DETERMINATION OF SURFACE PROPERTIES OF PROTECTIVE LAYERS BASED ON POLYMERIC NANOFIBERS

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Abstract

The potential of nanotechnology in the development of new materials (nanotextiles) in the civil engineering can provide advantage of new application. On the one hand, functionality of materials can be improved using nanotextiles and on the other hand, it could make possible a manufacture of nanotextiles with new properties. The surface properties of materials are relevant in many fields of industry such as civil engineering. Testing and characterizing of surface of nanotextiles are very important for developing a new class of protective layers for building materials based on polymeric nanofibers. One of suitable methods to characterize the surface and wetting behavior of nanotextile fibers is contact angle measurements. Contact angle was measured using optical tensiometer by placing a liquid drop onto the nanotextile fibers.

Keywords: Surface protection, polymer-based nanofibers, hydrophobicity

1. INTRODUCTION

Nanofibrous textiles consist of fibres with nanoscale dimensions. These nanofibres have a nanoscale cross-sectional area. Fabrication of such textiles requires a process that can create a lot of nanofibers very quickly, for example Nanospider technology. While research into nanofibrous textiles is widespread, their commercialization in civil engineering has not reached significant application. Its development may afford exciting applications and opportunities [1].

The durability of building construction is connected with protection of their surface layers. Volume of aggressive pollutants in air, water and ground water expands in these days. These chemical and biological agents permanently and effectively react on materials and structures, primarily on surfaces, and accelerate their degradation processes [2-3]. Therefore the protection of surface layers is so important and requires extra protection. Degradation processes of building construction are not possible to stop, but these processes can be markedly reduced and limited.

Protection of building constructions by paint systems is the most used technology in these days. This kind of protection closes and seals surfaces of building materials against water. Coating (weather-resistant paint) causes a decrease in void ratio of surface layers and creates thick film, which modify character of surface. Consequences are degradation of the adhesive bonds between the coating and the underlying surface (mostly in cold weather). Electrospun nanotextiles have unique non-woven porous structure, which offer small pores sizes. Their attributes can lead to an incremental improvement capability of building materials [4-5]. Therefore it is necessary to determine basic characteristics of nanofibers and find out their application in civil engineering.

In our study we have used nanofibers prepared using electrospinning machine equipped with stationary wire electrode. Stationary wire is coated by moving carriage that deposits uniform material (polymer). The thin stationary wire forms the nanofibre. Polymers are spun under the influence of electric field.

2. MORPHOLOGY

One of very important parameters is the magnitude of the catalytic surface, closely connected with S / V ratio (S is surface of given nanofibers, V is volume of nanofibers). The larger value of this ratio increases the effective surface of the system. Catalytic properties of the thin films consisting of polymer-based nanofibers can be influenced both by adequate adjustment of technological conditions during producing of nanofibers (mostly, intensity of electrostatic field).

Morphology of small samples of different electrospun nanotextiles was observed using SEM (Tescan Maia 3, ZEISS). The fibre diameters were measured on SEM images using Atlas software. Average fibre diameters were identified around 200 nm for PVDF nanotextiles (**Figure1**) and around 180 nm for PA6 nanotextiles (**Figure 2**). It is well known that structure and morphology can have a significant effect on the sensing properties of materials. It can be seen that the surface morphology of PA6 and PVDF nanofibers appeared smooth. The results revealed that when both textiles have the same surface density the average pore size increases with growing fibre diameter.

