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Review Article

Novel Materials as Consolidates for Stone Strengthening

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ABSTRACT

Deformations in the sculptures and monuments can be restored by the help of nanomaterials which can penetrate in it easily without any harm. Consolidation thus strengthens the object and improves the durability. Conservationist has developed new techniques to make stronger and longer shelf life of historic monuments. Nanotechnology has given us a path to maintain our cultural heritage. Major applications are reviewed and enlisted in detail including novel nanomaterials and consolidation procedure.

Keywords: Restoration; Nanotechnology; Consolidation; Shelf life

INTRODUCTION

Stone decay phenomena and deterioration are explained in various terminologies. Degradation, deterioration, weathering, disintegration, fragmentation, peeling, scaling, microkarst, missing part perforation, pitting, film, glossy aspect, graffiti, patina, soiling, subflorescence, lichen, moss, mould, plant, alteration, damage, decay, crack, deformation, blistering, bursting, delamination, alveolization, erosion, mechanical damage, crust deposit, discoloration, efflorescence, encrustation, biological colonization and algaare some of the terminologies used to explain different types of deformation in the sculptures.

The loss of cohesion and the subsequent erosion of the exposed stone surfaces in architectural objects have challenged masons, architects and curators. More recently, scientists have joined the group of active professionals searching for remedies of this long-standing and demanding conservation issue. The loss of the superficial layer of the stone brings about the loss of artistic value or when the material erosion is jeopardizing the overall structural stability of the object or its neighborhood.

Consolidation is the treatment of stone that restores the mechanical properties after they have been degraded by weathering. Consolidation is the "in depth" treatment of stone that has lost its cohesion to such a degree that its physical survival is imperiled. The disintegration of the stone may result from the dissolution of the material cementing the grains of the stone together or from the disruption of the intergranular bonds from increased tensile stresses caused by such processes as salt crystallization and thermal expansion. In this paper, numerous methods for consolidation of stone are discussed with respect to their chemical and structural properties. This type of study is highly essential and practical for the maintenance of stone for many years.

LITERATURE REVIEW

Consolidation also consists of impregnating deteriorated stone as well a substantial part of the underlying layer of sound stone with an appropriate material known as a consolidant. The consolidant, thus, imparts strength to the stone by effectively restoring the bonds between adjacent grains. Many of the consolidants available also impart hydrophobic property to the solid surface.

A full consolidation treatment is often irreversible and entails the introduction of a new material into the stone matrix. Consolidants must have the ability to improve the durability of deteriorated stone by restoring its physical properties such as abrasion resistance, hardness, tensile and compressive strength to near that of the original sound stone; must penetrate the full thickness of the deteriorated zone of stone; should be able to close and reduce the number of small pores in the stone, and thereby, increase its resistance to salt crystallization and frost damage; must retain or only cause minimal reduction in the

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water vapor permeability of the stone; should be compatible with the stone and not form any byproducts that can be harmful to stone; should not disrupt to the molecular structure of the stone due to similarity in molecular volume and thermal dimensional properties with those of sound stone; and cause minimal or no change in the appearance, color and optical properties of the stone [1].

Due to various limitations of commercial consolidants *i.e.*, cracking and shrinkage during drying process, novel materials and new technology is highly needed for heritage conservation. The use of improved methods and materials has found its way in heritage conservation. Nano-materials have several advantages such as good penetrating ability, low temperature sintering, improved dielectric properties, tribiological properties and increased resistance of the substrate, as well as the capacity to be polymerized after application to the materials thus reinforcing the structure. Nanoparticles grant a good penetration inside the paper and a quick carbonation due to their high surface reactivity. Moreover no surfactants are used to stabilize the alkaline nanoparticles.

A preliminary but detailed examination of stone is required prior to any conservation treatment. The physical and mechanical condition of the stone as well as all documentary evidence connected with the object or structure such as traces of painted decoration, incised lines drawings, inscriptions and tool mars must be recorded graphically and photographically. Consolidant materials should be similar with the heritage materials needed to be conserved. Therefore, the most efficient consolidants for silicate stone arealkoxysilanes. Most commonly used consolidants are inorganic materials *i.e.*, calcium hydroxide, barium hydroxide, silicon compounds, acrylic polymers and copolymers, vinyl polymers, epoxides, natural and synthetic waxes etc.

There has also been much interest in the use of resin based coatings to protect both old and new buildings, such treatments are designed to minimize water and oil penetration, dirt accumulation and the growth of lichen and moss, to be long lasting, invisible, UV resistant and yet to allow the natural material beneath to (have good air exchange) breathe. Their water resistant properties are thought to allow rain to form compact drops and to assist in the removal of particulates from the surface.

The application of nanotechnology in the cultural heritage conservation is marked by the possibility to design consolidant products highly compatible with the original stone substrate. Moreover, when particles have dimensions of about 1 nanometers–100 nanometers, the materials properties change significantly from those at larger scales. In this sense, nano-materials have larger surface areas than similar masses of larger-scale materials, which increase their chemical reactivity. In addition, these nano-materials present the possibility to penetrate deep into the damaged stone materials due to the particle size. On the other hand, atmospheric pollution is dramatically increasing the external degradation of monuments and buildings due to the deposition of organic matters and other contaminants on the stone substrates. The nanoparticles must have the following attributes: Stability and sustained photoactivity, biologically and chemically inert, nontoxic, low cost, suitability towards visible or near UV light, high conversion efficiency and high quantum yield, could be react with wide range of substrate and high adaptability to various environment and good adsorption in solar spectrum. In addition, these treatments can also have water repellent properties which favor this self-cleaning action, and prevent the generation of damage caused by water. The nanostructured particles can provide not only hydrophobic and repellence properties to the stone substrate but also super hydrophobic properties. The nanoparticles can also be used as additives in construction materials or to modify the synthetic polymers in order to enhance its outdoor performance, and its mechanical and thermal properties. Moreover, capsules with high initial flexibility are even used for self-healing concretes. On the other hand, the presence of soluble salts is recognized as an important decay agent of stone heritage. Thus, in the last few years, the study of the application of nanoparticles as a de-sulphating agent for stone, mortars and wall paintings are being carried out.

