Sperimentale della Seta (SSS) of Milan we developed a study taking into consideration a natural polymer, chitosan, previously proposed for a variety of applications including textile dyeing (Davarpanah et al. 2009; Chairat 2009), and a nanostructured hybrid (inorganic-organic) sol-gel (Bescher 2000; Zarraga et al. 2002; Bescher and Mackenzie 2005; Carmona et al. 2009), in this case, consisting of a sol-gel silicon dioxide modified with polyethylene glycol (PEG) 1000. Based on their chemical nature and their interaction with the substrate, chitosan and nanostructured sol-gel satisfy the criteria of "compatibility","durability" and "retreatability".

Compatibility with substrate

In terms of the chitosan, it is a linear chain polysaccharide, which is derived as a weak acid-soluble material by deacetylation from chitin commonly found in the outer skeleton of crustaceans and in the cell walls of fungi (Muzzarelli et al.1986). Depending on the chemical nature of the substrate undergoing chitosan coating, different interactions can be produced at the host-guest interface. Chitosan can interact with apolar substrates by means of its polysaccharide backbone and can generate strong and durable hydrogen bonds with polar substrates (e.g. silk) thanks to its amino and hydroxyl groups. In addition, in the presence of negatively charged functionalities, the cationic nature of chitosan can be exploited for creating very stable and long-lived electrostatic interactions (Dutta et al 2004). In its crystalline form, chitosan is normally insoluble in aqueous solutions above pH 6.0-6.5, for any temperature treatment. However, in dilute acids (pH < 6), the protonated free amino groups of glucosamine facilitate solubility of the molecule.

In terms of the sol-gel of nanostructured silicon dioxide modified with PEG 1000, it represents a state of matter in between molecules and bulk structures usually characterized by a large surface area that affects their physical-chemical properties. The sol-gel technique is a promising method that can be used to better control the size and shape of particles (Sakka 1990). This involves the phase transition of a system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. The starting materials are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol–gel process, the precursor is subjected to a series of hydrolysis and polymerisation reactions to form a colloidal suspension, or a "sol." Over time the "sol" turns into "gel" due to condensation reactions between the nanoparticles. With further drying and/or heat-treatment the "gel" is converted into an inorganic product like a glass, polycrystalline powder, dry gel or coating thin films. Due to the low temperature needed to process sol-gel materials and to the porosity of the 3D network formed, the inorganic matrix can be functionalized by organic molecules, giving rise to a hybrid material. The sol-gel matrices can be applied as protective coatings on the surface of materials. In this case, the sol-gel synthesis was performed by hydrolysis of metal-organic precursor, Tetraethylorthosilicate (TEOS) in acid water (pH 4.5) modified with PEG 1000 (0.25M). The organic and inorganic components are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure and the use of organic components (glycols) can give an improved flexibility to the inorganic network. Properties of these materials are the sum of the individual contributions of both phases thus rendering this consolidant versatile and suitable for application on both inorganic and organic substrates (as in our case). An improvement in terms of adhesion at the interface can be achieved through the use of hybrid precursors containing chemical functional groups that could give rise to strong covalent bonds between the polymeric substrate and the silicon groups.

If we consider the molecular characteristics of the two consolidants in question, we see: depending on the source and preparation procedure, the molecular weight of chitosan may range from 100 to over 500 kDa with a degree of deacetylation from 30% to 95%; instead, the sol-gel is characterized by particles smaller than 50 nm. Consequently, the reduced dimensions of the consolidants facilitate penetration into the yarn structure, settling between the fibres in order to evenly stabilize the fabric without coating the surface and retaining mechanical flexibility. In fact, one of the most attractive properties of chitosan is that it can be moulded in the form of films and membranes with high mechanical strength and resistance to stress, good elasticity and high permeability for vapour and gases (Matteini et al. 2010). The innovative applications of nanostructures are based on changes in reactivity and mechanical properties due to the small physical dimensions and large surface area. Additionally, the small particle size results in improved mechanical properties, like wear resistance and higher materials density, all of which are desirable characteristics in ultra high-strength structural materials (Baglioni, Giorgi 2006).

For both these consolidants, the colour on the surfaces of the silk samples was unchanged at the concentrations that were employed because after the treatment they maintained good optical transparency (see Tables 3-4).

Stability over time

An attractive characteristic of chitosan is its antifungal and antibacterical activity (Rossomacha et al. 2003), which may impart resistance to consolidated silk over time. The occurrence of light-stimulated modifications to the composition of chitosan films, which may impair their optical (transparency) properties, were previously studied under natural and artificial aging (Sionkowska et al. 2004). The inorganic nature of the sol-gel coatings contributes to its stability over time/aging. And they can act as protective barrier against the principal sources of chemical/bacterial and physical attacks. Currently, studies on the ageing of nanostructure treated textiles are on-going at the SSS laboratories in Milan.

