THE CURRENT STATE OF KNOWLEDGE IN THE FIELD OF THE USE OF SELECTED NANOSYSTEMS IN HERITAGE PRESERVATION - NANOTEXTILES AS BIOCIDAL PROTECTION OF HISTORIC WOOD

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ABSTRACT

The awareness of the need to protect wooden members dates back to the Middle Ages when the most common material for the protection of wood was oxblood. At present, there is a huge variety of biocidal chemical agents for wood protection available (such as Lignofix, Bochemit). Nanotextiles represent a novel method of enhanced biocidal protection of historic wood which has been intensively verified at the Faculty of Civil Engineering, CTU in Prague within the NAKI DG16P02M055 research. The paper will present partial results of experimental research into the effects of selected nanotextiles on the surface of historic wood applied for the purpose of biocidal protection. The research included the verification of the efficiency of nanotextiles without dopants and with dopants of Ag and TiO_2 nanoparticles. Surprisingly, a higher biocidal efficiency of nanotextiles without dopants was reached than in the case of nanotextiles with dopants.

INTRODUCTION

The history of nanomaterials dates back to over 1600 years ago – so-called Lykurgus cups of the 4th century AD are known to contain nanoparticles of an alloy based on copper and silver.

Other examples go back to the Middle Ages when glassmakers and potters created a shiny metallic film 200-500 nm in thickness on their artefacts with the content of spherical silver nano crystals (Horská 2011).

One of the first devoted and persistent pioneers in this modern scientific discipline was the American scientist and the Nobel Prize winner for physics, Richard Phillips Feynman, who pointed out the exploitation potential of the world of atoms and molecules in his lectures "There is Plenty of Room at the Bottom" of 1959 and "Tiny Machines" of 1984. Another pioneer in this field was Norio Taniguchi. Taniguchi coined the term nanotechnology denoting a new measurement method allowing the production of parts with a nanometre precision. In the 1970s, these ideas were further developed by the American physicist, Kim Eric Drexler, who suggested using proteins as fundamental building blocks in his article on molecular engineering. In his book called "Engines of Creation – The Coming Era of Nanotechnology" of 1986, he describes the world of miniature systems (nanorobots), which would behave similarly to living organisms having the abilities of self-replicating, mutual communication and self-improvement (Kubínek and Stránská 2011).

The prefix nano comes from Greek from the word nanos which is translated as a dwarf, indicating extreme smallness. A general definition says that nanotechnology is a scientific discipline, a branch of research and development, dealing with purposeful manipulation and use of material structures at a scale of several nanometres (Košťálová 2011). The characteristic size of nano dimensions ranges from 1 – 100 nanometres. In other words, we talk about a dimension of 10^{-9} m, i.e. one billionth of a metre.

A significant characteristic of the nano dimension is a giant growth in the ratio of the surface area to the nanomaterial particle volume. The number of atoms forming the surface of nanoparticles is incomparably higher than the number of atoms inside the particle (Kiliánová 2010). This ratio strongly affects the majority of chemical and physical bonds at the grain boundary in a material. Materials at a scale of nano dimensions, therefore, behave differently, they have different characteristics than materials at a scale of macro dimensions.

Application of nanotechnology in construction and heritage conservation practice

The last 20 years have seen a rapid development and utilization of nanotechnology focusing on a precise control of individual atoms and molecules to create some object (e.g. a chip, thousand times smaller than structures produced up to now with standard technology) or a structure with new characteristics (electrical, optical, physical, etc.) which may be understood and mastered. Nanotechnologies and nanomaterials have presently found their implementation in numerous areas of everyday life from electronics, medicine to the environment (Navrátil 2008).

There are successful applications known in construction as well, even though they exist at a significantly smaller scale than e.g. in medicine or electronics. There are e.g. nano coatings with high resistance to microbial attack by moulds, bacteria, coatings protecting surfaces from soaking, damage by graffiti, soiling, etc., or geopolymers used as plate panels increasing fire resistance, as thermal and sound insulation, or nano plasters protecting the façade from the effects of weathering, temperature fluctuations or solar radiation (Borovcová 2010).

