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USING NANOFIBERS IN THE RESTORATION OF HISTORIC COATINGS – RESISTANCE TO SALT CRYSTALLIZATION

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The paper presents partial results of research into the application of nanofibers in the stabilization, conservation, and strengthening of historic plasters. Nanotechnologies applied in all basic technical disciplines currently belong to the most popular fields of research. The restoration of historic and cultural heritage buildings must not in any way damage the preserved original coatings. The execution method and the choice of the suitability of used materials must respect the preserved condition based on the original plaster composition. The research addresses the above issues by applying nanofibers to textile carrier fabrics. The suitability of selected electrospun polymers and acrylates for the purposes of strengthening surface layers, and the application methods of nanotextiles on plasters, were investigated. The objective of this study is to verify whether the newly-designed methodology for the stabilization, conservation, and strengthening of historic plasters meets structural and technical demands, as well as the strict criteria set by cultural heritage conservation.

Keywords: Stabilization, Conservation, Strengthening, Historic plaster, Cultural heritage.

1 INTRODUCTION

The most common tasks in the restoration of historical buildings are, above all, the cleaning, desalination, and consolidation of different types of building matter. Water-soluble salts are considered to be the most common cause of damage to building materials. The reaction of $CaCO_3$ or $Ca(OH)_2$, which are significant components of lime mortars with solutions of weak acids (mostly sulphates, nitrates, chlorides and carbonates), produces soluble salts which subsequently crystallize on the surface of building structures. The washout of binder components from building materials impairs their mechanical properties, increasing the porosity and gradual weathering due to cyclical changes in temperature and humidity, accompanied by surface and internal corrosion. The continuous development of nanostructures, and the study of physical and chemical phenomena at the nanoscale, leads to novel methods that may slow down degradation processes (Baglioni at al. 2012, Chelazzi et al. 2012), increase the consistency of weathered materials, or remove the damage caused by, e.g., using improper restoration procedures (Grassi et al. 2007, Kotlík 2012).

Among unproven remediation methods of disintegrated building materials, mainly plasters but also stone and wood, there is the application of nanotextiles (Gavenda 2012, Machačko et al. 2012). All types of condensed substances, liquids, solutions, polymeric materials, glass, ceramics, ionic substances and metals or gels may theoretically be used for the production of nanofibers (Sodomka 2009). The most suitable substances for making nanofibers are fiber-forming materials such as polymers and carbon fibers. The actual spinning process is affected by numerous parameters, particularly molecular weight, the spatial arrangement of molecules, concentration of the solution, the surface stress of the polymeric solution, spinning voltage, electrical conductivity of the solution, the distance between the collector and the roller, the evaporation speed of the solvent, the type and speed of the textile carrier movement, the parameters of the environment, and others (Krňanský 2009). The application of nonwoven nanotextiles of ultra-thin fibers is presently growing, and their properties, such as a high surface-area-to-volume ratio, high porosity, and the nanoscale itself, enhance the potential of their utilization.

2 MATERIALS AND METHODS

The objective of laboratory testing is to verify the applicability and the effect of selected nanofibers and nanotextiles on characteristic properties of historic plasters, natural stone and wood—in particular their resistance to the impacts and effects of the external environment.

2.1 Test Specimens

Experimental testing involved the production of several sets of test specimens of different sizes and compositions. The tests were carried out using gothic, Renaissance and baroque plasters whose formulations were identified based on laboratory analysis as follows: a) gothic plaster (G): 5 kg of air lime, 16kg of river sand (fraction 0-4 mm), 4 l of water; b) Renaissance plaster (R): 5kg of dry hydrated lime, 10kg of river sand (fraction 0-2 mm), 3 l of water; c) baroque plaster (B): 5 kg of dry hydrated lime, 12.5 kg of river sand (fraction 0-2 mm), 3.5 l of water.

The plaster mixes were used for the production of test specimens in three sizes: a) circular with a diameter of ca. 100 mm, ca. 15 mm in thickness – for the nanotextile application and determination of adhesion plus for the needs of laboratory tests of mechanical and physical properties; b) circular with a diameter of ca. 20 mm, ca. 3 mm in thickness – for electron microscopy; c) test prisms with dimensions of 70 mm x 40 mm x 40 mm – for laboratory tests of resistance to salt crystallization.

A series of laboratory tests were executed using nanotextiles obtained by the electrospinning of Paraloid B72 acrylate and polyvinyl butyral polymers (PVB, solution in ethanol, 10wt%), polyacrylonitrile (PAN, solution in dimethylformamide, 15wt%), and polyvinylidene fluoride (PVDF, solution in a mixture of dimethylacetamide and acetone 8:2, 20wt%) (Figure 1). The PVB, PAN and PVDF polymers were spun using the needleless electrospinning technology (a string in the Nanospider^{TM} NS 4S1000U machine, TU Liberec), the applied voltage was -15.8 kV to the collector and +61.2 kV to the string, at a drawing speed of 10 mm/min (PVDF), 20 mm/min (PAN) or 45 mm/min (PVB). The Paraloid B72 acrylate was spun using the forcespinning technology (Pardam Company) in a toluene/acetylacetone mixture, at a concentration of 35wt%.