Nano sized barium, strontium and magnesium hydroxides emerged as efficient consolidants for porous stone and frescoes [2-5]. The potential of SiO_2 nanoparticles have been recently studied for conservation treatments of different stone substrates [6-7]. The efficacy of SiO_2 nanoparticles as a consolidating product of stone depends on the relative humidity of the exposure environment. Calcium alkoxides (Ca-alkoxides) have been studied mostly as suitable consolidating agents for carbonate stones, plasters and wall paintings in solution or as NP inorganic sols [8-12]. The mechanical properties of limestone can be significantly improved by *in situ* formed hydroxyapatite. Besides, in its various applications in materials science, medicine and archaeology, this calcium-containing compound is seen as a good inorganic consolidant for carbonate stones. The aqueous phosphate solution (diammoniumhydrogen phosphate, DAP) reacts with the calcite in the stone, leading to the formation of hydroxyapatite and by-products, which are not found to be harmful for the stone [13-17]. The suitability of the alkoxysilanes and their gels for stone consolidation is determined by their low viscosity and by their ability to form siloxane (Si-O-Si) bonds. Due to their first property, they can easily penetrate into the intergranular stone substrate where, due to their second property, they polymerize and through sol-gel process form siloxane stable bonds. In this way, the cohesion of the grains of the stone is improved [18].

Alkoxysilane solutions based on Tetraethoxysilane (TEOS) and Methyltrimethoxysilane (MTMOS) have been widely used for the consolidation of decaying heritage stone surfaces [19].

Hybrid nanocomposites based on silica and calcium oxalate improves the tensile strength of the treated stone, enhances the chemical and physical affinities for natural stone and exhibits a partial protective effect without altering the microstructure of the treated stone [20-21].

Novel consolidants

Organic-inorganic gel prepared by co-condensation of TEOS and an organosiloxane, Poly DiMethyl Siloxane (PDMS), provides excellent waterproofing to the stones reported by Mosquera et al. [22]. The new mesoporous silica avoids the main disadvantage of current commercial consolidants, which is their tendency to crack inside the pores of the stone. It is clear that the effect of the surfactant is to make the pore size of the gel network coarser, thus reducing the capillary pressure, which is responsible for the cracking. In addition, the surfactant decreases the surface tension of the solvent, which also contributes to reducing the capillary pressure. This single material provides both hydrophobicity and consolidation to the stones.

Consolidation effect of nanosized particles of calcium hydroxide dispersed in alcoholic medium on limestone has been studied by Omary et al. [23]. The efficacy of the consolidation material has been evaluated at various parameters *i.e.* porosity, water uptake, compressive strength, drilling resistance and salt crystallization damage resistance. Nanolime consolidant improved salt crystallization damage resistance by about 29% for fresh stone and by about 32% for archaeological samples. The main disadvantage of the nanolime consolidants is the relatively low penetration depth; the average consolidant uptake value ranged between 6.14 kg/m^2 hr 0.5 for archaeological stones and 1.52 kg/m^2hr 0.5 for fresh stone.

Mosquera, et al. prepared Gels from starting sol containing TEOS in the presence of an amine primary surfactant (n-octylamine). It has been reported, consolidation with the mixtures containing 1:7 and 1:11 TEOS: Ethanol molar ratios were more effective [24]. These two consolidants fill the rock pores more efficiently and provide a significantly greater increase in the compression strength of the stone than the commercial consolidant tested in this study.

Ksinopoulou, et al. reportedmodification of Si-based Consolidants by the addition of SiO_2-TiO_2 nanoparticles. The addition of inorganic nanoparticles into silica matrix seems to contribute to the reduction of shrinkage and cracking after solvent evaporation. Fifteen different compositions were developed, varying the concentrations of the reagents (TEOS and NH_3), to investigate their effect on both the final size of the particles, and the %content of solids in suspension [25]. According to the results of the qualitative characterization, which its composition contains less percentage of nano-particle dispersion TiO_2-SiO_2 (relative to the total volume), showed a greater stability in the liquid phase, while during drying it was deposited as a more cohesive white mass with a shorter shrinkage rate. This formulation appears to be more effective, both during application as well as after treatment, according to the evaluation methods applied.