"Retreatability" and flexibility of the treatment

In general the total Removability of consolidants from an artifact is always a problem. This is also true for both consolidants used in this study and it is due to the chemical and physical structure of the fabric's fibres.

Our objective in this study is the *Retreatability* of the object after consolidation and for all the conservation treatments to be. It is important to know that these consolidants interact directly with the fibres and not with the fabric's surface. Because of this particular interaction at a fiber level they permit restorers to retreat the samples both for fisical (microsuction cleaning, structural consolidation…) and chemical (cleaning and material consolidation…) conservation treatments. Furthermore the two consolidants tested can be applied in many ways: spray, immersion, immersion in ultrasonic bath, and application at room temperature.

Treatments and Results

It should be kept in mind that due to the experimental nature of this work, research and study is still on-going. The necessity to consolidate a very deteriorated three-dimensional work directed the initial research and the procedures. Consequently, both the experiments and the diagnostic investigations were planned and modified as the work progressed, and was based on the characteristics of the textile piece and the results obtained from the various treatments. The application method was also studied and was based on the nature and versatility of the consolidant.

The two different consolidation methods chosen to date are reported here:

The chitosan solution was prepared by dissolving chitosan powder in an acetic acid aqueous solution (pH 5) by magnetic stirring for approximately four hours at different concentrations (0.1% w/v, 0.3% w/v. 0.5% w/v, 1% w/v). The molar mass of the chitosan we used, as determined from the intrinsic viscosity reported by the manufacturer, has an average value of 120 kDa while the average degree of deacetylation was estimated around 83% by Fourier Transform infrared spectroscopy (FTIR) analysis. The testing was carried out on fragments of the silk that were no longer attached to the garment and on samples of old silk from OPD laboratory supplies. We decided to treat two groups of samples: the first group with a

15 minutes consolidation treatment in immersion with the use of ultrasonic, the second group with 15 minutes consolidation treatment in immersion. These two groups were then divided into two groups, half were rinsed for 5 min in continuous distilled water, half no rinsing. All samples were dried at room temperature.

The sol-gel synthesis was performed by hydrolysis of metal-organic precursor, TEOS in acid water (pH 4.5) modified with PEG 1000 (0.25M) with particle diameters smaller than 50 nm. The specific formulation is not commercially available but was prepared in the laboratories at the University of Bergamo. The tests themselves were carried out at the SSS laboratories on samples of new silk with density of 70 g/m^2. Samples were coated with the hybrid thin film using the application techniques of immersion in ultrasonic bath for one minute, or by spray-coating. After that, the treated samples were dried at room temperature and atmospheric pressure.

Analyses

The following techniques were used to document the consolidation achieved for both consolidants:

- documentation with stereomicroscope, optical microscope (MO) and scanning electron microscopy (SEM) in order to visually observe the distribution and placement of the consolidant on the samples.
- standard method to determine the physical-mechanical characteristics of an individual thread sample before and after treatment with the consolidant using costant rate of extension (CRE) tester UNI EN ISO 2062 CRE (Ente Nazionale Italiano di Unificazione 1997);

- standard method to determine the extent of the chemical changes of an individual thread sample before and after treatment with the consolidant, SNV 195595 (Schweizerische Normen Vereinung Association Suisse de Normalisation 1069);
- spectrophotometric method UV-Vis-NIR (whiteness value) to determine and evaluate any optical changes to the sample before and after treatment.

Results

Chitosan:

- under macroscopic observation after consolidation and a continuous rinsing in distilled water at 0.1% w/v, 0.3% w/v. 0.5% w/v, the “hand” of the sample does not appear to have been modified, at consolidant concentrations of 1%, the “hand” was altered.
- the hand was also altered when there was no rinsing subsequent to consolidation, and when rinsing was done without continuous flow replacement for at least 5 minutes
- the higher “Breaking Stress” value indicates that after treatment there was an increase in the fibre resistance under mechanical stress (e.g. +5; see Table 3);
- the decrease in the value of “Young’s Modulus” (e.g. -36.8) and the increase in the “Breaking Strain” (e.g. +26.2) value demonstrate a reduced rigidity and an increased flexibility of the silk, most likely a result of the “bridge” arrangement of the consolidant between the fibres (see Figure 5 and Figure 6);
- even in reduced concentrations of consolidant (e.g. 0.3%), stable bonds are formed between the polysaccharide and the protein resulting in increased integrity of the textile. This can be deduced because the sample, after consolidation treatment, is partially soluble in its specific solvent (see Table 3 Intrinsic Viscosity value)
- the difference in the “Whiteness Value” between the treated and untreated sample is negligible and is considered acceptable because there is an instrumental tolerance for check-white standards equal to ±5 units due to the non-significant difference on a visual level (see Table 3).
- by comparing the samples consolidated by immersion and by immersion in an ultrasonic bath, it can be inferred that the ultrasonic bath assists in improving the penetration of the consolidant into the textile structure, however, this aspect is still being examined and verified. Our experimentation with the cleaning by immersion showed that it is necessary to use ultrasonic baths in order to assist in the removal of the mud from the textile.