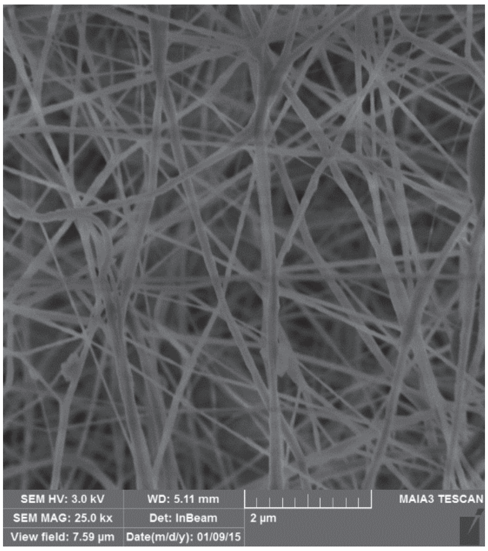

Figure 1 PVDF nanotextile

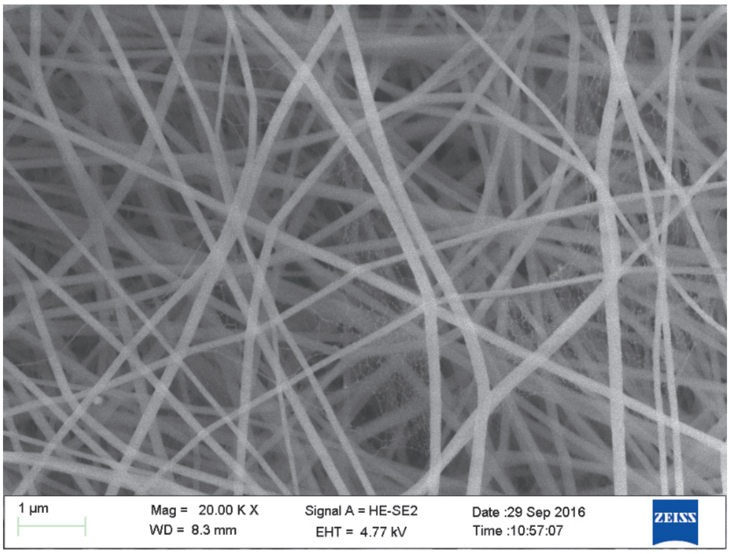

Figure 2 PA6 nanotextile

3. CONTACT ANGLE MEASUREMENTS

Wetting angle, typical macroparameter, comprises microscopic behaviour of the system. Its real value can be related to structural properties of thin film. One of the parameters characterizing the surfaces of materials is the surface free energy. The most common way to determine its value is to measure the surface tension by the drop method. The contact angles for a drop of distilled water on electrospun nanotextiles were measured using a contact angle set up at room temperature. A single drop of 0.3ml distilled water was dropped on the surface of a flat sample using a syringe and image captured after the water droplet became stable on the surface. In this case a contact angle between the surface and the edge of droplets of liquids is measured. This process was repeated five times on PA6 and PVDF nanotextiles. The contact angles were measured using the special software. Small contact angles (<90°) correspond to high wettability, while large contact angles (>90°) correspond to low wettability. The surface wetting analysis using contact angle measurements demonstrated no clear dependence of hydrophobicity on thickness of PVDF nanotextiles. The contact angle between the edge of a 0.3ml droplet of distilled water and the surface of different thickness of PVDF nanotextiles was measured to be around 130°. The contact angle of PA6 nanotextiles was found to be around 135°. Samples of PVDF and PA6 nanotextiles are hydrophobic.

4. TEST OF WATERTIGHTNESS

The basic aim of the measurement was to determine watertightness of nanotextiles, which were loaded by a 200 mm distilled water column for 15 minutes. The laboratory analysis consists of method to estimate the watertightness due to constant loading by a water column. The methodology of the laboratory measurement is in accord with European Standards EN 139859-1. The illustration of the laboratory device is presented in the **Figure 3**. The sample was placed over the plexiglass in the horizontal position. Between the sample and plexiglass is a laboratory filter, which indicates the water leakage through the sample.

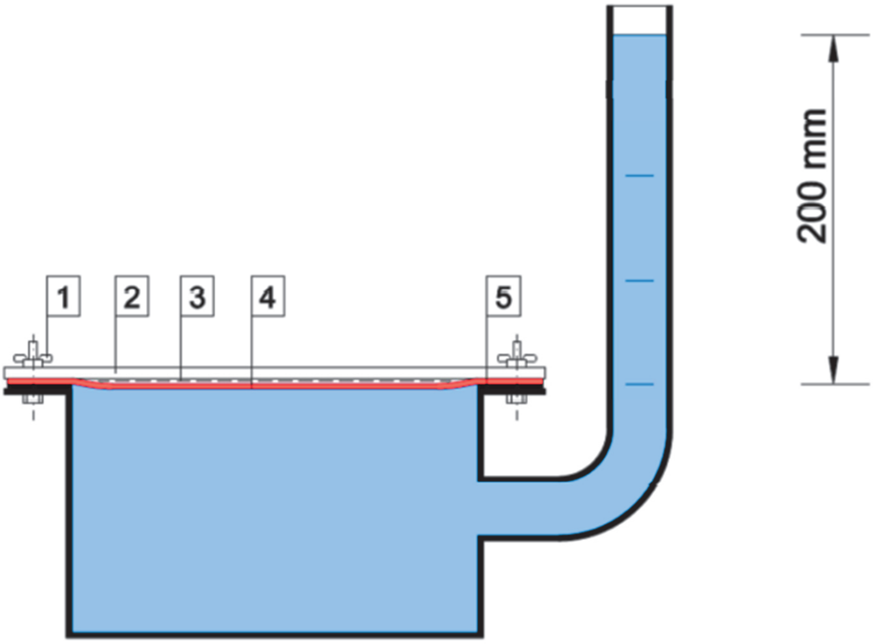

Figure 3 The schema of experimental device for measuring watertightness by the method of constant loading by a water column of 200 mm (1 - Sample holding device, 2 - Plexiglass, 3 - Laboratory filter paper indikates watertightness, 4 - Sample, 5 - Rubber ring)

During the testing all the samples achieved the results that are presented in the **Table 1**.