In the conservation of historical materials and structures, however, the application of nanomaterials still lacks behind, although it may be presumed that the exceptional properties of nanomaterials will allow their successful use in the restoration of heritage buildings, too. The application of nanomaterials in the heritage conservation in the last ca 15 years has been verified particularly in the form of nano dispersions and nano suspensions, or nano emulsions whose verified applications cover mainly the cleaning of surfaces of historic monuments (e.g. mural

paintings from 250-600 B.C. in Mexico, in the Acropolis Chik Naab in Calakmul where a nano dispersion-based coating of a mixture of calcium and barium hydroxide nanoparticles was used to remove degraded polymer coatings, (Giorgi et al. 2010), the consolidation of porous limestone-based materials (e.g. historic lime plasters of the 2nd overground storey of the arcaded walk of the former Rosa Coeli monastery in Dolní Kounice where the CaLoSiL E25 calcium hydroxide nano suspension was applied, (Machačko 2012) or the deacidification of valuable artefacts (e.g. a method based on the application of calcium hydroxide nanoparticles dispersed in an organic solvent was used for the removal of the continuously rising acidity of timber in the beams of the Swedish Vasa Warship, (Giorgi et al. 2005)). Calcium hydroxide nanoparticles have also been used to neutralise acetic acid and formic acid vapours, released from oak cabinets of a historic organ. The caustic agents released had caused extensive corrosion degradation of lead pipes (Giorgi et al. 2010).

Some parts of research projects NAKI DF12P01OVV37 "Progressive Non-invasive Methods for the Stabilization, Conservation and Strengthening of Historic Structures and their Parts with Composite Materials Based on Fibres and Nanofibres (2012 – 2015, MK0/DF) and NAKI DG16P02M055 "Development and Research of Materials, Methods and Technologies for the Restoration, Conservation and Strengthening of Historic Masonry Structures and Surfaces and Preventive Care Systems of Historic and Heritage Buildings Exposed to Anthropogenic and Natural Risks" (2016 – 2020, MK0/DG) address the issue of strengthening and stabilization of historic structures by applying carbon fibres and nanotextiles. The research involved the experimental verification of biocidal characteristics of certain historical material such as wood, masonry or stone (Witzany et al. 2008a, 2008b). The results shown presenting a subset of the project are focused on the not yet verified method of the restoration, stabilisation and conservation of historic materials, based on the application of nanofibre textiles produced by spinning. The research projects presently associate the following cooperating institutes: ICT Prague, Faculty of Chemical Technology, Department of Chemical Technology of Monument Conservation, TU Liberec, Institute for Nanomaterials, Advanced Technology and Innovation, and, last but not least, the Pardam Company.

MATERIAL AND METHODS

Nanotextiles

Nanotextiles usually represent "non-woven" material composed of very fine unarranged (acrylic) polymer fibres, which are chaotically laid onto the carrier substrate, so-called spunbond. They are manufactured from a liquid form of an (acrylic) polymer solution or a melt. The nanofibre preparation techniques are based on several methods, such as laboratory drawing of polymer (acrylic polymer or melt) threads from drops or extrusion of a solution through spinning nozzles and generation of small molecules by conjugation. Highly productive techniques are melt-blowing methods for the production of nanofibres and electrospinning for polymers (Doležal et al. 2011).

Two methods were used for the production of nanotextiles within the NAKI research projects. The first method used was so-called Electrospinning, or electrostatic spinning. The principle of this method is the generation of an electrostatic field between the electrospinning nozzle, through which the (acrylic) polymer solution is passed, the collector and the spunbond where the generated fibres are randomly laid after the solvent evaporation or the melt cooling. The second technology used for the production of nanofibre textiles was Forcespinning, or

centrifugal force spinning. In this case, the solution for the production of nanofibres is fed into the spinning head, which spins at high revolutions. By the action of centrifugal force, the material "jets" outside through miniature nozzles and is again deposited onto the spunbond in the form of nanofibres, placed this time under the spinning head.