Consolidation of carbonate stones: Influence of treatment procedures on the strengthening action of consolidants reported by Pinto et al. [26]. Four different carbonate stones *i.e.,* Anca and Boic¸ pure calcitic limestones formed almost exclusively of calcite with silica as the main, but relatively scarce, accessory mineral and Coimbra and Lisbon stones, two calciticdolostones and their chemical compositions include silica and alumina, which indicate the possible presence of clay minerals in both stones while Three different consolidants *i.e.,* ethyl silicate, acrylic, and epoxy resins were applied individually to samples of each stone type. The strengthening effect was quantified with microdrilling resistance, ultrasonic velocity, flexural strength and surface hardness. The results showed that the same consolidation product results in different strengthening actions when applied by different methods. The results also confirm the fact already widely proven that consolidation strongly depends on the stone properties, and show that some materials are almost impossible to consolidate, even when a fairly high porosity is present (see for instance the results of Coimbra stone with roughly 18% porosity). On the other hand, very porous stones (see for instance Anca stone with 27% porosity) may accept fairly large amounts of the consolidation product (Paraloid B72 by brushing may reach 2.1 kg/m^2) and still remain insufficiently (and possibly dangerously) consolidated. The formation of potentially harmful superficial strength peaks is highly probable in very porous stones and were found to be more intense when the product was applied by brushing (for Paraloid B72), and when applied by full immersion (for the epoxy resin).

Consolidant based on hydroxyapatite nanoparticles dispersed in alcohols reported by Ion, et al. [27]. Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), nanoparticle dispersions in alcohols may be applied by spraying or by impregnation. The structural, morphological and compositional aspects of chalk stone samples from Basarabi Chalk Church (Romania); treated with nanoparticles HAp has been tested. A complex collection of Dynamic Light Scattering (DLS), Scanning Electron Microscopy (SEM), FTIR and Raman spectra have been used in order to identify the major constituents of chalk stone, all these being useful for subsequently method of restoration. Some weak bonds are forming between chalk and HAp, and a strong homogeneous consolidation effect was visible from SEM images, where local white area could be observed, assigned to the new generated structure. The compressive strength indicated that HAp led to a good reconsolidation capacity of the chalk samples. Undoubtedly, this is caused by the network of hydroxyapatite, which can bind weathered stone blocks together providing a substantial reinforcement. The capillary water uptake decreased after the treatment with HAp, concluding that the treatment makes the stone samples more compact and less permeable to water. This method is a credible one for future building walls consolidation.

To avoid the fractures and to improve gel properties, a hybrid consolidant based on TEOS and fillers such as colloidal silica (200 nmin diameter) and hydroxy-terminated Polydimethylsiloxane (PDMS-OH) synthesized by Salazar-Hern ´andez et al.[28]. Both additives enhance gel properties such as porosity and elasticity, leading to the formation of non-fractured and permeable gels. Characterization of the hybrid xerogel was carried out by nitrogen adsorption and 29Si MAS-NMR. The properties of the hybrid xerogels were compared with those prepared from a formulation based on TEOS (T-ME) with a composition similar to a commercial product. Porosity in the final hybrid xerogels was significantly increased with the addition of colloidal silica, because the colloidal particles are caught in the TEOS matrix, forming micro and mesoporous structures depending on the percentage of SiO_2-ST in the hybrid structure. Moreover, the siloxane chains in the hybrid enable improved elasticity because PDMS-OH is chemically bonded to the inorganic silica skeleton (TEOS and colloidal silica), as was confirmed by 29Si MAS-NMR. The PDMS-OH fragment crosslinks with the agglomerate of silica particles in the hybrid microstructure. Thus, the flexibility and mobility of such fragments lends support to the capillary tension generated during the drying stage. The stone treated with the hybrid (TEOS–SiO_2-ST–PDMS-OH) formulations showed a major increase in hardness, a significant change in water-accessible porosity and a major salt crystallization resistance. Although the amounts of consolidant deposited by H1-ME and T-ME were similar, a greater increase in hardness was observed for the samples consolidated with the hybrid formulation. Furthermore, PDMS-OH significantly modifies the hydrophobic properties of the stone, and thus its percentage in the formulation is critical.

Consolidation of Stone by Mixtures of Alkoxysilane and Acrylic Polymer (Ethylsilicate 40 and Paraloid B-72) reported by Jiti et al. [29] The composition of the mixtures under evaluation was chosen so that the effects on consolidation quality of the addition of Paraloid B-72 and of various catalysts (*i.e.*, Dibutyltindilaurate (DBTDL), Hydrochloric Acid (HCl) p.a., Lovogen Mg (manganese salt of 2-ethylhexanoic acid), morpholine p.a., anhydrous sodium sulphate p.a.,) have been assessed. Strength was increased by 75% on average. Sample treatment led to a reduction in water absorption capacity and to an increase in resistivity to crystallizing salts. Although absolute values of these quantities differ considerably, depending on the catalysts used, the presence of Paraloid B-72 has a positive effect. From the rate and height of capillary rise it appears that mixtures containing Ethylsilicate 40 and Paraloid B-72 can be used successfully as a stone consolidant although the presence of this polymer decreases the mobility of the mixture. Of particular importance is the fact that surface stone porosity and the appearance of the stone were not greatly affected by consolidation.

Surface consolidation of natural stone materials using Microbial Induced Calcite Precipitation (MCP) reported by Richardson, et al. [30]. This study has shown that stone particle cementation is possible using microbial precipitation. MCP is presented as a possible repair agent when used in surface repair of calcareous sandstone and limestone alike. Multiple coats of bacteria were more beneficial than a single application and this was due to the increase in surface coated mass recorded. It is likely that the calcite formations in the micro cracks would reduce natural weathering actions on exposed stone. Adopting a bacterial solution of OD 0.9 proved adequate for the surface treatment experiment despite its minimal cementitious properties. *Sporosarcinapasteurii* has shown to be a highly active bacterium for the production of calcite through hydrolysis but the cell quantity could be increased to produce more effective deposition and cementation. A method for obtaining optimal results in terms of surface treatment would involve reducing the time between mixing and application, this would require having the two reaction constituents mixed only seconds before use. Using a late mix spray application system has the potential to allow the two mixtures to combine in the spray nozzle whilst exiting the apparatus. An additional benefit may occur from this process in so much as it may prevent calcite formation building up within the spray system that would damage the equipment and hinder operations. Conservation of stone masonry substrates may be possible through the application of calcite derived MICP for external surface treatment of friable surfaces. The application of a microbial-based surface treatment may reduce the rate of decay of stone based materials.

