MODIFICATION OF CEMENT PASTE SURFACE USING NANOFIBERS BASED ON POLY(VINYL-ALCOHOL) (PVA)

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Abstract
The difference in size of nano- and macro-materials (or in their volume) is an obstacle for the application of nanofibers in civil engineering. The synergy of these scales can be utilized when macro-material surface is protected by nanofibers. The proposed experiment investigated the possibility of utilizing the nanofiber textile on cement-based materials. The surface of fresh cement paste was coated by Poly(vinyl-alcohol) (PVA) based nanofibers. Nanofiber textiles were laid in three different weights per unit area (namely 0.1, 5.0 and 10.0 g/m²). The weight loss due to water movement through the material surface was monitored for the first 28 days. Reference samples without nanofiber coating were monitored for comparison as well. All the measurements took place in a laboratory environment and it is obvious from the results that there is no influence of nanofibers on cement paste drying. The surface of samples was optically investigated after the first experiment and in case of higher nanofiber weights per unit area there was an observable shrinkage of the nanofiber coating. The images from electron microscope also confirmed the interaction between the cement paste and the nanofibers. Thicker nanofiber coatings (>10 g/m²) could be peeled off from the samples, unlike those having a smaller weight, being perfectly attached.

Keywords: Nanofiber, electro-spinning, cement paste, surface protection, coating

1. INTRODUCTION
Surface protection of various materials or products has been developed since the ancient times. In most cases its purpose is to protect the surface from the negative effects of environment without need to modify the entire volume of the protected material and therefore to reduce costs. For this purpose nanofiber textiles made of various materials are used in many industries [1]. Needleless electro-spinning can be utilized, allowing to prepare the nanofiber samples in a big volume (or area) and thanks to the increasing popularity of nanotechnology in the recent years it became quite cheap. Therefore, the price of the final product is nowadays comparable to the price of commonly used materials.

The nanofiber textiles are widely utilized also in biomedicine, where the Poly(lactic-co-glycolic acid) based nanofibers can be exploited for the growth of cells [2, 3]. According to a comprehensive literature study it seems that nanofibers have not been, with a few exceptions, used for the surface protection of porous building materials. Poly(vinyl-alcohol) based polymers are most often used for the electrospinning and they seem to be as suitable choice for such application mainly because of their relatively low price and solubility in water. PVA is commercially available in the form of water solution or in a solid state [1].

The influence of the PVA protection coating has been investigated on composite wood-based materials. This research was focused on an influence of nanofibers on the material surface and its relative humidity [4]. Otherwise, the nanofibers are used in civil engineering rather as an additive to the building materials in order to modify or improve their properties. Nowadays, most of the nano-research is focused on improvement of concrete, into which the nanoparticles added in order to reach a higher strength and durability. The use of nanoparticles and nanofibers in a cement matrix as randomly distributed nano-reinforcements helps to prevent crack initiation during the concrete hydration and drying shrinkage. Such reinforcement should cause
an elimination of micro- and macro-cracking, which is very common phenomenon in the cement based materials and causes strength reduction and also limited durability of concrete structures. The effort to suppress the concrete cracking by the addition of PVA-base nanofibers into the cement matrix was most successful when all the fibers had the same properties, geometry and were uniformly distributed [5]. The number of fibers and their distribution in the cement-based composites were microscopically investigated on the samples containing fluorescent fibers [6]. The interaction of PVA fibers with the cement-based material and their bond have been investigated rather on a macro-level. The three-point bending tests focused on the investigation of crack development were carried out, using the fibers of different length, diameter and volume. It was found that the composites containing 2% of fibers per volume of a higher average length (12 or 24 mm) and 1% having smaller average length (6 mm) showed the best results [7].

The solubility of PVA in water introduces a difficulty; the PVA-based nanofibers have to be stabilized before their use and preferably immediately after their production. There are two ways of stabilization — the first possibility is using physical stabilization and the second possibility is to use a technique called cross-linking. During the physical stabilization the nanofiber is exposed to the temperatures higher than 140°C. On the other hand, cross-linking is a chemical stabilization when the nanofibers are after their production submerged into methanol and methanol-glutaraldehyde. The latter approach seems to be more advantageous if a high biocompatibility is not required, because the morphology of the fibers is not altered [8].

