VERIFICATION OF THE USE OF PVA BASED NANOFIBER TEXTILES AS A REHABILITATION FOR THE STRUCTURES ATTACK BY WOOD DECAYING FUNGI

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Abstract
Timber structures and components made of wood are used worldwide and their popularity is still increasing, especially in developed countries. The problem of newly built, but mainly of the historical monuments is that they suffer from degradation caused by wood decaying fungi. As a result, the attacked structures lose their load-bearing capacity, which is not only dangerous, but decreases the aesthetic value. The presented paper is focused on the investigation of antifungal properties of nanofiber PVA-based textiles with incorporated copper and silver ions. In particular, the ability to prevent the growth of Dry rot fungus (Serpula lacrymans) was studied in laboratory conditions. For that purpose, the Petri dishes with malt agar were inoculated with square cut-outs of seed stocks, consequently covered by the nanofiber textiles and kept in an incubator at 28 °C. The fungal growth has been monitored and recorded at regular intervals for 28 days. The comparison of the individual treatments (PVA, PVA + Ag, PVA + Cu, PVA + Ag + Cu) is finally discussed.

Keywords: Nanofiber textiles, Dry rot fungus, PVA, metal ions

1. INTRODUCTION
The antimicrobial surface treatment of building materials is the current problem encountered in building industry [1]. Specific material in this regard is wood, since it is very popular all over the world and struggles the attacks by various bacteria, algae and fungi. Wood-decaying fungi represent a separate group of biodeteriogens. One of the most dangerous kind of wood-decaying fungi is Dry rot fungus. There have been developed many kinds of more or less successful protections of wood against wood-destroying fungi and other degradation phenomena, which have been used for thousands of years. However, the proper design of structural details has proven to be the most successful [2].

The protection of wood against wood-decaying fungi is possible to accomplish in several ways, paintings and penetrations are among the oldest. The ancestors also tried to eliminate the contact of timber elements wet environment or changing moisture [3]. Nowadays, there are emerging new types of protection, e.g. nanofiber textiles augmented by incorporated nanoparticles. The textiles can be produced of various polymers, based on required properties. Their properties may be further enhanced and modified by the addition nanoparticles, such as nanodiamonds, or Ag, Cu or Ti ions [4,5,6,7].

Because of the specific and extraordinary properties of nanofiber textiles, such as low weight per unit area or large specific area, it is possible to apply the nanofiber coating directly on the surface of the protected materials. This layer creates a thin film, since the fibers are only 100-500 mm thin [8], a therefore the host material (e.g. wood) does not lose its color or texture. According to our, yet unpublished, the application of textiles having their weight higher than 5 g/m² can be considered in the case of materials commonly used in the building industry [9].

The incorporated particles within the polymer-based nanofiber textiles are, due to the large specific area of the substrate textile, very effective even at low concentrations [10]. Last but not least mentioned advantage of the use of nanofiber textiles for the application of antibacterial or antifungal agents is that they can carry aggressive agents that could damage the protected material if applied directly [11].
Currently available open literature does not deal with the application of nanofibers with dispersed particles for the purposes of timber protection against wood-decaying fungi. On the other hand, the exploitation of nanoparticles to improve the properties of timber is extensively studied and it is assumed that this area has a huge potential for the future use in the industry [6,11].

2. MATERIAL

The PVA-based nanofiber textiles were spun and tested at the Center for Nanotechnology in Civil Engineering, at the Faculty of Civil Engineering, Czech Technical University (CTU) in Prague, Czech Republic. For the needleless electrospinning the device NS Lab 500 device was used, in particular the laboratory version of this equipment, with the 600 mm wide cylinder rotating electrode. The nanofiber textiles were prepared at common laboratory conditions at the temperature of 23°C and relative humidity of about 40 %. The nanofibers themselves were spun on a polymeric support textile substrate. A polypropylene (PP) base substrate with the width 500 mm, weight of 18 g/m² and an antistatic treatment was used. The reference plain PVA polymer and PVA polymer with incorporated metal ions were prepared for the analysis. In particular, there were prepared three PVA-based textiles with silver ions, with copper ions and also those with copper and silver ions together.

The basic solution for electrospinning was prepared from PVA polymer, for that purpose a commercial product was used. The solution consisted of the following items: 375 g of PVA (Sloviol 16 %), 117 g of demineralized water, 4.4 g of glyoxal, and 3 g of phosphoric acid (75 %). Glyoxal and phosphoric acid was used as cross-linking agents and for better consistency of the solution [12].

