

POTENTIAL APPLICATIONS OF TRANSPARENT FABRIC BASED ON NANOFIBRES FOR THE STRENGTHENING OF PLASTERS DECORATED WITH PAINTINGS AND FRESCOES

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ABSTRACT

Nanomaterials have been increasingly used in the construction industry in the last decades. Nanomaterials have been tested in specific applications focusing on the restoration and conservation of heritage buildings, mainly their surfaces. Nanofibre materials represent a separate area within this field of research and their applications in the construction and conservation practice are still very limited. The article summarizes the possibilities of strengthening plasters decorated with wall paintings with nanomaterials.

KEYWORDS

Nanotextiles, plasters, paintings, degradation

INTRODUCTION

The surface treatment of buildings, both in the exterior and interior, is an integral part of their appearance and value (Fig.1). Apart from the technical importance of protecting the building and its surface, this treatment has always had an aesthetic function subject to changing trends. In all historical periods, surface coatings have participated in creating the building's appearance adding the final touch to it and improving its surface.

Historical plaster represents a tangible proof of craftsmanship, the degree of technical skills and creates a credible and coherent final appearance of plastered historic buildings. The preservation of historic coatings, plasters or plasters decorated with wall paintings belongs to key issues of top quality heritage conservation. The appearance of each building results from the combination of many components, e.g. the application method, surface treatment, grain size, colour, and, last but not least, the artistic impact, etc. [6]. Numerous techniques of mural painting have developed over the centuries; they can be divided into two basic groups according to the nature of the substrate: paintings on dry plaster and paintings on fresh i.e. wet plaster. According to the type of technique selected for mural painting (buon fresco, secco, Kalkmalerei, tempera, oil, etc.), the required plaster treatment was performed. In the case of mural painting, the readiness and type of the substrate for painting is quite significant – a normal fresh plaster substrate coated with so-called intonaco (final, very thin layer made of a mixture of plaster and fine sand or ground marble dust) sufficed for the traditional, so-called classic, fresco technique, but for the tempera technique the wall had to be previously coated with white pasty sealant (with a spatula) made from e.g. washed chalk or ground gypsum (so-called gesso).



Fig. 1: Bečov Castle – authenticity of plaster surfaces: a) southern facade, b) the Annunciation Chapel, c) corner room in the donjon) stress the genuine historical appearance of buildings

Before taking any preservation or restoration steps, however, detailed historical, construction and technical, conservation and other surveys of plasters and related structures must be done. Based on the results of the surveys, a suitable procedure is selected for the damaged historical surface restoration. The conservation of historic plasters is an interdisciplinary branch combining the expertise of specialists from among architects, designers, heritage preservation specialists, heritage technologists, restorers and, last but not least, craftsmen who perform the restoration [13]. At this point, it must be noted that the restoration of multi-layer plasters should be preceded by the restoration of the historic structure as a whole.

The conservation and restoration of plasters decorated with wall paintings include the performance of many procedures, such as, for example, the consolidation, cleaning, removal of accessories and retouching, cementing, new retouching and others. The application of nanomaterials in some of the above procedures belongs to advanced technologies that are slowly gaining ground in building construction as well. Nanomaterials are made up of a cluster of several thousand atoms and exhibit properties somewhere at the intersection between properties at the level of molecules and matter [1, 8]. This characteristic results from the high surface area of their clusters, which significantly affects the physical and mechanical properties of these systems. Among the benefits obtained from the material nanostructure, there is, for example, high chemical performance, superior plastic, consolidation and diffusion properties, low sintering temperature, cleaning capabilities, etc. It is, therefore, easy to understand that these innovative materials are the subject of major research interest.