To simplify the nanotextile's application and handling on the plaster, electrospun polymers and acrylates were applied on textile carrier fabrics that may be removed after the nanotextile's application onto a plaster specimen.

2.2 Verification of Nanotextile's Adhesion to Plaster Surface

The results presented below include the experimental verification of the applicability of materials described above. Eight different compositions were tested under laboratory conditions for the application of nanotextiles onto a substrate: ethanol, acetone, dimethylformamide, xylene, polyvinil acetate dispersion, Veropal UV40, lime water, and water. Laboratory conditions were at a temperature of 23°C and humidity of 52%. To ensure the nanotextile's adhesion to the plaster (Figure 1), the upper, coarse-grained side of test specimens (diameter of 10 cm, 2 cm) whose structure most approximates the surface of historic plasters, was fitted with an appropriate solvent using a brush, and a nanotextile was successively applied onto the surface and pressed with a sponge.

After applying nanotextiles and after the solvent dried, the degree of surface adhesion to the plaster surface was verified by the subjective assessment, using visual assessment and the scratch test. The visual assessment evaluated primarily optical changes of the plaster surface after the application of nanotextiles (e.g., specimen's optical clarity, nanotextile's shrinking, etc.). The results are summed up in Table 1.

2.3 Resistance of Nanotextiles to Salt Crystallization

The experimental tests presented below were focused on the verification of the possibility of using nanotextiles to protect plasters (or mural paintings) and other coatings of historic buildings from crystallizing salts. The test executed under the DIN 5211 standard was modified with respect to the nanotextile application, and carried out on special test specimens of gothic mortar with dimensions of 70 mm x 40 mm x 40 mm.

Based on the degree of adhesion, adhesives and nanotextiles with the highest degree of adhesion were selected. The selected PVB, PVDF, and Paraloid B72 nanotextiles were applied onto the upper bases of test prisms using suitable agents (PVDF with lime water (A), PVB with lime water (B) and Paraloid B72 with ethanol (C)) (Figure 2).

The test specimens were placed in glass beakers on a mat resting on their bottom base (without nanotextiles), and weighed with a precision of 0.001g at preset time intervals (after 24 h). The prisms were immersed 20 mm in 10% salt solutions of NaCl and Na_2SO_4, resting in a semi-enclosed space (a beaker, see Figure 3) for 5 days.

The salt solution was changed and the capillary elevation of salt solutions into test prisms was monitored every day. The capillary elevation of salt solutions led to the formation of efflorescence on the surface (the upper base of the test specimen fitted with nanotextiles) (Figure 4).

Figure 1. Test specimens with applied nanotextiles obtained by electrospinning Paraloid B72 acrylate, with images from the Tescan Vega 3 scanning electron microscope with a 570x magnification: a) Paraloid B72 with lime water; b) Paraloid B72 with ethanol.

Table 1. The summary of the results of nanotextiles' application onto the surface of historic plasters using selected agents.

	ETHANOL	H_2O	ACETONE	DIMETHYL FORMAMIDE	LIME WATER	XYLENE	POLYVINYL ACETATE DISPERSION	VEROPAL UV40
PVDF	0	2	0	1	3	0	0	0
PVB	3	**5**	0	1	**5**	0	0	0
PAN	2	0	0	2	6	0	0	0
PARALOID B72	6	0	**5**	6	4	6	0	0

Legend: 0 – no nanotextile adhesion or reaction with the solvent, i.e., the nanotextile remained in unchanged condition; 1 – the nanotextile was partially dissolved without adhesion to the test specimen; 2 – nanotextile was not transferred onto the test specimen; it was etched, shrunk or otherwise damaged; 3 – nanotextile was transferred onto the test specimen, it did not adhere with all of its surface; a visible milky layer of the nanotextile remains on the plaster; 4 – all-surface nanotextile adhesion to the plaster structure occurred; the layer is slightly white colored; 5 – all-surface nanotextile adhesion to the test specimen's structure occurred, and the nanotextile layer became transparent; 6 – the nanotextile was dissolved in the applied solution.

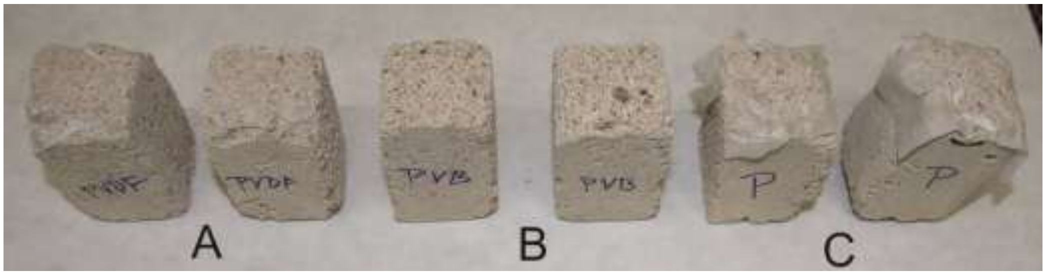

Figure 2. Test specimens.