Table 3. Results of the analyses of activity of the 0.3% w/v chitosan consolidant on samples of treated silk in ultrasonic immersion and rinsing.

Chitosan 0.3% (the results are obtained from the average taken from c. 10 samples)			
Direction	**Weft**		
Test sample: Silk twill (90 g/m^2)	**Untreated**	**Treated**	**Change due to treatment (%) [(treated-untreated)/untreated]x100**

Breaking Stress centiNewton cN Standard deviation cN	279 ± 2.7	293 ± 0.9	+5.0
Breaking Strain % Standard deviation %	10.3 ± 2.9	13 ± 0.8	+26.2
Young’s Modulus g/den Standard deviation g/den	63.9 ± 11.2	40.4 ± 11.6	-36.8
Intrinsic Viscosity dl/g (lithium bromide)	0.34	the sample proved to be partially soluble in the specific solvent	-
Whiteness Value Index illuminant D65 Observer 2°	47.04	42.99	-

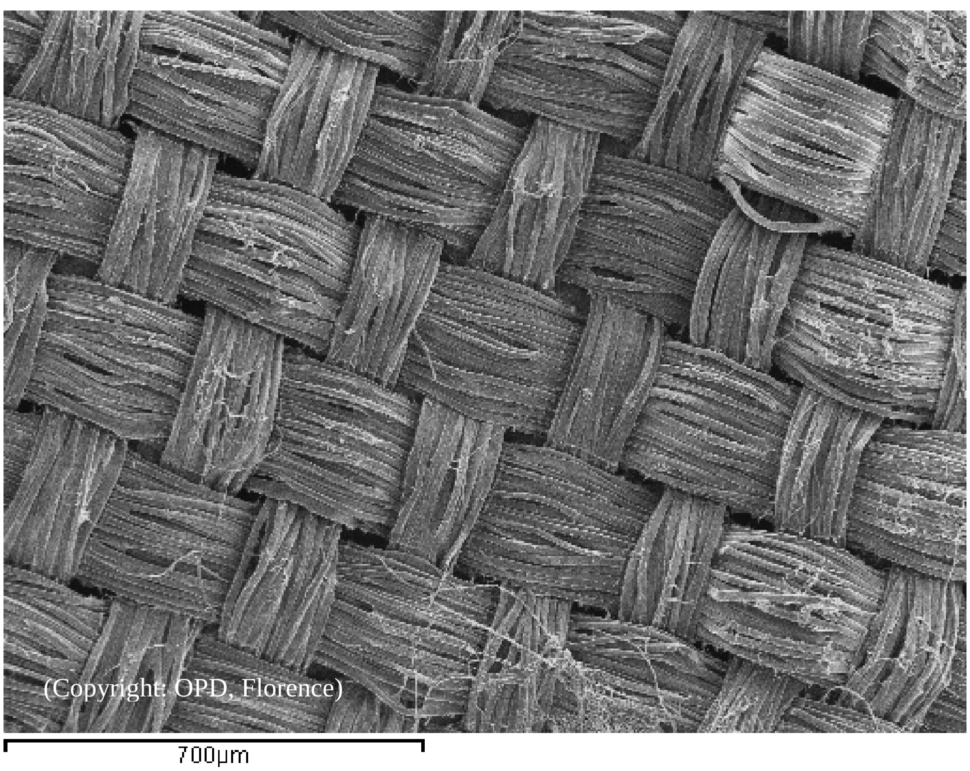

Figure 5. (SEM) Old silk taffeta from the laboratory supply (the pilling occurred prior to treatment) treated with 0.3% chitosan. Even at these magnifications the consolidant does not show up as uneven deposits on the yarns.

