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MICROSTRUCTURAL AND PHYSICAL-MECHANICAL ANALYSES OF THE PERFORMANCE OF NANOSTRUCTURED AND OTHER COMPATIBLE CONSOLIDATION PRODUCTS FOR HISTORICAL RENDERS

MIKROSTRUKTURA IN FIZIKALNO-MEHANSKE LASTNOSTI NANOSTRUKTURNIH IN DRUGIH KOMPATIBILNIH PROIZVODOV ZA UTRJEVANJE ZGODOVINSKIH OMETOV

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The surface consolidation of historical renders, directed to restore cohesion and stability, is based on the use of materials with aggregating properties. This operation is usually achieved with the use of inorganic or mineral consolidants, which are preferred to organic ones, due to the better compatibility and durability.
Based on the results of previous studies, two mineral-compatible products were selected: a commercial dispersion of calcium hydroxide nanoparticles in propanol and a calcium-silicate product, consisting of a limewater dispersion of ethyl silicate. The consolidation products were applied to mortar specimens in order to assess their efficacy by determining their microstructural and physical-mechanical properties, before and after the consolidation treatment. Microstructural (optical and SEM microscopy) and chemical analyses of the consolidation products and of the consolidated samples were performed. The physical-mechanical analyses, i.e., the superficial hardness, is reported too.

Keywords: consolidation products, compatibility, nanoproducts, SEM/EDS

Utrjevanje površine zgodovinskih ometov z vidika ohranjanja kohezije in stabilnosti temelji na uporabi materialov z vezivno sposobnostjo. To se navadno doseže z uporabo neorganskih ali mineralnih utrjevalcev, ki so v prednosti pred organskimi zaradi boljše skladnosti in zdržljivosti.
Na podlagi predhodnih študij sta bili izbrani dve vezivi: komercialna disperzija delcev kalcijevega hidroksida v propanolu in proizvod na osnovi kalcijevega silikata, ki vsebuje apnovico, dispergirano v etil silikatu. Namen uporabe vzorcev veziv na vzorcih malte je bil ugotoviti njihovo učinkovitost z določitvijo mikrostrukture in fizikalno-mehanskih lastnosti, pred obdelavo z vezivom in po njej. Izvršene so bile raziskave mikrostrukture (svetlobna in SEM-mikroskopija), kemijska analiza vzorcev veziv in vzorcev po utrjevanju, fizikalno-mehanski preizkusi, poročamo pa tudi o trdoti površine.

Ključne besede: utrjeni proizvodi, kompatibilnost, nanoproizvodi, SEM/EDS

1 INTRODUCTION

A common degradation phenomenon in historic mortars is the loss of cohesion of the binder-aggregate system, which is usually followed by the superficial material loss and a loss of mechanical strength, usually as a consequence of chemical and biological phenomena that can modify the nature of the binder[1].

The restitution of cohesion between the mortar's particles, turned friable by the loss of binder, is achieved through the application of organic or mineral consolidants. The first experimentations on silicates, fluorides, barite and limewater were done in the 19th century[2]; subsequently in the 20th century there was the introduction of polymers, such as acrylics and epoxy resins, which are easier to apply and present better adhesiveness, but do not obey the fundamental rules of physical-chemical compatibility with the substrate. Inorganic consolidants are becoming preferred due to their better compatibility and durability; the best known inorganic consolidants are calcium hydroxide (limewater), barium hydroxide, ethyl silicate, calcium oxalate and calcium tartrate.

The aim of this work is the experimental characterization of two different, compatible, consolidant products, i.e., a traditional compatible product, such as a limewater, mixed with ethyl silicate, and a commercial alcoholic dispersion of nanoparticles of calcium hydroxide, which presents an innovative consolidant product.

2 MATERIALS

2.1 Specimens – Mortar samples preparation

In order to simulate a mortar with a loss of cohesion, different mortar specimens were prepared; the binder/aggregate ratio of 1 : 4 (in volume) was chosen in order to get the desired effect of a low-cohesion mortar, without significant loss of material. The aggregate used was graduated siliceous sand obtained from a mixture of three different calibrated sands with mean particle sizes <2 mm. After the optimization of the mortar composition, different samples were prepared, such as mortar prisms 40 mm × 40 mm × 160 mm and ceramic bricks 28 cm × 19 cm with a single mortar layer of 1.5 cm thickness.