It may be assumed and has been confirmed by the research conducted to-date, e.g. in Italy, that applications of nanotechnology in the restoration and preservation of historic plaster surfaces decorated with mural paintings belong to progressive conservation procedures [2, 3, 5]. The used and presently verified technologies for reinforcing plasters include mainly nanosuspensions containing calcium hydroxide nanoparticles and nanomaterials based on barium hydroxide or sulphates [7]. The active substances are dispersed in alcohols, which is also advisable in the technological perspective, as, first, there is no repetitive wetting of surfaces with water, and secondly, their application in relation to the risk of their freezing is not limited. Among the currently already commercially available products there is so-called nanolime - nanosuspension with the trade name “CaLoSil” (in Germany) or Nanorestore (in Italy), which is mainly used for the consolidation of materials containing calcium carbonate (e.g. arenaceous marl, limestone, lime plasters) [11, 12]. The particle size of calcium hydroxide in this nanosuspension ranges from 50 to

200 nm, which creates a limitation in relation to the pore size of the treated material. An indisputable advantage is a significant reduction in impregnation cycles - several applications of nanolime ensures reinforcement which may only be reached after thousands of cycles when using lime water. Nanolime may also be advisably used for the removal of mould, realkalisation of paper, coatings, adhesives, surface layers, preservation of wood, etc.

The success of the consolidation process using nanomaterials is affected by the mineralogical and chemical composition of the treated material, the characteristics of the pore system, surface structure, degree of hardening before the treatment, properties of the active substance in the reinforcing agent (size of ions and particles, chemical composition, concentration, drying and hardening rate, etc.), and, finally, by the temperature and moisture conditions during the application.

Compared to nanosuspensions, nanoemulsions and nanogels, the consolidation of surfaces of historic buildings, mainly plasters or plasters decorated by wall paintings, based on the application of nanotextiles produced by electrospinning falls behind as an unverified technique. Nanotextile is a non-woven fabric, formed by chaotic lying of ultrafine fibres on a flat textile substrate (so-called spunbond) or directly on the surface of the treated material. The best choices for the production of nanofibres are fibre-forming materials, such as polymers and carbon fibres [16]. Nanotextile properties can be further improved by means of additives, e.g. some metals. The application of this composite structure can e.g. enhance the resistance of surfaces against aggressive components of the environment (e.g. bacteria) or their self-cleaning capabilities [4, 14, 15].

MATERIALS AND METHODS

Extensive experimental research is currently running at the Faculty of Civil Engineering CTU in Prague within the NAKI project addressing the possibilities of the consolidation, stabilisation and cleaning of plastered surfaces by means of nanotextiles. The research aims to verify the applicability of nanotextiles and the effectiveness of selected PVB and Paraloid B72 nanotextiles without dopants and PVB and Paraloid B72 nanotextiles doped with Ag and TiO₂ nanoparticles. The research is carried out in the laboratories of the Faculty of Civil Engineering CTU and under in-situ conditions in an agricultural building of the Premonstrate Monastery complex at Teplá.

The specimens of all the above mentioned nanotextiles were prepared in the laboratory of the Pardan Company on the FE production line using the forcespinning technology.

PVB without admixtures was electrospun using the standard forcespinning technology process. In cooperation with the Nanotrade Company, a spinning solution was prepared containing 100mh.ppm of Ag nanoparticles 40-50nm in size, the resulting nanofibre layer has a basis weight of 1.6 g/m². To produce nanofibres with TiO₂ dopants, a 5% Degussa Aeroxid P25 solution was prepared using the Schwego ultrasonic dispergator, the resulting nanofibre layer has a basis weight of 1.6 g/m².

The production process was further modified to electrospin Paraloid B72 where 14.5 g/m² of nanofibres had to be applied to create a solid peelable layer. Ag and TiO₂ dopants were additionally applied onto the Paraloid B72 nanofibre layer with a manual sprayer. In the case of Ag nanoparticles, 588 ppm of Ag were applied onto the nanofibre layer with a basis weight of 10 g/m². The mean concentration of TiO₂ nanoparticles corresponds to 2% of dry matter (polymer and binder) of the nanofibre layer with a basis weight of 10 g/m².