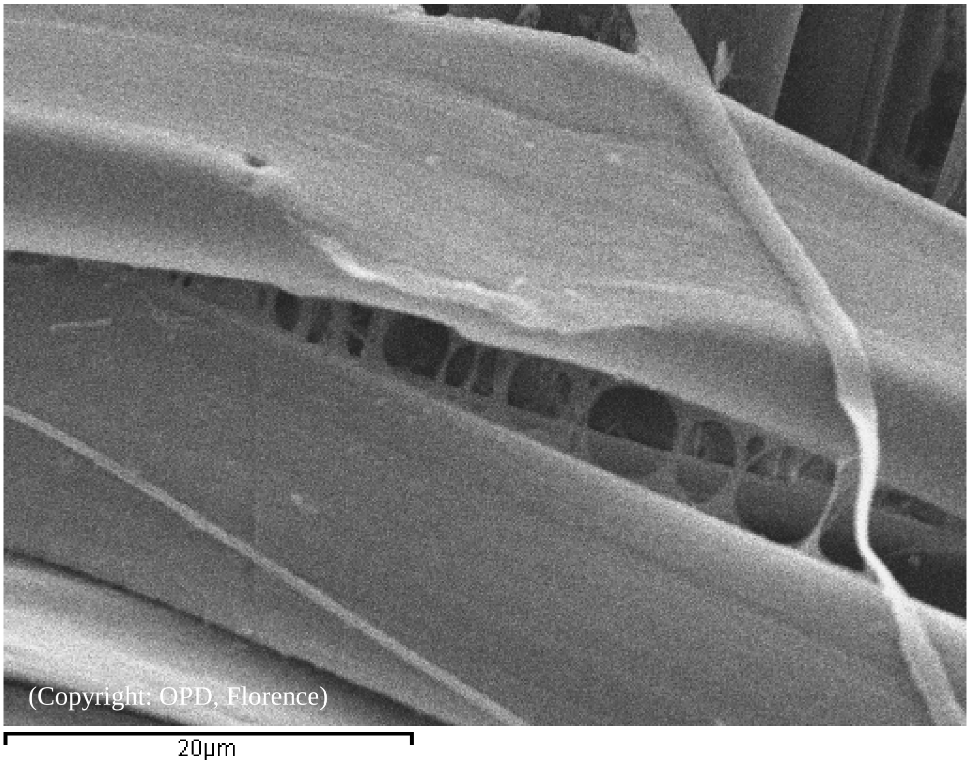

Figure 6. (SEM) Detail of the chitosan (0.3%)“bridges” deposited between the fibres on the samples.

Nanostructured sol-gel:

- under MO and SEM the consolidant (one minute application) appears to have been distributed in a uniform manner on the entire surface of the treated sample;
- the higher “Breaking Stress” value (e.g. +7.4, see Table 4) and the increase in the “Breaking Load” value (e.g. + 7.3, see Table 4) indicate that after treatment there was an increase in the fibre resistance under mechanical stress. The increase in the values is most likely due to its “protection” of the individual fibres (Figures 7 & 8);
- the decrease in the value of “Young’s Modulus” (e.g. -18.8 see Table 4) and the increase in the “Breaking Strain” (e.g. +7.3, see Table 4) value demonstrate a reduced rigidity and an increased flexibility of the silk after the treatment;
- the percentage variation in the “Viscosity” value (e.g. +2.9 see Table 4) most likely indicates that the nanostructured solution does not create bonds that modify the molecular arrangement of the silk; it is hypothesized that hydrogen bonds and ionic bonds form leaving the fibre more resistant to depolymerization;
- the slight reduction in the “Whiteness Value” is considered to be non-relevant. The consolidant appears not to have affected the colour in the treated sample, for the same reasons given above;
- the sol-gel can be applied either in an ultrasonic bath or in the spray-coating distribution but spray distribution method does not seem to guarantee uniformity even if hand and

colour are considered to be good; the application at low temperatures and atmospheric pressure is particularly well suited to this type of treatment;

Table 4. Results of the analyses of activity of the Hybrid SiO_2 /PEG 1000 sol-gel consolidant on samples of silk in ultrasonic immersion and rinsing.

Hybrid SiO_2 /PEG 1000 Sol-Gel (the results are obtained from the average taken from c. 10 samples)			
Direction	**Weft**		
Test sample: Silk twill (70 g/m^2)	**Untreated**	**Treated**	**Change due to treatment (%) [(treated-untreated)/untreated]x100**
Breaking Stress cN Standard deviation cN	373.4 ± 2.8	400.9 ± 8.1	+7.4
Breaking Strain % Standard deviation %	16.5 ± 1.4	17.7 ± 1.0	+7.3
Young's modulus g/den Standard deviation g/den	58.4 ± 8.9	47.4 ± 8.9	-18.8
Intrinsic Viscosity dl/g (lithium bromide)	0.34	0.35	+2.9
Whiteness Value Index illuminant D65 Observer 2°	63.5	62.7	-