Experimental research

Experimental research was divided into three basic phases. In the first research phase, laboratory works were focused on setting the demands for the characteristics of nanotextiles and historic wood after the nanotextile application, with a subsequent identification of materials suitable for spinning. Based on identified characteristics, materials suitable for spinning were selected. The second research phase dealt with the application conditions and successive securing of the interaction of the nanotextile layer with the historic wood surface. In the last, third, phase of research, basic experimental laboratory tests were carried out with the aim of the verification of the positive or negative efficiency of the nanotextiles applied on the surface of historic wood.

Specimens of historic spruce wood from the 18th century sampled from the ceiling joists of the Hájčí Dvůr historic building in Prague 5 were prepared for experimental testing with a volume density of 420 kg.m^{-3}, a circular cross section of 6 cm and ca 1 cm in thickness.

1st research phase – Definition of requirements on properties nanotextiles

The criteria for the selection of nanotextiles are very restrictive and, basically, it is impossible to find an ideal material meeting all requirements, both in building technical terms and in terms of the strict criteria demanded by heritage conservation. The selection of nanotextiles must always be carefully considered with respect to the fact onto what material and under what conditions they will be applied.

The initial step which had to be taken before the very production of nanotextiles was to define the requirements for the nanotextiles, but also the material properties for the nanotextile application. These requirements included the following: sufficient cohesion of the nanotextile with the substrate, substrate strengthening, reversibility, resistance to salts (chlorides, sulphates, nitrates, ammonium salts), resistance to biochemical degradation, resistance to moisture and washing away, resistance to dust particles and soiling, resistance to cyclic temperature and moisture loading, resistance to shock temperature and moisture changes, resistance to extreme temperatures, resistance UV radiation, colour stability and removability.

Based on the above requirements and verification tests, three polymers were selected for experimental research: PVB (polyvinyl butyral, solution in ethanol, 10 wt %), PVDF (polyvinyldenefluoride, solution in a mixture of dimethylacetamide and acetone 8:2, 20 wt %) and Paraloid B72 (P) (toluene/acetylacetone solution, 35 wt %), which is commonly used in conservation and restoration practice.

The spinning took place at a temperature of 22°C and relative humidity of 40 %. PVB nanotextiles (the resulting volume density of the nanotextile layer was 1.6 g.m^{-2}) were spun in cooperation with TU Liberec using the needleless electrospinning technology (string on the NANOSPIDER^{TM} NS 4S1000U machine). The used voltage was -15.8 on the collector and +61.2 kV on the string at a traction speed of 10 mm.min^{-1}. The other materials (Paraloid B672 and PVDF) were spun in cooperation with the Pardam Company using the Forcespinning technology (Cyclone F.E.1.1 machine). In the case of spinning the Paraloid B72 acrylic polymer (the resulting volume density of the nanofibre layer was 14.5 g.m^{-2}) and PVDF polymer (the resulting volume density of the nanofibre layer was 4 g.m^{-2}), the materials were extruded through nozzles by centrifugal force to form the structure of submicrone fibres, which were successively

deposited in the chamber under low pressure onto the carrier fabric. The spinneret spinning speed was 6000 rev.min^{-1}, the nanotextile shift speed 0.4 m.min^{-1}. The spinneret height over the textile was 8 cm. The flow through the spinneret was set at 8 ml.min^{-1}.

Numerous problems appeared during the spinning of Paraloid B72. The spun layers dried too slowly, they got stuck onto the winding cylinder, and after drying they were brittle and contained a lot of defects and undrawn thick fibres. The nanofibres of pure PVDF could not be prepared on the production line due to the low stability of the spinning solution and gel formation in the spinning head of the production machine. The specimens had been prepared of the PVDF-HFP copolymer from the Solvay Company with a molecular weight of 670 – 600 kDa, which was more easily soluble and formed more stable solutions (material characteristics of this copolymer are similar to those of pure PVDF). All the above nanotextiles, i.e. PVB, Paraloid B72 and PVDF, were applied onto the carrier substrate, so-called spunbond, which allowed easier nanotextile handling, during production.