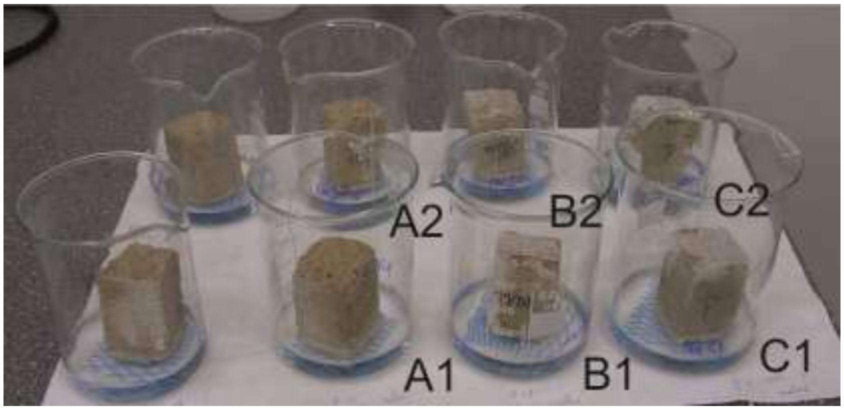

Figure 3. Test system – immersion of specimens in 10% salt solutions with front specimens in a 10% NaCl solution. Front row: Specimen 1 – gothic plaster without a nanotextile; specimen 2 (A1) – gothic plaster with PVB; specimen 3 (B1) – gothic plaster with PVDF; specimen 4 (C1) – gothic plaster with Paraloid B72.
Back row: specimen 1 – gothic plaster without a nanotextile; specimen 2 (A2) – gothic plaster with PVB; specimen 3 (B2) – gothic plaster with PVDF; specimen 4 (C2) – gothic plaster with Paraloid B72.

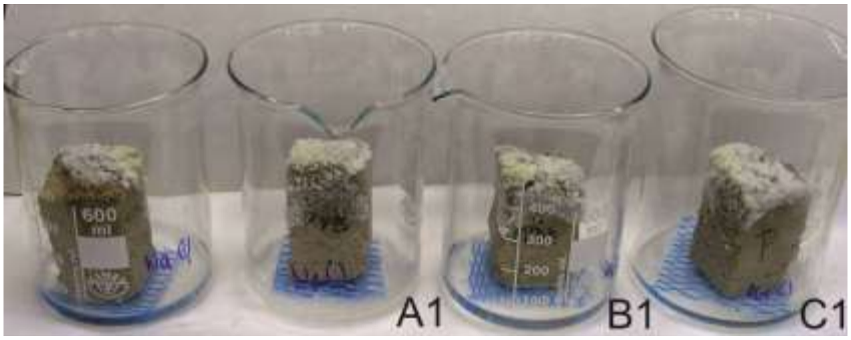

Figure 4. The solution test after 5 days in NaCl: specimen 1 – gothic plaster without a nanotextile; specimen 2 (A1) – gothic plaster with PVB; specimen 3 (B1) – gothic plaster with PVDF; specimen 4 (C1) – gothic plaster with Paraloid B72.

3 CONCLUSION

Nanotextile bonding into the structure of a building material is unsatisfactory in some cases using the subjective test evaluation, in particular in the case of electrospun PAN and PVDF polymers. The nanotextiles based on PVB and Paraloid B72 were, to some extent, bonded into the plaster structure; they showed no change in color and their surface was slightly glossy. However, weak physical bonds were most likely formed.

The results of the tests lead to the conclusion that the efflorescence of salts occurred significantly on the surface of nanotextiles, except for PVB specimens. In the case of specimens with the applied PVB nanotextile, a behavior pattern analogical to specimens of untreated gothic plaster occurred. The efflorescence on test specimens immersed in a 10% NaCl solution had the intensity of weak salt efflorescence (pursuant to ČSN 72 1565 Part 13). The efflorescence on test specimens immersed in a 10% Na_2SO_4 solution had a significantly higher intensity of efflorescence—strong efflorescence of salts (pursuant to ČSN 72 1565 Part 13). The nanotextile itself does not affect the development or the improvement of resistance to salt crystallization.

It may be concluded that the remediation potential of historic plasters using nanofibers and nanotextiles is significantly affected by the choice of polymers and the conditions of their application. Furthermore, we may conclude that the technologies known up to now only allow the application of nanofibers and nanotextiles on a small scale. The above issues will require further research.

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