The active nanoparticles particles were added into plain PVA solution in the form of metal ions. For that purpose the particles were obtained by dissolving the silver (Ag) – and copper (Cu) – based compounds in water and then dispersed within the polymer solution. The silver ions were extracted from a silver nitrate (AgNO₃) and the cooper ions from a pentahydrate of copper sulphate (CuSO₄·5H₂O). UV sonification was used three times for the period of one minute to prevent clustering. Finally, it was necessary to thermally stabilize all the spun nanofiber textiles before their use. The stabilization was accomplished by exposing the samples to the temperature about 140°C for 10 minutes [7].

3. EXPERIMENTAL METHOD

Dry rot fungus was chosen as the model organism. It is a frequent wood-decaying fungi, famous for its ability to reproduce easily and destroy timber structures when infested. Square segments of area 100 mm² were extracted from the host fungus. These samples were placed into the sterilized Petri dishes with malt agar (Sigma-Aldrich, Germany). By this way the sample was allowed to grow and circular samples of area 490 mm² were produced.

The samples of the infested material were finally covered by the nanofiber textiles with the treatment of by metal ions and prior to that, the supporting textile that strengthens the nanofibers before their application was removed. A schematic composition of studied Petri dishes is shown in Fig. 1.
The infested material was incubated at the temperature of 28 °C and the growth of fungi was regularly monitored in two- to three-day intervals for the period of one month. The data from the monitoring are summarized in Tables 1 and 2. The provided data from the 6th, 16th and 25th day are related to the day of textile application. The photo documentation was complemented by the measurement of the growth of fungi inside the dishes, with the initial length of 10 mm. The maximum length of the attacked are reached up to 90 mm which represents fully infested dish and the measurement was stopped at that moment, while the photo documentation was done beyond that limit.

The measurement was carried out also on the samples without any treatment or covering. All types the treatments were represented by three samples, the scheme of the investigated materials is depicted in Fig. 2.
4. RESULTS AND DISCUSSION

The results presented in Fig. 3 indicate that the application of nanofiber textiles influences the growth of Dry rot. All types of investigated nanofiber textiles exhibit antifungal properties and therefore inhibited the growth and development of fungi. In the beginning the textile itself created a barrier for the growth and the largest antifungal effect was reached in case of textiles enriched by the silver and copper ions.

On the other hand the plain PVA-based textile without any fungicide agents had no effect on the development of the fungi. The fungicide agents appeared to be most effective in the initial phase of the fungi development and their affectivity when applied directly or using nanofiber textiles is the same [3, 6].
However, if the medium is rich in nutrients and the infested material is placed in optimal environment, the concentration of the agents appears to be too low. Also the methodology for the assessment of the protective ability has to be also established for future research. The above described study and results should contribute to the development of methods and methodology for the application of nanofiber textiles on-site. Therefore, the future research will be focused on the investigation of the protective properties of enhanced textiles on the timber structures and elements exposed to outdoor environment.

Table 2 Photo documentation of the experiment; growth of dry rot

<table>
<thead>
<tr>
<th>Sample/Day</th>
<th>6th</th>
<th>11th</th>
<th>25th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag + Cu</td>
<td><img src="image1.jpg" alt="Image" /></td>
<td><img src="image2.jpg" alt="Image" /></td>
<td><img src="image3.jpg" alt="Image" /></td>
</tr>
<tr>
<td>Control sample</td>
<td><img src="image4.jpg" alt="Image" /></td>
<td><img src="image5.jpg" alt="Image" /></td>
<td><img src="image6.jpg" alt="Image" /></td>
</tr>
</tbody>
</table>

Fig. 3 Dependence growth of dry rot on time
5. CONCLUSIONS

The PVA-based nanofiber textiles with incorporated ions to give the textiles antifungal character were prepared and investigated. The study was focused on the ability of individual agents to inhibit the growth of commonly encountered Dry rot fungi. It appears that the use of the textiles for remedy on the existing infested structures. On the other hand, the textiles could be easily used as prevention without any impact on the appearance and texture of wood. The fungicidal properties of the PVA-based textiles were observed only in the case of the nanofibers with incorporated particles, and in a limited time period without the desired killing effect. However the initial barrier properties were clearly observed and that could provide a reliable protection of newly built structures.

ACKNOWLEDGEMENT

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LITERATURE