Experimental testing also included the preparation of PVB and Paraloid B72 nanotextiles with silver and titanium oxide nanoparticles for the verification of potential biocidal protection effects and cleaning of historic material surfaces.

100 hm.ppm of Ag nanoparticles 40 – 50 nm in size were added in the PVB spinning solution (the resulting volume density of the nanofibre layer was 1.6 g.m^{-2}). To produce nanofibres with TiO$_2$ dopants a 5 % Degussa Aeroxid P25 solution was prepared using the Schwego ultrasonic dispergator. The average size of original nanoparticles was 21 nm (the resulting volume density of the nanofibre layer was 1.6 g.m^{-2}).

Some complications occurred during the preparation of doped spinning solutions of Paraloid B72, which was incompatible with the Ag and TiO$_2$ nanoparticle dispersion components, and the polymer coagulated after mixing. The Paraloid B72 nanofibre layers were additionally functionalised by applying a nanoparticle dispersion containing a binder for their attachment to the nanofibre surface. The application was manual by means of a sprayer. In the case of the Ag nanoparticle application, 200 g of a dispersion with a concentration of 50 hm.ppm of Ag nanoparticles and 1 % of a binder (sodium silicate) was gradually applied onto a surface area of 1.5 m^2 of the nanofibre layer with a volume density of 10 g.m^{-2}. In the case of the TiO$_2$ nanoparticle application, 35 g of a dispersion with a concentration of 0.87 of TiO$_2$ nanoparticles and 0.48 % of a binder was gradually applied onto a surface area of 1.5 m^2 of the nanofibre layer with a volume density of 10 g.m^{-2} (Tab. 1).

Tab. 1: List of tested nanotextiles.

Sample identification	Polymer	Dopants	Nanofibre layer (g.m^{-2})
PVB	PVB	withour dopants	1.6
PVB + Ag	PVB	100 hm.ppm Ag	1.6
PVB + TiO$_2$	PVB	5% TiO$_2$	1.6
P	Paraloid	without dopants	14.5
P + Ag	Paraloid	50 hm.ppm Ag	10.0
P + TiO$_2$	Paraloid	2% TiO$_2$	10.0
PVDF	PVDF-CTFE	without dopants	4.0

PVB, PVDF and Paraloid B72 nanotextiles without dopants, PVB nanotextiles with Ag and TiO$_2$ dopants and Paraloid B72 nanotextiles doped with TiO$_2$ nanoparticles have a pale, milky to white shade. The exception is the nanotextile produced by the spinning of Paraloid B72 doped with Ag, nanoparticles, which has a light yellow to ochre shade and is very brittle.

2nd research phase – Adhesives

The subject of the second phase of experimental research was the specification of substances, or adhesives respectively, for the application of nanotextiles onto the surface of historic wood. The adhesion of the nanotextiles themselves to the surface of historic wood   without adhesives was very poor or zero. In order to secure the adhesion of the nanotextile to the spunbond a total of 8 agents were originally tested in cooperation with ICT: acetone, ethanol, water, lime water, dimethylformamide, xylene, polyvinylacetate dispersion and Veropal UV40.

The laboratory verification of the nanotextile adhesion to the surface of historic wood was carried out under laboratory conditions at a temperature of 23°C and relative humidity of 52 %. To secure the nanotextile (PVB, P and PVDF without/with dopant(s)) adhesion to the surface of historic wood the upper part of the tested specimen was fitted with the respective adhesive (acetone, ethanol, etc.) with a brush, and, successively, the nanotextile was applied and pressed in with a sponge. The visual assessment of specimens was primarily concentrated on the nanotextile optical clarity, nanotextile shrinkage, nanotextile adhesion rate or the dissolution of fibres.

Based on the first results of adhesion tests (Tab. 2), only the adhesives: acetone, ethanol and lime water were used for further experimental tests. In the other cases, the nanotextiles had neither adhered to the historical specimen surface, nor reacted with the adhesives, the nanotextiles had remained unchanged.