Behavior during drying of two stone consolidants *i.e.*, Wacker OH and Tegovakon V, containing tetraethoxysilane has been evaluated by Mosquera et al. The rigidity of the gel network has been evaluated by mercury porosimetry, while pore size, which controls capillary pressure, has been determined by nitrogen adsorption. The shrinkage of gels under mercury pressure is characterized by high moduli. This fact suggests a high rigidity of the networks. The small pore radii found in the network (<3 nm) indicate that high capillary pressures are generated within the gel network. The high values of the bulk moduli of the network and their elastic behavior are consequences of their low porosity. Pore size of the dry gels is estimated to be low. Such small pores give rise to high capillary pressure during gel drying inside the stone pore structure. In gels formed on the surface of stone, the high rigidity of networks implies that stress would be also controlled by capillary pressure.

Three different inorganic consolidants *i.e.*, Calcite *In-situ* Precipitation System (CIPS); CaLoSil and ammonium oxalate treatment for use on museum artefacts in comparison to organo silanes assessed by Booth, et al. overall colour change for all replicates was at a level detectable by the human eye. The lowest values were for those treated with CIPS, although this treatment did change the gloss of the surface in a noticeable way. Next lowest were the replicates treated with ammonium oxalate, which were below the values for the replicates treated with Wacker OH. The replicates treated with CaLoSil developed a very obvious white bloom on the surface; shown by the extremely high ΔE00 values. The colour change was so severe that further experiments to try and reduce/ prevent this white bloom would be needed before any recommendation for trialling on museum artefacts could be made. Karsten tube tests to analyse water penetration showed replicates treated with CIPS, ammonium oxalate, and Wacker OH, all had a significant decrease in water penetration with virtually no water penetrating into the Wacker OH replicates. Some individual CaLoSil replicates had a decrease in water penetration, however overall there was not a statistically significant difference. These treatments were all designed as consolidants, not as hydrophobic coatings. Whilst some decrease in water penetration could be expected, blocking all water penetration could be detrimental to an object. No one parameter can be used on its own to make a decision about whether any of these three inorganic consolidants hold potential for use on limestone artefacts in the British Museum, or are a more preferable option than previously used Wacker OH. This decision will be made once results from the destructive tests are in. However, information from these non-destructive tests can be used to focus on certain areas during the destructive testing. The results here seem to show the ammonium oxalate treatment succeeding more than the other two inorganic consolidants and indeed outperforming the Wacker OH. However, it will be really important to analyze if this treatment is consolidating the stone substrate, or just has just formed a very hard superficial layer.

Consolidation of porous carbonate stones by an innovative phosphate treatment: Mechanical strengthening and physical-microstructural compatibility in comparison with TEOS based treatments reported by Graziani et al. From the tests carried out on Globigerina Limestone (GL) and Giallo Terra di Siena (GS), the following conclusions can be derived. Both consolidants proved to be effective on the selected lithotypes, as they caused significant improvements in mechanical properties of both GL and GS. The HAP mechanical efficacy was found to be comparable to that of TEOS, when isopropyl alcohol was employed to reduce ethyl silicate toxicity (GS samples), while TEOS efficacy proved to be higher than that of HAP when white spirit was used as solvent (GL samples). TEOS efficacy proved to be much dependent on the product formulation: when isopropyl alcohol is used instead of white spirit, TEOS efficacy dramatically decreases. In terms of alterations in porosity, both consolidants can be considered as fairly compatible with GL and GS; in particular, HAP leads to basically no alteration in total open porosity and a very slight alteration in pore size distribution, whereas TEOS is responsible for more pronounced open porosity reductions; in terms of alterations in liquid water transport properties, HAP demonstrated a much higher compatibility than TEOS, as the former treatment caused no substantial alterations, while the latter treatment induced temporary hydrophobicity in the treated stones. This makes the application of water based treatments impossible for several months after treatment and may give rise to salt and freezing related problems, in case water is present behind the consolidated, hydrophobic layer. For these reasons, HAP seems to be a valuable alternative to TEOS for the selected litho types, as it allows obtaining a good efficacy in a much shorter curing time and a higher compatibility with the substrate. Additional parameters on which the treatment compatibility depends (e.g. alteration in water vapour permeability, colour change, etc.) have given promising results in previous studies on different lithotypes. Further tests to assess the durability of HAP-treated samples are currently in progress.