From the above it follows that the compatibility between materials should be ensured, as it is in case of nanofibers blended with cement paste [9], if the PVA nanofibres are applied on the surface of cement-based materials. It also follows that the susceptibility to damage by humidity should not be a big obstacle.

2. MATERIALS AND SAMPLES

The nanofiber textiles of different weights (0.1; 5 and 10 g/m²) were spun at the Center for Nanotechnology at Faculty of Civil Engineering, Czech Technical University in Prague, using the NanoSpider device Elmarco NS Lab 500 S. This equipment produces randomly oriented electro-spun nanofiber textiles suitable for research purposes.

The solution of PVA for electro-spinning was prepared in a volume of 500 ml, which is corresponding to the volume of one cathode beaker. This volume contains 375 g of PVA (produced under the brand name Sloviol 16%), into which the other substances are added during the continuous stirring: 117 g of distilled water, 4.4 g of glyoxal and 3 g of phosphoric acid (75%). Glyoxal and phosphoric acid were used as the agents for cross-linking and the PVA-based nanofiber textiles were finally stabilized in elevated temperature approximately 140°C (exposition time 10 minutes) [8]. The nanofiber itself was spun on a polymeric supporting substrate (spunbond) made of polypropylene (PP) with an antistatic treatment and having the weight of about 18 g/m².

The electrode width in the spinning device was 600 mm, distance between electrodes 126 mm, spinning voltage 70 kV, substrate (spunbond) frequency 10 Hz, and electrode frequency 8 Hz. The nanofiber textiles were prepared continuously on the substrate of width 500 mm.

The temperature during the preparation of the cement paste samples, onto which the nanofiber textiles were applied, was 22 ± 1°C and relative humidity 31 ± 3%. Six different sets of samples were tested, denoted A (samples without surface treatment and being the reference samples), B (samples with the spunbond only), C (samples with the nanofibers and the spunbond above the nanofibers having the weight of about 0.1 g/m²), D (samples with the nanofibers, having the weight of about 5 g/m², and the spunbond), E (samples with the nanofibers, having the weight of about 10 g/m², and the spunbond), and finally F (samples with the nanofibers of thickness of about 1 mm, applied on a free surface of the tested samples). The nanofiber textiles of the higher weights per unit area were made as double-layered.

The tested cement paste samples were prepared from the ordinary Portland cement, CEM 42.5 R (Mokrá, Czech Republic). The water/cement ratio was set to 0.41; the mixing was carried out by hands. The cement
paste was placed into cylindrical containers having the diameter 100 mm and depth 15 mm, and into the forms with the following dimensions 20 x 20 x 100 mm. Surface of the tested samples was modified using the nanofiber textiles or the nanofiber textiles with the spunbond.

The PVA nanofiber textiles laid on the fresh cement paste samples were cut off the spun textile. Immediately afterwards the water from the paste samples soaked through the textiles and PP spunbond, ensuring the adhesion to the paste samples. Finally, the samples were cured at the laboratory conditions at the temperature 20 ± 2°C and relative humidity 40 ± 2%.

The specification of the samples is summarized in Tab. 1. The mass of the nanofiber textiles was determined using high precision scale and the weights per unit area were determined from the known mass and area of the samples [10]; the standard deviation was approximately 4%.

### Tab. 1 Specification of tested samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Surface coating</th>
<th>Nanofiber textile [g.m⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>B</td>
<td>spun bond</td>
<td>none</td>
</tr>
<tr>
<td>C</td>
<td>spun bond with the nanofiber textile</td>
<td>0.1</td>
</tr>
<tr>
<td>D</td>
<td>spun bond with the nanofiber textile</td>
<td>5</td>
</tr>
<tr>
<td>E</td>
<td>spun bond with the nanofiber textile</td>
<td>10</td>
</tr>
<tr>
<td>F</td>
<td>1 mm layer of PVA</td>
<td>none</td>
</tr>
</tbody>
</table>

### 3. METHODS AND RESULTS

The first experiment carried out on the samples was a measurement of the weight loss in the individual samples. After their production, the samples were stored in the laboratory conditions as described above and their weight loss was monitored for the first 28 days using the scales with the accuracy 0.01 g. The weight development can be clearly seen in Fig. 1, the standard deviation of the measured data was about 5%. From the obtained values it is obvious that the coating does not have almost any influence on the weight development during the first 28 days.