Tab. 2: Results of nanotextile adhesion to historic wood surfaces.

	Acetone	Ethanol	Lime water	Water	Dimethyl-formamide	Xylene	Polyvinyl acetate dispersion	Veropal Uv40
PVB	5	5	4	0	0	0	0	0
P	5	5	3	0	5	5	0	0
PVDF	5	0	3	0	1	0	0	0

Legend:

0 – nanotextile neither adhered nor reacted with the solvent, the nanotextile remained unchanged

1 - nanotextile partially dissolved without adhering to the test specimen

2 – nanotextile was not trasnferred onto the test specimen, it was etched, contracted or damaged

3 – nanotextile was transferred onto the test specimen, but it did not adhere to it over its whole area, a visible milky layer

4 – nanotextile adhered to the plaster structure over the whole area, the layer is slightly whitish

5 – nanotextile adhered to the specimen structure over the whole area and the nanotextile layer became transparent (the nanotextile had dissolved).

It is evident from the results of adhesion tests (Fig. 1) of the nanotextiles with acetone, ethanol and lime water and scanning electron microscopy that in the case of using organic adhesives (except for the PVDF nanotextile with ethanol), the fibres dissolved into the wood structure after the nanotextile application thus changing its matter.

PVB			Paraloid B72			PVDF		
Acetone	Ethanol	Lime water	Acetone	Ethanol	Lime water	Acetone	Ethanol	Lime water
reference sample n.1	reference sample n.2	reference sample n.3	reference sample n.4	reference sample n.5	reference sample n.6	reference sample n.7	reference sample n.8	reference sample n.9
not visible	not visible	visible surface lightly whitish	not visible	not visible	visible	not visible	visible surface whitish (brittle)	visible surface whitish (brittle)

Fig.1 : Results of nanotextile application on historic wood surfaces.

No change in the colour of the wood specimen occurred visually. In the case of the applications with lime water and ethanol (in the case of the PVDF nanotextile), the nanotextiles failed to integrate into the wood structure. The nanotextiles remained on the specimen surface where they formed a milky to white layer affecting significantly the appearance of historic wood (Fig. 2).
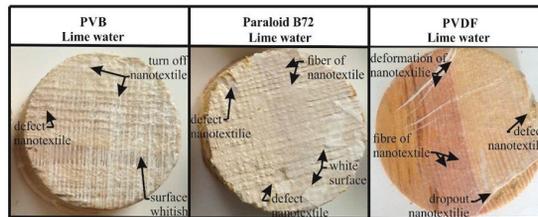
Fig. 2: Details of nanotextile application on historic wood surfaces with lime water.

The results of the adhesion of nanotextiles with Ag and TiO_2 dopants were similar to the case of nanotextiles without dopants. Using organic solvents caused the dissolution of nanotextiles into the wood structure in the case of PVB and P nanotextiles. No change in colour occurred visually. In the case of lime water, the nanotextiles failed to integrate into the wood structure (Fig. 3).

PVDF			PVDF + TiO₂			PVDF + Ag		
Acetone	Ethanol	Lime water	Acetone	Ethanol	Lime water	Acetone	Ethanol	Lime water
reference sample n.7	reference sample n.8	reference sample n.9	reference sample n.22	reference sample n.23	reference sample n.24	reference sample n.25	reference sample n.26	reference sample n.27
not visible	visible surface whitish (brittle)	visible surface whitish (brittle)	dissolved the remains of nano	non-adhered	visible the remains of nano	not visible	visible non-adhered (bright ochre)	rozpuštěná zbytky (dark ocher)

Fig. 3: Results of PVDF nanotextile application with dopants on the surface of historic wood with lime water.