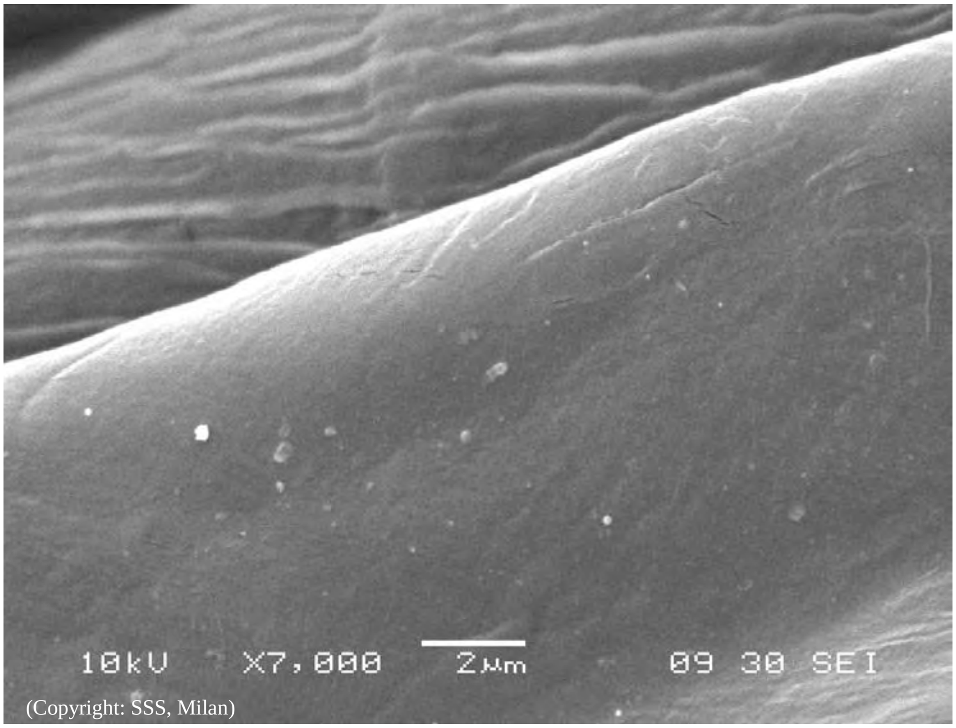

Figure 7. (SEM) Detail of the silk twill before treatment with nanostructured silica sol-gel

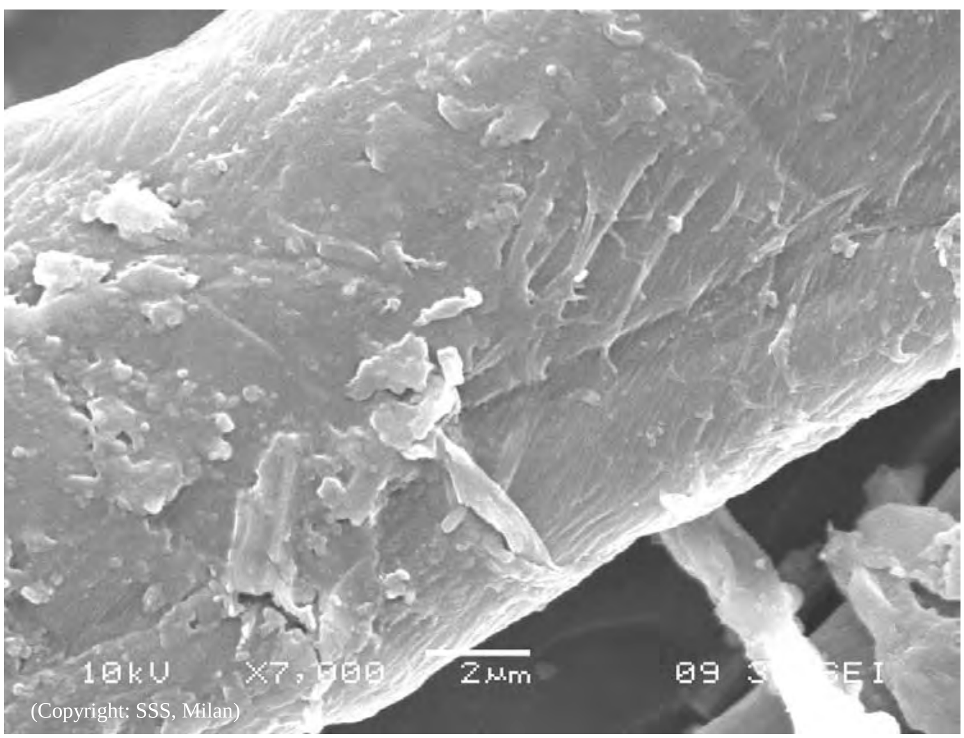

Figure 8. (SEM) Detail of the silk twill after ultrasonic treatment with nanostructured silica sol-gel, where the "protection" of the single fibres can be seen.