Effectiveness and durability of nanolime and nanosilica-based consolidants applied on heated granite and limestone has been assessed by Pozo-Antonio, et al. They were applied on two stones with different mineralogy and texture (granite and a limestone). Both stones were previously weathered to obtain a loss of cohesion and increase the open porosity. Samples were subjected to 500°C and rapidly cooled by tap water jet, simulating the effect caused by firefighters' intervention in a fire. After 500°C, granite showed the highest increase of open porosity, which is associated to the fissures occurred after the heating and cooling down. Regarding the method used to applied both nanoconsolidants, different number of applications were used following Karsten pipe method; regardless of the product, higher number of applications were made in the granite and subsequently, higher dry matter was obtained. Nano Estel and Nanorestore induced different results due to their composition and the mineralogy of the stone. In the case of granite, similar reduction of the porosity and similar resistance to salt crystallization cycles were achieved. However, in the limestone, nano-restore, despite having a composition similar to the stone mineralogy, yielded lower effectiveness in terms of dry matter, porosity and water absorption by capillary coefficient, comparatively to the nanosilica consolidant. The lack of effectiveness was attributed to the low penetration of nanolime particles in the fine pore structure of this stone. However, the nanosilica consolidant Nano Estel on the limestone induced higher levels of decay after crystallization cycles due to the difficulty to bond silicate materials to fine porous calcite-based substrates. Regarding the influence of the consolidant in the colour of the surfaces, granite yielded the highest surface colour alterations on samples treated with nano Estel due to the appearance of yellow spots.

Suitability of silica nanoparticles for tuff consolidation analyzed by Iucolano, et al. The consolidant consists of an aqueous suspension of nano-silica particles (diameter of 10/20 nm) and despite its lower penetration capacity than ethyl-silicate based consolidants, takes advantage of less toxicity, a fast-enough setting time. Moreover, it induces not-relevant chromatic alterations on specimens' surface. For this purpose, two series of specimens have been dipped one or two times in the consolidating solution (1:1 dilution). After treatment by immersion, a considerable amount of solvent evaporated, but a continuous silica gel film permeated the pores of stone surface layers, thereby reducing the stone susceptibility to decay mechanisms related to the action of water, mainlythe water absorption by capillarity and permeability. The consolidating action promoted also a moderate strengthening effect, increasing the cohesion of tuff as evidenced by unconfined compressive and flexural strength tests. Finally, ageing tests (freeze-thaw cycles) have provided additional data that support the suitability of silica nanoparticles for conservation/ restauration of tuff.

Novel nanomaterials, such as nanosilica or nano-titanium oxide for the conservation of built heritage synthesized byBorsoi, et al. Among nanomaterials, nanolimes have acquired a considerable relevance due to their potentialities as consolidant product. The so-called nanolimes, colloidal dispersions of calcium hydroxide nanoparticles in alcohols, have been successfully applied as pre-consolidants on frescos and paper, and their use has later been extended to plasters, renders and stone. Nanolimes have better potentialities compared to conventional inorganic consolidants based on limewater (e.g. faster carbonation rate and higher calcium hydroxide concentration). Moreover, nanolimes are considered more compatible with $CaCO_3$ based substrates than alkoxysilanes (e.g. TEOS), the most widely used consolidant products. Nanolimes can guarantee the recovery of the superficial cohesion of degraded materials. However, when a mass consolidation is required, like in the case of decayed stone, nanolimes show some limitations. One of the problems is caused by nanolime accumulation at or just beneath the surface of the treated material. The absorption and drying behaviour of nanolime in this limestone was measured and nanolime deposition in the stone was studied by optical and scanning electron microscopy. The results show that nanolime transport is strictly related to the properties of the solvent. The alcoholic solvent guarantees a stable dispersion that penetrates in depth in the material, but is partially back-transported to surface. The high volatility of the solvent and the high stability of the dispersion favour the partial back-migration of lime nanoparticles to the surface during drying. The dense nanolime layer accumulated beneath the drying surface may impair the quality of consolidation and also limit the penetration of successive consolidant applications, hindering effective consolidation. These results suggest that, in order to improve nanolime precipitation in depth, the transport and deposition mechanism of nanolime should be modified. This might be obtained by slowing down the drying rate (e.g. by applying a covering, as a water-filled cellulose compress, on the treatment) and/oraltering the kinetic stability of the dispersion (e.g. by modifying the solvent of the dispersion). Both these facts are expected to avoid the nanolime back-migration and favour nanoparticle deposition in depth in the substrate.

$Sr(OH)_2$ nanoparticles synthesis in homogeneous phase at low temperature reported by Ciliberto et al. This has been achieved *via* homogeneous precipitation by the salt solution method, a synthetic route which starts from low cost raw materials, operates at low temperature and in aqueous medium. The process avoids the use of organic solvents, specialized equipment, long processing times, or expensive special chemicals. The experimental conditions to reach a high supersaturation degree were set at 60°C by using $Sr(NO_3)_2$ and NaOH solutions 0.7 and 0.3 M respectively. The nanospecies obtained consist of regularly shaped, homogeneous and nearly rounded particles, which have a narrow distribution and an average particle diameter of about 30 nm. The experimental data collected and the results reported in this work suggest that $Sr(OH)_2$ nanocrystals could represent a good alternative to other more traditional methods in the protection and consolidation of cultural heritage artefacts. In fact, *in vitro* experiences have revealed that $Sr(OH)_2$ is able to react both with atmospheric carbon dioxide and with sulphate ions arising from gypsum. Thus as a new sacrificial material it can be used inwall painting and plaster restoration without the toxicity problems typical of barium hydroxide solutions. This synthetic technique can probably be applied to the preparation of other nanosized particles of moderately/highly soluble inorganic compounds and represents an innovative technological route in nano-material chemistry.