Visible changes occurred in the case of using the PVDF nanotextile. In one case of using acetone, i.e. the PVDF nanotextile with Ag dopants, the nanotextile was dissolved. In the case

of using ethanol and lime water, the nanotextiles remained on the specimen surface. Changes in colour occurred in PVDF nanotextiles with Ag dopants where the specimen surface turned into a light ochre to dark ochre shade (Fig. 4).
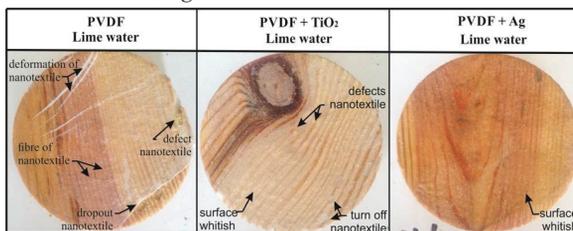

Fig. 4: Details of PVDF nanotextile application with dopants on the surface of historic wood with lime water.

3rd research phase – Experimental tests

In the 3rd phase of research, basic experimental tests were performed. Historic wood was tested for changes in colour after the application of nanotextiles, changes in colour after UV exposure, changes in colour after the removal of nanotextiles, removability of nanotextiles by means of infrared spectroscopy and by means of the contact angle measurement and the verification of a potential increase in the biocidal efficiency of nanotextiles.

Biocidal efficiency of nanotextiles

The specimens for testing the biocidal efficiency of nanotextiles were fitted with nanotextiles (PVB, P and PVDF) using selected adhesives (acetone, ethanol, lime water) and applying the identical procedure (see 2nd research phase – Adhesives). The specimens prepared in this way were put in Petri dishes in the FCE CTU laboratory; the Petri dishes contained a preinfected nutrient broth produced on the basis of in-situ sampling from the Premonstrate complex at Teplá. In the laboratory, the specimens were placed in the BT120 biological thermostat at a temperature of 24°C and humidity of 95 %. The growth of mould was monitored for a period of two or three weeks (Figs. 5, 6).

Fig. 5: Results of biocidal efficiency of nanotextiles without dopants.

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Reference sample	PVB Lime water	PVDF Ethanol	PVB Ethanol	PVDF Acetone
45%	4%	4%	5%	6%
Clean sample great develop. od mold	Surface whitish small develop of mold	Non visible small develop of mold	Non visible small develop of mold	Non visible small develop of mold

Fig. 6: The best results of biocidal efficiency of nanotextiles without dopants.

To be able to compare the results, a reference specimen of wood with no nanotextile application was prepared. In the reference specimen of wood (i.e. untreated wood), the total growth of mould had affected roughly 45 % of the specimen area. It is evident from partial results of the biocidal efficiency of nanotextiles reached that the nanotextiles without dopants positively affected, i.e. improved, the biocidal efficiency of wood.

The best results, i.e. a low growth of mould, was reached in the case of:
- PVB nanotextiles with lime water and PVDF with ethanol where the mould had spread over ca 4 % of the specimen area,
- PVB nanotextile with ethanol where the specimen surface had been covered with mould in 5 % and
- PVDF nanotextile with acetone where the mould growth had been found in 6 % of the specimen area (Fig. 6).

In a similar way, the test specimens of wood were fitted with nanotextiles (PVB and P) with Ag and TiO$_2$ dopants. The specimens were successively placed in Petri dishes with a preinfected nutrient broth and the growth of mould was monitored for a period of two to three weeks (Figs. 7, 8).

Fig. 7: Results of biocidal efficiency of PVB nanotextiles with Ag and TiO$_2$ dopants.

	10.10.2014			16.10.2014			24.10.2014		
	Aceton	Ethanol	Lime water	Aceton	Ethanol	Lime water	Aceton	Ethanol	Lime water
P + Ag	non visible	non visible	surface whitish	non visible no mold	non visible development of mold	destruction of nanotextiles no modl	non visible small develop of mold	non visible great develop of mold	destruction of nanotextiles small - modl
P + TiO₂	non visible	non visible	surface whitish	non visible no mold	non visible no mold	destruction of nanotextiles no modl	non visible small develop of mold	non visible small develop of mold	destruction of nanotextiles great - modl

Fig. 8: Results of biocidal efficiency of P nanotextiles with Ag and TiO$_2$ dopants.