Discussion

The study we have described is aimed at finding a consolidation method linked with the cleaning treatment that is suitable for a highly deteriorated three-dimensional textile. The initial results are very encouraging for further research. The ultrasonic bath does not appear to cause mechanical deterioration of the sample, but simply serves as an aid to remove the mud from the textile and the homogeneous distribution of the consolidant. This will be confirmed by more analyses. It was important to understand that all the immersion liquid should not be totally removed during treatments in order to avoid flattening, and thus adhering, the different layers of the fabric to one another. It was noted that in both cases (chitosan and sol-gel), the consolidation improved the mechanical and chemical properties of silk fibres and improved the flexibility without stiffness and breakage. Neither of the consolidants creates non-homogeneous films covering the exterior. Chitosan creates a bridge between the fibres, thus stabilizing the structure rendering it more flexible. The sol-gel consolidant coats the individual fibres strengthening and giving body to the fabric.

It should be kept in mind that these are results obtained from experiments made on silk that was not in the same condition as our artifact. The fragments from the burial garment were also consolidated with both compounds, however, their small size, the small number of available samples, and the current inability to remove all the deposits on the fabric do not allow us to obtain repeatable and comparable results at this time.

Conclusion

This research is clearly still in the initial phases and a further phase of study is necessary. It is impossible to identify which of the two consolidants is better and more suitable at this time. The benefits of ultrasonic baths in the consolidation phase will continue to be tested. A lower molecular weight chitosan will be tested. In terms of the sol-gel, the process of consolidation first with ultrasonic immersion followed by spray coating will be evaluated to see if better results can be obtained. After aging tests will be carried out on silk fragments of the garment as well as samples of the silk from other sources in order to assess the results. This will be monitored over time in order to identify the treatment that will be carried out on garment n. 29. It is clear how important this experimentation has been in terms of innovation and in the implications it holds for conservation strategies applied to highly degraded textile materials.

Acknowledgements

In this type of collaboration, thanks must go to so many individuals that it is difficult to list them all separately. Here, the authors would like to thank the following groups and institutions for their generosity and cooperation: the public and private institutions that participated in the "Progetto Medici", the Opificio delle Pietre Dure and the University of Bergamo, in particular Dr. Claudio Colleoni for the nano-silica preparation.

Endnotes

1.This project began in 2003 on the mortal remains of the members of the Medici family buried in the Medici Chapels in the Laurentian Complex in Florence.

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Materials and Suppliers

Chitosan: Sigma-Aldrich S.r.l. Milan, Italy
120 kDa, deacetylation was estimated around 83%,
http://www.sigmaaldrich.com/italy.html

Silicon dioxide modified with PEG (polyethylene glycol) 1000 in ratio 0.05:
silk + Sol-gel 0.125 M in acid water pH 4.5
University of Bergamo and Stazione Sperimentale della Seta di Milano
http://www.ssiseta.it/index.php

Author Biographies and Contact Information

Susanna Conti has a degree in Conservation from the School of Higher Education, Opificio delle Pietre Dure (OPD) in Florence, Italy and has worked in the field of textile conservation for more than 30 years. She founded the textile restoration sector at the Opificio delle Pietre Dure e Laboratori di Restauro in 1981, and today she manages this sector as Technical Director and Coordinator. She began teaching at the OPD School of Higher Education in 1980. The main focus of her teaching and research has been the development of non-invasive diagnostic and conservation techniques coupled with experimentation on the consolidation of textile materials. She is currently involved in collaborative research with other institutions and universities studying the consolidation of archaeological silk using nanotechnologies, in addition to coordinating numerous conservation projects. She has authored many publications and has been active in conferences and collaborative projects with both Italian and international organizations.

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Susanna Conti détient un diplôme en conservation-restauration de l’école d’enseignement supérieur de l’Opificio delle Pietre Dure (OPD), à Florence, en Italie, et il y a plus de 30 ans qu’elle travaille dans le domaine de la restauration des textiles. En 1981, elle créait le secteur de la restauration des textiles à l’Opificio delle Pietre Dure e Laboratori di Restauro, et elle dirige actuellement ce secteur à titre de directrice et coordinatrice technique. Elle a commencé à donner des cours à l’école d’enseignement supérieur de l’OPD en 1980. Son enseignement et ses travaux de recherche portent en grande partie sur l’établissement de diagnoctis non effractifs et les techniques de restauration; elle conjugue à ces activités des expériences sur la consolidation des matériaux textiles. Elle réalise actuellement des recherches en collaboration avec d’autres établissements d’enseignement et universités sur la consolidation de la soie archéologique dans le cadre desquelles les nanotechnologies sont mises à contribution, et ce, tout en coordonnant divers projets de restauration. Elle a rédigé de nombreux articles et ouvrages, et elle a participé à des conférences et à différents projets conjoints menés sous l’égide d’organisations tant italiennes qu’internationales.