2.2 Properties and application of the consolidant products on lime-mortar specimens

The effectiveness of the limewater, considered the most traditional consolidant product, is known and previous studies provided good results[3,4], beyond the economic advantage and full compatibility. However, limewater usually contains not more than 2 g/L of calcium hydroxide, which only guarantees a low consolidation effect[2], unless it is applied in a large number of cycles.

We have decided to explore the efficiency of limewater, matured in a closed container for some years, mixed with a commercial ethyl silicate (Estel 1000®, CTS). The application of this product causes the formation of amorphous silica gels, which act as a consolidant, ensuring an increase of the mechanical resistance[5]. A low concentration of ethyl silicate was used (5 %), in order to moderately increase the mechanical strength.

Nanolime dispersions of calcium hydroxide are white-to-opal solutions containing stable calcium hydroxide nanoparticles dispersed in an alcoholic medium, usually isopropanol. The nanoparticles have a hexagonal-shaped form and a size range between 50 nm and 600 nm[6]; the reduced dimension of $Ca(OH)_2$ particles guarantees a deeper penetration inside the smaller pores. We have used a commercial nanolime (Nanorestore®, CTS).

An analysis of the selected consolidation products was made considering the important characteristics linked to an optimal application, including the pH, setting times and dry residues (**Table 1**).

Table 1: Characteristics of the consolidation products
Tabela 1: Značilnosti veziv

Consolidation product	pH	Dry residue (g/L)	Setting time (min)
Limewater + Ethyl Silicate (5 %)	9.2	3.51	20
Nanolime	7.2	1.78	120

The applications were made in a conditioned room, at 23 °C and 50 % RH, using a manual-spraying technique (ten consecutive applications) at a distance of 20–30 cm [3,7].

3 METHODS

3.1 Characterization of the consolidant treatments

The evaluation of the efficacy of the consolidant treatments was carried out through the use of different tests, executed before and after treatments (90 d from the consolidant product application).

The improvement of the mechanical resistance was checked by the durometer hardness (Shore A, PCE Group)[8,9]. The surfaces of mortar specimens were observed with an Olympus SZH stereoscopic microscope and the images were recorded digitally.

The microstructural observations and the elemental analyses were performed on specimens previously sputtered with a gold film by SEM JEOL JSM-6400, coupled with an Oxford Instruments energy-dispersive spectrometer (EDS).

4 RESULTS AND DISCUSSION

4.1 Durometer hardness (Shore A)

The superficial hardness of the specimens was verified 90 d after the application of the product through a durometer (Shore A). As shown in **Figure 1**, an improvement in the superficial hardness of the treated specimens is evident.

The nanolime consolidant presents a moderate increase in the superficial hardness (18 %) compared to the untreated specimens, while the treatment of limewater mixed with ethyl silicate registered a greater increase (28 %); the values reflected the trend of previous studies that were made on ancient lime-based mortars[7,10].

4.2 Microscopic observations by stereozoom microscopy

Stereozoom observations were made in order to evaluate the morphological and microstructural variations due to the consolidation treatments. In comparison with the untreated specimens (**Figure 2a**), which present wide pores and micro-cracks, the specimens treated with a limewater dispersion of ethyl silicate (**Figure 2b**) show a more compact surface and an increase in the porosity. Otherwise, the product presents a discontinuous distribution, forming planar agglomerates in the surface.

On the other hand, specimens treated with nanolime (**Figure 2c**) present a more uniform distribution of the consolidation product and homogeneous infilling of the matrix voids; moreover, fewer microcracks were visible.