- in the case of PVB nanotextiles with Ag dopants, the biodegradation results were similar to the reference specimen, i.e. neither an improvement nor a significant deterioration in the biocidal efficiency of historic wood occurred. The growth of mould ranged around 43 – 44 % of the specimen area (Fig. 9),

PVB + Ag Ethanol	PVB + Ag Lime water	PVB + Ag Acetone	P + Ag Ethanol	P + TiO₂ Ethanol
43% Non visible great develop. of mold	43% Surface whitish great develop. of mold	44% Non visible great develop. of mold	48% Non visible great develop. of mold	50% Non visible small develop of mold

Fig. 9: Worst results of biocidal efficiency of nanotextiles with dopants.

- PVB nanotextile with TiO$_2$ dopants had positively affected the biocidal efficiency of the specimens compared to the reference specimen. The growth of mould over the specimen area ranged within 23 – 35 %,
- in the case of P nanotextiles with Ag dopants, the biocidal efficiency (18 % growth of mould) improved in two cases (acetone, lime water) compared to the reference specimen.
- in the case of P nanotextiles with Ag dopants with ethanol, the biocidal efficiency deteriorated compared to the reference specimen where the growth of mould had covered 48 % of the specimen area.
- P nanotextiles with TiO$_2$ dopants (acetone, ethanol) positively affected the biocidal efficiency of the specimen compared to the reference specimen, the growth of mould accounted for 10 %.

Fig. 10: Evaluation of the results of biocidal efficiency of nanotextiles.

- in the case of the P nanotextile with TiO_2 and lime water, there was a significant deterioration in the biocidal efficiency against the reference specimen (50 % growth of mould) (Fig. 10).

RESULTS AND DISCUSSION

The experimental verification of the bond strength of nanotextiles on the surface of historic wood was carried out under laboratory conditions and manifested the unsuitability of some adhesives (dimethylformamide, xylene, polyvinylacetate dispersion and Veropal UV 40). Selected nanotextiles (PVB, PVDF and Paraloid B72 without/with dopant(s)) were subsequently subjected to laboratory tests focused on the verification of the biocidal efficiency of nanotextiles.

The partial results reached allow us to state that the results of the adhesion rate and biocidal efficiency of nanotextiles are significantly affected by the selection of (acrylic) polymers, adhesives (acetone, ethanol, lime water) and the method or conditions of their application.

The analysis of the results of the biocidal efficiency of nanotextiles has manifested that the nanotextiles with Ag and TiO_2 dopants reached a far lower biocidal efficiency than in the case of "pure" nanotextiles, i.e. nanotextiles without dopants. The best results of the biocidal efficiency of nanotextiles were reached in PVDF + E, PVB + LW,

PVB + E and PVDF + A nanotextiles where the biocidal efficiency of the above nanotextiles was by 91.2 – 86.7 % higher compared to the reference specimen. The dopants themselves, which caused that the nanotextiles "became brittle", cannot be ruled out as the reason for the deterioration in the brittle", cannot be ruled out as the season for the deterioration in the biocidal efficiency of nanotextiles with nanoparticles.

We may also conclude that the up-to-now known technologies allow the application of nanofibres and nanotextiles only to a very limited extent as they are difficult to handle. Futher research should be focused on the nanotextile application methodology.

CONCLUSIONS

The objective of the research was the verification of existing knowledge and the design of a new method for the protection of historic materials by nanotextile surface treatment preserving

the characteristic material properties to stop or significantly eliminate degradation processes and thus extend their service life. In the case of nanotextiles (unlike nano suspensions or other agents), the situation is serious with respect of the issue of the interaction of the nanotextile and the substance by means of which it is applied onto the surface and meeting all the requirements set by present-day heritage conservation. It is evident that the nanotextile application process onto the substrate and the use of nanomaterials and nanotechnologies in heritage conservation will go through a series of further laboratory and verification steps. The finding and identification of suitable combinations of (acrylic) polymers and applicators could lead to the practical usage of nanotextiles in construction and heritage conservation practice.

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