Essa, et al. reported Copper has strong biocidal activity with non-specific mode of action against microbial cells that make it ideal antimicrobial agent. CuNPs were prepared through novel bioprocess that utilizes volatile metabolites of *E. coli* to aggregate Cu ions into nanometal structures away from the bacterial cells. This bioprocess is inexpensive and eco-friendly. Besides, uncontaminated bacterial biomass could be used safely in different applications. The incorporation of CuNPs into polymer matrix produced nanocopper composites with remarkable antimicrobial capability. The antimicrobial activity of CuNPs was evaluated against the bacterial strains *Bacillus subtilis*, *Micrococcus luteus*, *Streptomyces parvulus*, *E coli*, *Pseudomonas aeruginosaas* well as some fungal strains *Aspergillusniger*, *Aspergillusflavus*, *Penicilliumchrysogenum*, *Fusariumsolani* and *Alternariasolani*. The functionalized consolidation polymers could be used not only to inhibit the microbial growth on the surfaces of historical stones but also to improve physical and mechanical properties of the treated stones. Additional research is required to evaluate the application of consolidation polymers loaded with nanoparticles of copper *in situ* treatment. At the same time, limestone and sandstone blocks treated with consolidation polymers functionalized with CuNPs recorded apparent antimicrobial activity against *E. coli*, *S. parvulus* and *B. subtilis* in addition to an improvement in the physical and mechanical characters of the treated stones. Furthermore, the elemental composition of CuNPs was elucidated using electron dispersive x-ray system connected with the scanning electron microscope.

The two tested consolidant products, namely a limewater dispersion of 5% ethyl silicate and a commercial alcoholic dispersion of nanostructured calcium hydroxide, proved to be effective in improving the cohesion of weak lime mortars confirmed by Borsoi, et al. Nevertheless, the mechanical resistance results showed some differences between the two consolidant products. Higher mechanical increases were obtained with the 5% ethyl silicate limewater dispersion. However, it presents reduced penetration depth due to the rapid reaction of the ethyl silicate with limewater, which forms platelike silica gels. Instead, the alcoholic dispersion of nanolime particles, probably due to the reduced concentration of the nanostructured calcium hydroxide, guarantees a moderate improvement of the mechanical resistance. On the other hand, this nanolime product reveals excellent penetration capacity, due to the alcoholic solvent. Microstructural observations through stereozoom and SEM illustrate that the limewater dispersion of ethyl silicate has consolidation efficiency on the treated surface. This is related to the mixture of colloidal silica with the calcium carbonate crystals, as a result of limewater carbonation. Moreover, carbonation seems to interfere in the solidification of the xerogel formed from the ethyl silicate, promoting the development of planar structures. These plates like colloidal silica formations, however, could reduce the consolidant penetration depth. Due to the reduced depth penetration, this product is recommended only for lime mortars with superficial loss of cohesion. According to our results, nano lime particles permit homogeneous distribution and optimum penetration on the treated substrate. The plate like nanoparticles present specific crystallographic orientation that could contribute to an agglomeration process and therefore improve the mechanical resistance of the treated surface. Since this dispersion does not guarantee high mechanical resistance improvement, the use of nano lime is recommended for lime mortars with reduced loss of cohesion, or in combination with other consolidation products. Otherwise it will be necessary to proceed to a larger number of applications or to use more concentrated dispersions. The development of nanoparticle materials offers new tools in conservation science and constitutes one of the most advanced systems for consolidation of renders and plasters. As a future prospective, combined application of the two analyzed products, with higher concentration of calcium hydroxide nanoparticles, will be considered.

The promising results from this innovative research reported by Otero, et al. showed that the use of sticky rice alone or in combination with LAQ nanolime yields a higher degree of consolidation than that attained by a simple nanolime consolidation. However, the consolidation effectiveness of sticky rice decreases when the treated samples are exposed to weathering processes. More research needs to be carried out to fully understand the sticky rice weathering process to optimize its consolidation mechanism. This study concludes that the sticky rice solution has low viscosity which favors good penetration into the porous substrate. FTIR and the iodine test confirm that the sticky rice starch is composed mainly of amylopectin. The morphological properties of the dried gelatinized sticky rice show that it presents an uneven structure formed by a film with several granular nodules tightly packed and clustered into compound grains. All treated samples, either with nanolime (LAQ), Sticky Rice (SR) or their combination (SR-LAQ), had a lower porosity. The highest porosity decrease was observed for samples treated withSR-LAQ (~22.9% decrease), followed by thosetreated with SR (12.8%). MIP results clearly show that the reduction in porosity corresponds to the filling of pores with diameters between 2 and 11 lm in all treatments. Both treated samples involving nanolime, *i.e.*, LAQ and SR-LAQ, also showed a reduction in the smaller pore range with diameter between 0.01 and 0.3 μm and confirming that LAQ can partially fill these finer pores.

A significant increase of surface cohesion. The samples treated with only sticky rice showed the highest increase in the superficial cohesion followed by samples treated with sticky rice and nanolime. A certain degree of hydrophobicity was imparted to the sample surface by the application of the SR, but it decreases when nanolime is applied subsequently. Further studies are required to elucidate this behavior.

The drilling resistance increases for all treated samples, especially those pre-treated with stickyrice, where the treatment certainly reached 2 cm (half the length of the sample reached by the drilling) while those treated only with LAQmerely reach 6 mm. The increase in the drilling resistance is fairly constant throughout the drilling depth, confirming that sticky rice starch increases the mechanical resistance of samples providing a deeper consolidation of the mortar independent of the use of nanolime in combination with it. The increased durability of the SRLA Q treatment could be attributed to the stickyrice which apparently improved nanolime distribution throughout the sample. Further research is required to elucidate this hypothesis and to study the total penetration depth of the sticky rice independent of the use of nanolime in combination with it. Colorimetric results showed that both samples involving nanolime (LAQ and SR-LAQ) caused as light whitening of the surface with both ΔE^* and ΔL^* values above 5. The surface cohesion, hydrophobicity and drilling resistance of sticky rice samples significantly decreased after exposure of the samples to the AWT-1 (T=40–60°C) weathering which may be attributed to the irreversible starch gelatinization process. A lower decrease in the consolidation was noticeable after exposure of the samples to the AWT-2 (T=40–30°C) and similar results were obtained after wet–dry cycles. These results confirm that starch still degrades at medium or room temperatures after several moisture cycles. FTIR analysis of the water from wet–dry cycles shows that small amounts of sticky rice starch were dissolved in the water.