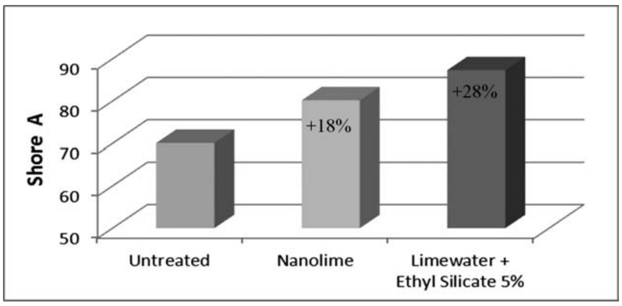

Figure 1: Superficial hardness and relative increases of the treated mortars (durometer Shore A)
Slika 1: Trdota površine in njeno relativno povečanje v obdelanih maltah (trdometer Shore A)

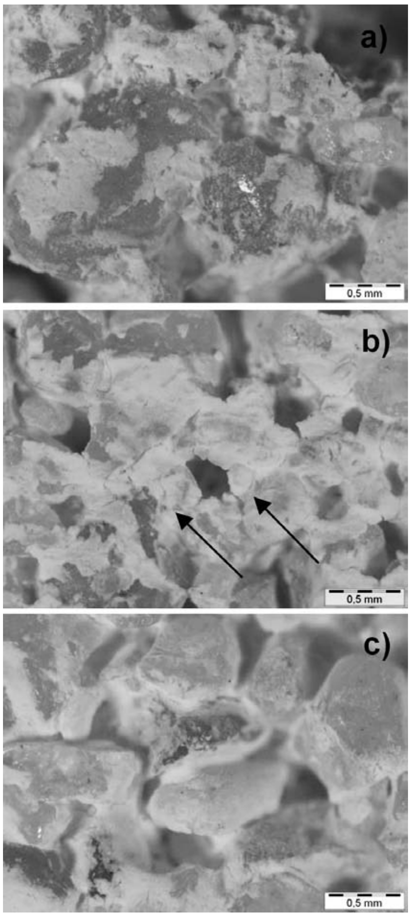

Figure 2: Stereozoom microphotographs (magnification 40-times): a) untreated specimen; b) specimen treated with limewater solution of 5% ethyl silicate and relative planar aggregates (arrows); c) specimen treated with nanolime

Slika 2: Posnetki s stereomikroskopom (povečava 40-kratna): a) neobdelan vzorec; b) vzorec, obdelan s 5-odstotno raztopino apnovice in etil silikata in relativno ploskimi površinami veziva (puščica); c) vzorec, obdelan z nanodelci apna

Macroscopically, both products show few differences in comparison to the untreated mortar, and seem to induce only a slight whitening on the surface.

4.3 Microstructural observations by SEM-EDS

The specimen treated using limewater with ethyl silicate (**Figure 3a, b**) shows the formation of platelike aggregates of calcium-silica gels. Indeed, the quick reaction in the alkaline aqueous solution of limewater rapidly forms calcium-silica gel; this gel transforms itself into a xerogel due to the evaporation of the solvent, and the presence of $CaCO_3$ seems to modify the xerogel vesicular microstructure.

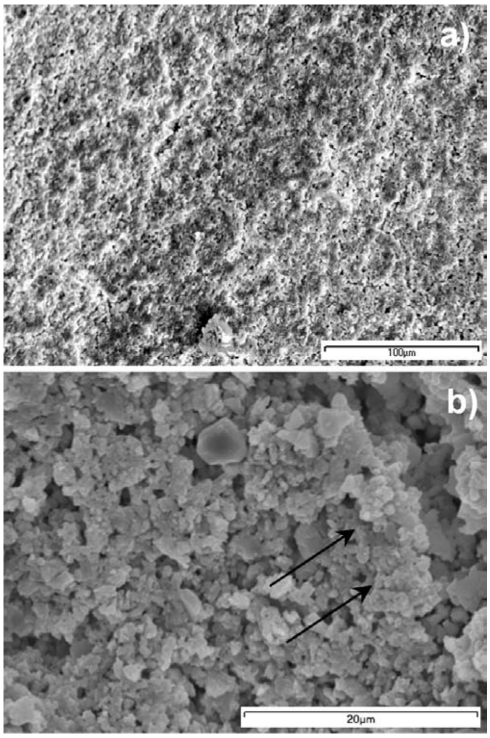

Figure 4: SEM microphotographs of the mortar, treated with nanolime: a) homogeneous distribution of the nanolime in the mortar paste; b) clusters of nanolime particles (arrows) mixed with the original binder