PVB and Paraloid B72 nanotextiles without dopants, the PVB nanotextile with Ag or TiO₂ dopants and the Paraloid B72 nanotextile doped with TiO₂ have light, milky colour. The exception is electrospun Paraloid B72 doped with Ag, which has light, yellow-brown colour and is very brittle (Fig.2).



Fig. 2: a) Paraloid B72 nanotextile doped with TiO₂, b) Paraloid B72 doped with Ag

The plaster samples were prepared 100mm in diameter and 15 mm in thickness to verify the possibility of using nanotextiles for the stabilisation of surfaces treated with colour paint. The plaster composition formula was designed based on the laboratory analysis of a historic Renaissance plaster: 5 kg of dry hydrated lime, 10 kg of river sand - fraction 0-2 mm, 3 litres of water (= dry mixture composition). After drying, the surfaces of the samples were wetted with lime water the day before and immediately before the application and natural colour pigments diluted in water in the shade of blue and ochre by the Picasa Company were applied onto them. Based on the previous testing of adhesives [9, 10, 17], nanotextile specimens were applied onto the lime plaster samples using acetone, ethanol and lime water at a surface temperature of 23° C and a relative humidity of 52%.

Before the nanotextile was applied on the plaster, its surface had been wetted with corresponding solvents and individual nanotextiles on the spunbond were successively applied onto the plaster surface (PVB without nanoparticles, PVB with Ag and TiO₂ nanoparticles, Paraloid B72 without nanoparticles, Paraloid B72 with Ag and TiO₂ nanoparticles). The spunbond was easily removed after the application of the nanotextiles on the coloured surface of the historical plaster.

Subjective evaluation of the effectiveness of the nanomaterial application was performed by simple tests directly on the surface of the samples - visual assessment, the indentation test and the estimate of the depth of consolidant's penetration. In the case of applications by means of acetone and ethanol in laboratory conditions, nanotextiles are not visible on the plaster surface. The plaster surface remains unchanged and no whitish haze is created on its surface. As a result of the dissolution of nanotextiles, surface penetration of the material into the plaster sample occurred. Visible changes are apparent only in cases where lime water was used as an adhesive. In these cases, the nanotextile poorly adheres to the surface of the plaster; it does not exhibit the necessary cohesiveness and falls off.

The nanotextile's integration into the plaster structure is unsatisfactory in some cases. In the case of PVB applications using limewater, the nanotextile's application onto the specimen failed, and in eight cases the nanotextiles dissolved. In nine cases, the nanotextile is visible on the surface, but does not exhibit the required cohesiveness, it peels off, the surface is slightly whitish or the nanotextile is not completely dissolved and remains on the surface of the sample. These problems occur in particular in the case of the electrospun PVB polymer with lime water, PVB with TiO₂ dopants with acetone and lime water, PVB with Ag dopants with lime water, then in the electrospun Paraloid B72 acrylic resin with lime water, Paraloid B72 with TiO₂ dopants with acetone and lime water and Paraloid B72 with Ag dopants with acetone, ethanol and lime water. Satisfactory results in terms of application include PVB nanotextiles with acetone and ethanol, PVB with TiO₂ dopants

with ethanol, PVB with Ag dopants with acetone and ethanol, Paraloid B72 with acetone and ethanol and Paraloid B72 with TiO₂ dopants with ethanol. In these samples, the nanotextiles interlocked with the surface structure of the plaster and there was no discolouration.

CONCLUSION

Based on the results of laboratory tests, we may summarize that working with nanotextiles does not seem promising in applications on historical material or any mature construction material. The application itself remains the fundamental problem: the nanotextile dissolves if an adhesive (acetone, ethanol) is used. In the case of applications using lime water, the adhesion of the nanotextile to the substrate could not be secured – it remained tightly stretched over protruding uneven parts and, therefore, not integrated into the plaster structure. Another problem is the depth of its effectiveness – the nanotextiles remain in layers close to the surface or on the surface. Their effectiveness in relation to the consolidation of historical material is, therefore, negligible or none at all.