Nanosilica and nanotitania nanoparticles produced by CO_2 laser pyrolysis reported by Gancristofaro, et al. have been applied as nanometric filler to siloxane polymeric dispersions. The preservation properties of our nanocomposites were tested the application on two dfferent lito types, very common in outdoor cultural heritage: white marble (statuary and veined carrara) and travertine. Samples of treated stone were submitted to artificial aging processes, both in climatic chamber and in solar box, to access and compare the performance *vs.* nanocomposites. Rhodorsil RC80 modified with nanosilica and nanotitania have shown an appreciable enhancement of the conservative performances on both the tested specimens and the best behavior, in terms of protection capability and durability, has been noted on the nanocomposites RC80/SiO_2 (1% w/v). A good resistance has been observed also in the samples treated with RC80/SiO_2 (0.2% w/v)/TiO_2 (0.2% w/v).

SEM mages and LIF spectra let have a morphological investigation and a molecular study on the treated stone surfaces. The LIF technique presents the advantage to be a non-invasive and a remote application. The colorimetric variations, measured before and after the accelerated aging processes, say that the optical surface alterations remain acceptable (ΔE value is always under 5).

The contact angle, measuring the wettability, has shown the nanoparticles capability to enhance the hydrophobicity in a conservative polymeric material inducing a better durability of the stone substrates treated by the different nanomixtures. This property becomes primarily important in case of artistic and monument stone exposed to real outdoor conditions and extends the application of hydrophobic coatings to the field of cultural heritage conservation.

Conservation of stone and mortars by a Three-Layered Compatible Treatment of TEOS-Nano-Calcium Oxalate Consolidant and TEOS-PDMS-TiO_2 hydrophobic/photoactive hybrid nanomaterials synthesized by Kapridaki et al. This conservation approach was implemented treating lithotypes and mortars of different porosity and petrographic characteristics with a three-layered treatment comprising *i.e.*, a consolidant, Tetraethoxysilane(TEOS)-Nano-Calcium Oxalate (TCO); a hydrophobic layer of TEOS-Poly Dimethyl Siloxane (PDMS) (SP); and a self-cleaning layer of TiO_2 nanoparticles from titanium tetra-isopropoxide with oxalic acid (T) as hole-scavenger. After the three-layered treatment, the surface hydrophobicity was improved due to PDMS and nano-TiO_2 in the interface substrate/atmosphere, as proven by the homogeneity and the Si–O–Ti hetero-linkages of the blend protective/self-cleaning layers observed by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Fourier-Transform Infrared Spectroscopy (FTIR). The aesthetic, microstructural, mechanical and permeable compatibility of the majority of treated substrates ranged within acceptability limits. The improved photo-catalytic activity, as proven by the total discoloration of methylene blue in the majority of cases, was attributed to the anchorage of TiO_2, through the Si–O–Ti bonds to SiO_2, in the interface with the atmosphere, thus enhancing photo-activation. The hydrophobic properties improved after SP and T treatment for all the studied substrates, as proven by the contact angle and capillary water absorption values. The three-layered treatment re-aggregated the structure and adhered well to the surface, since an insignificant amount of material was removed with the peeling test. The water vapor permeability is ensured for the majority of the studied lithotypes with an exception of PRC, where the significant reduction is related to the high amount of TCO and SP and T absorbed. The aesthetic compatibility of the TCO and SP and T treatment was compromised in the case of ceramic material with values exceeding the acceptability limits. Discolouration experiments of MB on the various litho types demonstrated that the new application protocol of TCO and SP and T treatment exhibited enhanced self-cleaning performance, achieving total discoloration of MB in the majority of the substrates as a result of the incorporation of nano-TiO_2 into the silica network, as evidenced by the formation of stable Si–O–Ti bonds identified by FTIR. The TCO and SP and T three-layered treatment ensured the re-aggregation of the grains in the majority of studied litho types with different petrographic characteristics and porosity. Moreover, protection against water action with the SP hydrophobic layer and a self-cleaning ability with the nano-TiO_2 anchored on the interface of the protective layer/atmosphere, were also accomplished.

Study of sol-gel process by using Dynasylan 40 with the addition of nanoparticles of SiO_2, Al2O_3, TiO_2 and $CaCO_3$ reported by Adela, et al. The addition of nanoparticles influences the time of gelation, which translates to the working time for the real consolidation. Adding nanoparticles decreases the working time by accelerating the gelation phase. The nanoparticles also influence the extent of shrinking and cracking. Gels containing SiO_2 nanoparticles had the least amount of cracking but also the largest shrinkage. The best shrinkage/cracking ratio had gels with $CaCO_3$ nanoparticles. Choosing the right type and concentration of nanoparticles can reduce the cracking, possibly improving the efficiency of consolidation.