Slika 4: SEM-posnetek malte, obdelane z nanodelci apna: a) homogena razporeditev nanodelcev apna v malti; b) skupek nanodelcev apna (puščica), zmešan s prvotnim vezivom

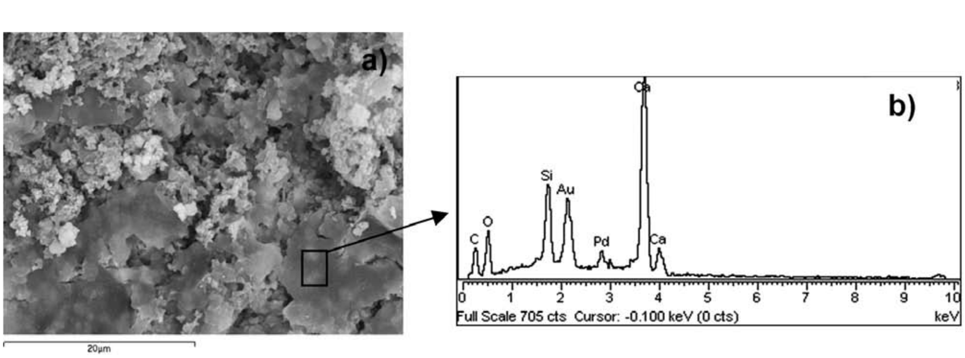

Figure 3: SEM/EDS images of the specimen, treated with limewater-ethyl silicate solution: a) presence of platelike shaped of calcium-silica gel on the mortar surface and b) corresponding EDS spectrum

Slika 3: SEM/EDS-sliki vzorca, obdelanega z raztopino etil silikata v apnovici: a) prisotnost ploščatih oblik kalcij-silicijevega gela na površini vzorca malte in b) ustrezen EDS-spekter

According to recent studies[11], calcium carbonate actually aids the development of shorter linear chains of tetrahedral silica and linear silicate structure, which can explain the rapid formation of a granular gel with a platelike shape.

The SEM/EDS observations of the mortars treated with the nanolime product show micro-sized clusters of calcitic formations; the distribution and morphology of these nanostructured particles show a homogeneous consolidation film. The consolidation film of nanolime is characterized by the presence of plate-like nanoparticles that aggregate into micro-sized clusters, which are compact and polydispersed (**Figure 4**).

According to previous studies[12], the carbonation of nanolime particles originate in oriented crystal grains, which promote the agglomeration of the particles.

Moreover, beyond the chemical, physical and mechanical compatibility, Rodriguez-Navarro et al.[13] have shown that plate-like lime nanoparticles have a great capacity to absorb water (which acts as a lubricating film), guaranteeing a good plasticity and avoiding the mechanical stress inside the treated mortar.

5 CONCLUSIONS

The analysis evidenced some differences between the two products. The obtained results of the mechanical resistance, evaluated through the durometer hardness and the flexural and compressive strength, show that the highest mechanical increase was obtained with the limewater dispersion of ethyl silicate, while the alcoholic dispersion of nanolime particles guarantees a moderate improvement in the mechanical resistance. Microscopical and microstructural observations using stereozoom microscopy and scanning electron microscopy show that the limewater dispersion of ethyl silicate has a consolidation effectiveness on the treated surface, due to the formation of plate-like aggregates of calcium silica gels; however, these planar aggregates can physically interfere in the penetration depth of the consolidant. A limewater dispersion of ethyl silicate is also a good consolidation product, ensuring the restitution of superficial cohesion to the treated mortar. In any case it is recommended only for mortars with a superficial loss of cohesion, because of the reduced depth penetration.

Otherwise, nanolime particles permit a homogeneous distribution on the treated substrate; the platelike nanoparticles present a specific crystallographic orientation that could contribute to an agglomeration process. The nanolime dispersion appears as promising consolidant product for lime mortars with a loss of cohesion, ensuring an optimum penetration and distribution in the matrix binder; however, this dispersion does not seem to guarantee a large improvement in the mechanical resistance, so the use of nanolime is recommended for mortars with reduced loss of cohesion, or to combine the use of this product with other consolidation product.

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