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REFERENCES

- [1] BAGLIONI, P., GIORGI, R., DEI, L., 2012. Soft condensed matter for the conservation of cultural heritage, *C.R.Chimie*, Vol.12, p.61-69
- [2] BAGLIONI, P., et al., 2005. Microemulsions and micellar solution for the cleaning of wall paintings, *Studies in Conservation* 50,128–136, <http://dx.doi.org/10.1179/sic.2005.50.2.128>.
- [3] GIORGI, R., et al., 2008. Nanoparticles for Cultural Heritage Conservation: Calcium and Barium Hydroxide Nanoparticles for Wall Painting Consolidation, *Chemistry a European Journal* 16, 9374–9382, <http://dx.doi.org/10.1016/j.culher.2008.06.012>.
- [4] GRAZIANI, L., et al., 2013. Evaluation of inhibitory effect of TiO₂ nanocoatings against microalgal growth on clay brick facades under weak UV exposure conditions, *Building and Environment*, Vol.64, p.38-45
- [5] GRASSI, S., et al., 2007. The conservation of the Vecchietta's wall paintings in the Old Sacristy of Santa Maria della Scala in Siena: The use of nanotechnological cleaning agents, *Journal of Cultural Heritage*, vol.8, no.2, p.119-125
- [6] HOŠEK, J., MUK, J., 1989. *Omítky historických staveb*, ISBN 80-04=23349-x
- [7] CHELAZZI, D., et al., 2012. Hydroxide nanoparticles for cultural heritage: Consolidation and protection of wall paintings and carbonate materials. *Journal of Colloid Interface Science*, <http://dx.doi.org/10.1016/j.jcis.2012.09.069>
- [8] KOTLÍK, P., 2012. Možnosti využití nanomateriálů v památkové praxi, *Sborník semináře Nanomateriály v památkové péči*, STOP, str. 4-9
- [9] KROFTOVÁ, K., ŠMIDTOVÁ, M., 2013. Stabilizace, konzervace a zpevňování historických omítek pomocí nanovláken, conference WTA, Praha

- [10] KROFTOVÁ, K., ŠMIDTOVÁ, M., 2014. Užití nanovláken při obnově historických povrchových úprav – odolnost krystalizujícím solím, conference ISEC, Bankog
- [11] MACHAČKO, L., et al., 2012. Konsolidace historických omítkových vrstev v druhém NP ambitu bývalého kláštera Rosa Coeli v Dolních Kounicích pomocí vápenné nanosuspenze CaLoSiL. Zpráva památkové péče, roč.72, č.2, str.122-128
- [12] MACHAČKO, L., et al. 2012. Testování „nanosuspenzí“ na bázi hydroxidu vápenatého v rámci projektu Stonecore, Nanomateriály v památkové péči, seminář STOP 32–36.
- [13] MICHONOVÁ, D., 2006. Příprava vápenných malt v péči o stavební památky, nakl. ČKAIT Praha, ISBN 80-86769-81-x
- [14] QUAGLIARINI, E., et al., 2012. Smart surfaces for architectural heritage: Preliminary results about the application of TiO₂ based coating on travertine, Journal of Cultural Heritage, Vol.13, p.204-209
- [15] QUAGLIARINI, E., et al., 2013. Self-cleaning materials on Architectural Heritage: Kompatibility of photo-induced hydrophobicity of TiO₂ coatingy on stone surfaces, Journal of Cultural Heritage, Vol.14, p.1-7
- [16] SODOMKA, L., 2009. Jednoduché teoretické úvahy ke zvláknování nanovláken, konference Nanocon.
- [17] ŠMIDTOVÁ, M., KROFTOVÁ, K., 2014. The possibility of using nanotextiles in the restoration and conservation of plaster, conference NANS, Praha