TEOS-based three-component stone consolidants has been prepared by sol–gel process reported by Liu, et al. The composite consolidants consist of 15 nm silica particles, α, ω-hydroxyl-terminated Poly Dimethyl Silane (PDMS-OH) and TEOS. In this system, due to the hydrophobic nature of TEOS (before hydrolysis), the hydroxyl-terminated PDMS molecules tend to stay on the hydrophilic surface of nano-SiO_2. By wrapping around the nanoparticles, PDMS not only prevents the particle from agglomeration, but also functions as a bridge to mediate the interfacial difference between nano-SiO_2 and bulky gels. Thus PDMS significantly reduces the color alteration caused by nano-SiO_2. Due to the synergistic effects with PDMS, the three-component composite also has smallest volume shrinkage and best heat-aging resistance, even better than TEOS/nano-SiO_2 system. In general, by the synergistic effect among the three components, the three-component composite stone consolidant exhibits the best overall performance.

DISCUSSION

Mosquera, et al. reported the synthesis of organically modified silicate (ormosil) by the co-condensation of Tetra Ethoxysilane (TEOS) and hydroxyl terminated Poly Dimethyl Siloxane (PDMS) in the presence of a nonionic surfactant (n-octylamine). The role played by the surfactant in the assembly of the organic-inorganic hybrid silica gel was investigated. Crack free material has been prepared using the same synthesis method but without adding PDMS to the starting sol. n-octylamine acts to direct the formation of the pore structure, creating a nanomaterial with uniform pore radius. Cracking of the gel is prevented as a result of the role played by n-octylamine and PDMS. The surfactant prevents gel cracking by coarsening the pores of the material and by reducing the surface tension of the solvent. PDMS enhances the flexibility of the material, increasing the shrinkage and subsequently preventing cracking. In addition, n-octylamine plays a significant role in the co-condensation of TEOS and PDMS, which allows a homogeneous organic-inorganic hybridxerogel to be created in which PDMS is perfectly integrated into the silica skeleton. Removal of the surfactant by simple drying under laboratory conditions is confirmed by FTIR. To demonstrate the effectiveness of the new nanomaterial in stone restoration, it have been shown that it increases the mechanical resistance of the stone and creates a hydrophobic coating. The exceptionally high contact angles obtained are discussed with reference to the roughness of the surface. Finally, no negative effects on the treated stone are observed.

Werf, et al. synthesized zinc oxide nanoparticles by means of simple and reproducible electrochemical procedures. Products based on tetraethoxysilane and/or polysiloxanes were tested. In a first step the nano-materials were applied on stone samples and studied with scanning electron microscopy and spectrophotocolorimetry. Then, *in situ* experimentation was undertaken by applying nanocomposite coatings on the exterior of a 12th century church in the south of Italy. The performances of the ZnO-nanoparticles based composite coating were compared with a previously investigated copper nanoparticles based material, successfully tested and monitored *in situ* for more than two years. Finally, preliminary tests on the inhibitory effect on the growth of the fungus *Aspergillus niger* were also carried out. The results showed that in case of zinc oxide a tenfold higher concentration of nanoparticles as compared with Cu-NPs can be utilized in the matrices without affecting the colour of the stone substrate, which means that the new material should be able to exert a long-lasting biocide activity. Laboratory and *in situ* tests of the developed innovative nanomaterials yielded very promising, though preliminary, results in terms of chromatic changes, morphological characteristics and bioactivity. Constant monitoring of the coatings will be continued in order to obtain all necessary information on their long term behaviour and inhibition of biological colonisation.

Properties of consolidant and protective materials (Paraloid B72) modified with nanoparticles (SiO_2 and TiO_2 nanoparticles) onto marble samples have been analyzed by D'Amato et al. Laser pyrolysis method has been employed for the synthesis of nanoparticles. The technique of CO_2 laser pyrolysis of gas and vapour phase reactants appears as a scalable synthesis route for preparing nanoparticles with control able morphology and in quantities sufficient to be tested for structural and functional applications. This analyses provided a useful insight in terms of homogeneous surface morphology so that it was possible to select only theoptimal nanoparticle concentration for each kind of nanocomposite (silica–Paraloid, titania–Paraloid, silicaandtitania mixture–Paraloid) for subsequent evaluationtests: SiO_2=1% w/v, TiO_2=0.2% w/v, SiO_2/TiO_2=0.2%/0.2% w/v and SiO_2/TiO_2=1%/0.1%w/v. The best behavior, in terms of protection capability with respect to the negative water effect present in the environment, has been observed with the addition of SiO_2 (1% w/v); for the nano-oxide mixtures of SiO_2 and TiO_2, the best results have been reached when SiO_2 concentration is 1%, allowing us to say that this is the more effective concentration. The preliminary results demonstrate that capability of nanoparticles to enhance the hydrophobicity in a conservative polymeric material induces a better durability of the stone substrates treated by the different nanomixtures. This property becomes primarily important in case of artistic and monument stone exposed to real outdoor conditions and extends the application of hydrophobic nanoparticle coatings to the field of cultural heritage conservation. Development of nanocomposites for conservation of artistic stones.

CONCLUSION

Nanotechnology and nanomaterials have proven as best consolidants for the conservation of cultural heritage. Paraloid B72, tetraethoxysilane and polysiloxanes nanomaterials, CaLoSil, TEOS-PDMS-TiO_2 Hydrophobic/Photoactive Hybrid Nanomaterials, Rhodorsil RC80 modified with nanosilica and nanotitania have shown an appreciable enhancement of the conservative performances. This review paper provides a broad knowledge in the field of conservation including specifically nanomaterials and consolidation procedures, which will surely provide new methodologies to chemists as well as conservationists.

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