For the other experiments the spunbond was removed from the samples. It was easily possible in all the samples except B, where the spunbond became interconnected with the cement paste and it had to be removed mechanically from the paste surface. Some of the PP fibres from the spunbond remained fixed in the surface of the B samples and the pattern of the PP spunbond was imprinted into the surface. None of the tested samples contained cracks and the samples were not damaged due to cement paste shrinkage.

It could be observed that the PVA nanofiber textiles became incorporated into the surface of the cement paste in the samples C to E. Unlike in the other samples, a difference in paste and fibre expansion could be observed in the sample E, being covered by the textiles of weight about 10 g/m² (Fig. 2). The separation and shrinkage of the PVA nanofiber textile on the E samples was probably present immediately after the application of the textile with a spunbond on the fresh paste surface. This phenomenon was probably caused due to high moisture content and different expansion of the PP spunbond and PVA textile, having relatively high thickness. The rate of shrinkage was approximately 17 mm/m ± 8%.
In another experiment the surface of the E samples of cement paste and separated textile (having the weight 10 g/m²) were investigated using the electron microscope. On the samples covered by the lighter textiles it was not possible to extract the nanofibers from the hardened cement paste (after 28 days) – the textile became inseparable part of the samples. This can be explained by consideration of the forces acting against each other – one force holds the textile attached to the hardened cement paste and the other force, caused by the differential expansion, tends to separate the layers. The latter force is higher with the increasing weight of the textiles. There are the same phenomena on the interface between the nanofiber textile and the cement paste surface as in the case of cement matrix reinforced by PVA nanofibers [6, 7].

It was observed during the scanning electron microscopy (SEM) analysis (the electron microscope XL ESEM TMP Philips) that the nanofiber textile transformed into a PVA-based coating, which was compact and without characteristics of a textile [11, 12]. This was probably caused by the high moisture content in the surface layer of the cement putty and consequent segregation of the cement and water in the very acid
environment (pH up to 13) typical for cement-based materials during setting and hardening. Even though the nanofibers were stabilized [8], they degraded and dissolved in the water solution with the high pH value [13]. Among other phenomena, growing of hydration products through the nanofiber could be observed, see Fig. 3. It gives an evidence about the compatibility between the cement matrix and PVA-based materials. The interface between the paste and PVA coating can be also clearly seen in Fig. 3. The surface of the cement paste in the figure is disturbed by the separation of the PVA layer from the cement matrix. The interconnection between the cement matrix (its hydration products) and nanofibers can be observed in Fig. 4 (left) on the reverse side of the PVA layer.

Fig. 3: Front side of PVA nanofiber textile (left), interface between PVA nanofiber and cement paste

Fig. 4: Reverse side of separated PVA textiles (left), cross-section image of separated PVA textile (right)

4. CONCLUSIONS

The presented results indicate that the utilization of nanofiber textiles in civil engineering might be possible. In particular the PVA based textiles used as a protection coating on the cement paste were investigated and tested. It follows from the study that PVA-based materials can very well interact with a surface of cement-based materials, however, if the material is not suitable (e.g. PLGA) the nanofiber textile does not form a continuous coating, but instead retains its original properties.
The use of nanofibers for the protection coating on cement-based materials has a great potential, but a comprehensive research is needed in this area. The basic task for a real life application is the choice of the most suitable polymer for different types of surfaces and materials (lime, cement, gypsum, or combination of these materials). Also the negative factors of the external environment, such as wind, high humidity or UV radiation, have to be investigated and tackled in order to make the application of nanofibers in the exterior possible.

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LITERATURE