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Isetta Tosini received a degree from the Department of Mathematics, Physics, and Natural Sciences at the University of Florence, Italy in 1980. She has worked in the Scientific Lab of the Opificio delle Pietre Dure (OPD) in Florence since 1985. Now the Director-Coordinator of the OPD Biological Lab for different types of artworks, she collaborates closely with the Textile, Tapestry, Paper, and Parchment conservation labs and also identifies wood species used in wooden sculptures and supports. She carries out studies, research, and planning for new methodologies and techniques of analysis using specialized instruments and equipment for analytic and research aims. She has also coordinated the Mould Technical Office at the OPD since 1992, carrying out research and experiments on materials and mould-making methods for historical and artistic artifacts. She teaches Biology at the OPD School of Higher Education and at the Mosaic Restoration School in Ravenna.

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Isetta Tosini obtient son diplôme du département de mathématiques, physique et sciences naturelles de l'Université de Florence, en Italie, en 1980. Elle travaille depuis 1985 au laboratoire scientifique de l'Opificio delle Pietre Dure (OPD), à Florence. Elle est actuellement la directrice-coordinatrice du laboratoire de biologie de l'OPD pour différents types d'œuvre d'art, elle collabore étroitement avec les laboratoires de restauration des textiles, des tapisseries, du papier et des parchemins, et elle identifie les essences des bois utilisés dans les sculptures et supports en bois. Elle mène des études et des recherches et planifie les travaux pour établir de nouvelles méthodes et techniques d'analyse au moyen d'instruments et d'équipements spécialisés à des fins d'analyse et de recherche. Elle coordonne de plus le bureau technique de moulage de l'OPD depuis 1992, où elle mène des études théoriques et effectue des expériences sur les matériaux et les méthodes de fabrication des moules utilisés avec les artefacts historiques et les objets d'art. Elle enseigne la biologie à l'école d'enseignement supérieur de l'OPD et à l'école de restauration des mosaïques de Ravenne.

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Elisa Bracaloni has been a freelance textile conservator since 2010. She has a scientific preparatory secondary education as well as a degree from the University of Florence, Italy (2005) with a thesis entitled *Studies, Hypothesis and Operative Methods Applied to an Embroidered Bedspread*. In 2006, she won a nationwide entrance examination to the Advanced Professional Training program at the School of Opificio delle Pietre Dure in Florence concentrating in textile conservation. She graduated from this program in 2009 with a thesis on her experimental studies for cleaning and consolidating archaeological silk. She is currently part of the research project "Tecniche avanzate per la conoscenza materica e la conservazione del patrimonio storico-artistico" (TEMART) under the auspices of the Tuscan Region. Her studies address many aspects of conservation, from documentation and condition reporting to diagnostic surveys, conservation treatments, and historical-artistic research. She has also worked in the private sector, where she continues to develop her manual skills and concentrate on the application of conservation techniques.

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Elisa Bracaloni est restauratrice de textiles à la pige depuis 2010. Elle a suivi une formation préparatoire en sciences, puis elle a obtenu un diplôme de l'Université de Florence, en Italie (2005); son mémoire s'intitulait *Études, hypothèses et méthodes pratiques appliquées aux couvre-lits brodés*. En 2006, elle faisait partie des candidats choisis à l'échelle du pays pour passer l'examen d'entrée au programme supérieur de formation professionnelle de l'école Opificio delle Pietre Dure, à Florence, où elle a surtout étudié la restauration des textiles. En 2009, elle devenait une diplômée du programme avec un mémoire sur les expériences qu'elle avait réalisées sur le nettoyage et la consolidation de la soie archéologique. Elle participe actuellement au projet de recherche « Tecniche avanzate per la conoscenza materica e la conservazione del patrimonio storico-artistico » (TEMART) sous les auspices des autorités de la région toscane. Elle aborde, dans le cadre de ses travaux, de nombreux aspects de la restauration, allant de la documentation et de la description des conditions jusqu'aux enquêtes de diagnostic, aux traitements de restauration et aux recherches historico-artistiques. Elle a également travaillé dans le secteur privé, où elle a continué de peaufiner ses habiletés manuelles et d'approfondir l'application des techniques de restauration.

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Mauro Matteini is an expert in conservation science who currently works as a private consultant. He is a former Director of both the Scientific Laboratories at the Opificio delle Pietre Dure in Florence, Italy (1975–2002) and the CNR Institute for the Conservation and Promotion of Cultural Heritage (Florence, Milan, and Rome) (1972–1975). He has authored or co-authored more than 350 scientific publications in the field of conservation (including books on the Chemistry of Conservation adopted in many Italian and foreign universities); been a visiting professor at the universities of Bologna, Syracuse, Siena, Pisa, London, and Thessaloniki; and coordinated research projects on the diagnostics and monitoring of important monumental artistic works such as *David* by Michelangelo, *The Rape of the Sabine Women* by Giambologna, the *Gates of Paradise* by Lorenzo Ghiberti. His current research involves investigation into innovative methods for consolidating and protecting wall paintings and stone artifacts.

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Mauro Matteini est spécialiste des sciences de la restauration; il travaille actuellement comme consultant privé. Il a déjà occupé le poste de directeur des laboratoires scientifiques de l'Opificio delle Pietre Dure, à Florence en Italie (de 1975 à 2002) et de l'Institut de conservation et valorisation du patrimoine culturel du CNR (Florence, Milan et Rome) (de 1972 à 1975). Il est l'auteur ou le coauteur de plus de 350 ouvrages et articles scientifiques dans le domaine de la restauration (dont des manuels de chimie de la restauration qui sont employés dans de nombreuses universités italiennes et étrangères). Il a été professeur invité aux universités de Bologne, de Syracuse, de Sienne, de Pise, de Londres et de Salonique. Il a coordonné des projets de recherche sur les diagnostics et le suivi d'importantes œuvres d'art monumentales comme le *David* de Michel-Ange, *L'enlèvement des Sabines* de Giovanni Bologna et *Les portes du paradis* de Lorenzo Ghiberti. Dans le cadre de ses travaux en cours, il étudie des méthodes novatrices de consolidation et de protection des peintures murales et des objets de pierre.

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Maria Rosaria Massafra is a senior chemical researcher and scientific manager at the Ministero dello Sviluppo Economico in Italy (since 1979). She is the Scientific Director of the laboratories at the Stazione Sperimentale per la Seta in Milan and coordinates research projects and analytical structures. Her accomplishments include more than 150 papers (published in Italian and international journals), several monographs, books, and patents developed in the following fields: natural and man-made textile products (chemical and technological), auxiliaries and dyeing of textiles, nanotechnology applied to textiles, and innovation in textile restoration. She is an inspector (since 1995) Accredia (Italian accreditation body) and a professor of Textile Technology and Quality in various courses and seminars: FSE, laboratories, associations, and universities (the Engineering Department at the University of Bergamo, the Physics Department at the University of Milan Bicocca, and the Chemistry Department at the University of Milan).

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Paolo Matteini obtained a degree in Chemistry from the University of Florence in Italy in 2004. He worked in the field of fluorescence microscopy of natural compounds and of biological tissues during 2005 before continuing his education. In 2009, he received a PhD in Chemical Sciences from the Institute of Applied Physics – National Research Council of Italy (IFAC-CNR) in Florence, working on the molecular mechanism of photothermal denaturation of proteins and on laser-induced modifications to extracellular biomolecules. Since 2010, he has held a postdoctoral position at IFAC. His current research interests include the study of photothermal processes; the development of polymeric scaffolds, films, and hydrogels for laser applications in biomedicine; the fabrication of temperature- and light-responsive biopolymeric and metal nanoparticles; and the development of nanostructured and biocompatible drug-delivery systems.

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Roberto Pini is a physicist and a Senior Scientist at the Institute of Applied Physics – National Research Council of Italy (IFAC-CNR) in Florence, where he is the leader of the Biophotonics and Nanomedicine Lab. He also holds the Chair of Optics at the University of Florence, Faculty of Medicine and Surgery, and the Chair of Biomedical Optics at the Faculty of Optics and Optometry. His main research interests are related to studies on light propagation in biological tissues; development and applications of laser-activated gold nanoparticles and nanostructured chromophores for medical use; microscopic analyses on photothermal modifications of proteins; development of new medical laser devices; and preclinical and clinical studies on the use of laser and other optoelectronic devices for minimally invasive surgery (e.g. in ophthalmology, microvascular surgery, and dermatology). He is co-author of about 200 scientific publications, including 6 books, and 15 patents.

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Roberto Pini est physicien et préposé principal à la recherche à l'Institut de physique appliquée du Conseil national de recherches de l'Italie (IFAC-CNR), à Florence, où il est responsable du laboratoire de biophotonique et de nanomédicine. À l'Université de Florence, il occupe la chaire d'optique, à la faculté de médecine et de chirurgie, et la chaire d'optique biomédicale de la faculté d'optique et d'optométrie. Ses travaux de recherche portent sur la propagation de la lumière à travers les tissus biologiques, la production de nanoparticules d'or et chromophores nanostructurés activés par laser et leurs applications à des fins médicales, les analyses microscopiques des modifications photothermiques des protéines, la mise au point de nouveaux dispositifs à laser médical et les études précliniques et cliniques sur les appareils à laser et autres dispositifs optoélectroniques utilisés en micromanipulation chirurgicale (p. ex. en ophthalmologie, en microchirurgie vasculaire et en dermatologie). Il est le coauteur de près de 200 publications scientifiques, dont six livres et quinze brevets.

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