Table 1 Results of the laboratory watertightness measurement

Material	Surface density [g/m^2]	Number of samples	Resistance to water penetration
PVDF	31.3 ± 0.4	1	Not leaked through
	12.6 ± 0.4	1	Not leaked through
		2	Leaked
	8.0 ± 0.4	1	Leaked
		2	Leaked
PA6	5 ± 0.4	1	Not leaked
		2	Leaked

The watertightness results of PVDF and PA6 nanotextiles were different. As it is obvious from the laboratory measurements, watertightness of PVDF nanotextiles depends on their thickness (weight per unit area). No water penetration was found in any of the tested PVDF samples with 31,3 g/m². The reason is due to the structure of the material. It is a compact material made of PVDF fibres with a high degree of density.

5. DIFFUSION TEST

The effects of thickness of electrospun PVDF, PA6 nanotextiles on their permeability were tested using a diffusion tube. The relative humidity and temperature inside of the tube were monitored all time when the samples were weighted. The schema of the experimental apparatus is shown in the **Figure 4**. The vapour flux goes from the environment (chamber with water) with higher humidity, through a sample, to the environment with lower humidity (chamber with silica gel). Temperature is the same for both environments. The experiment was run for 20 hours.

Diffusion properties of thin products are most commonly described by the water vapour diffusion equivalent air layer thickness s_d. The sd-value expresses the thickness of a static air layer with the same water vapour resistance as the sample. It is an expression of resistance to diffusion of water vapour. The sd-value [m] is defined as follows (**Figure 5**):

$$s_d = \frac{A \cdot \tau \cdot \Delta p \cdot \delta_a}{\Delta m_i} \qquad (1)$$

where A is the effective area of the sample (m²), τ is the time period (s), Δp is difference of water vapor partial pressures (Pa), Δm is the change of the mass (kg) and water vapour diffusion coefficient in air δ_a (kg/(m.s.Pa)) is calculated from the equation:

$$\delta_a = \frac{2{,}306 \cdot 10^{-5}}{R_{H_2O} \cdot T} \cdot \frac{p_o}{p_a} \cdot \left(\frac{T}{273{,}15}\right)^{1{,}81} \qquad (2)$$

where T is the absolute temperature (K), R_{H2O} is the gas constant for water vapour (J / kg.K), p_o is the reference pressure in air (Pa), p_a is atmospheric pressure (Pa).

We fitted our experimental data in equations 1 and 2 to obtain the water vapour diffusion equivalent air layer thickness sd of the nanotextiles.

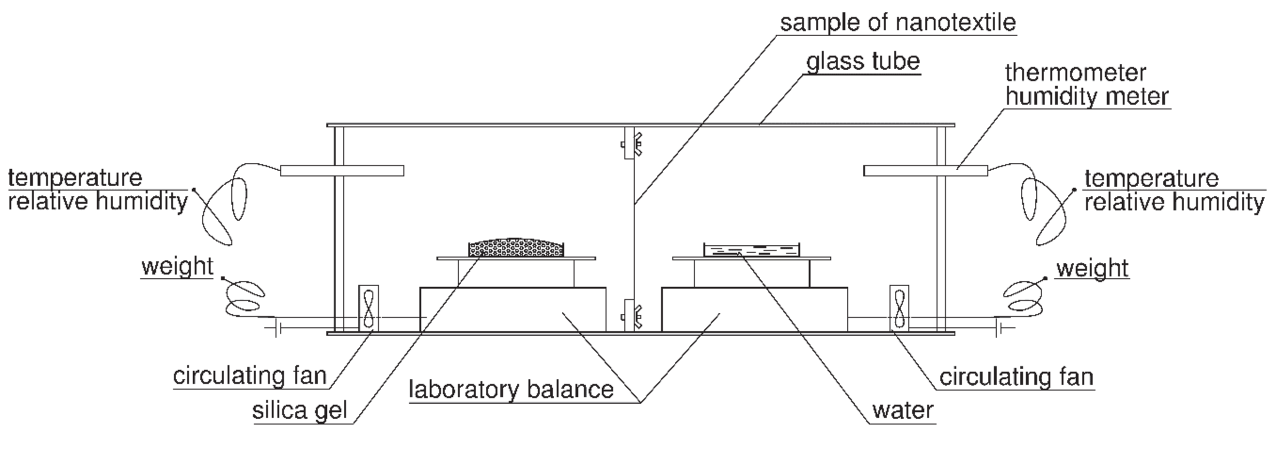

Figure 4 Schematic representation of experimental device for measuring of diffusion properties of thin layers

Diffusion tests showed the low s_d-value of nanotextiles. Samples are vapour permeable. Vapour permeability of samples is not dependent on thickness or type of the nanotextile. Transport properties of nanotextiles (in particular, diffusion of water molecules) are mostly affected also by distribution function of porous system of nanotextiles. The decrease of fibre diameter leads to decrease of the average pore size.

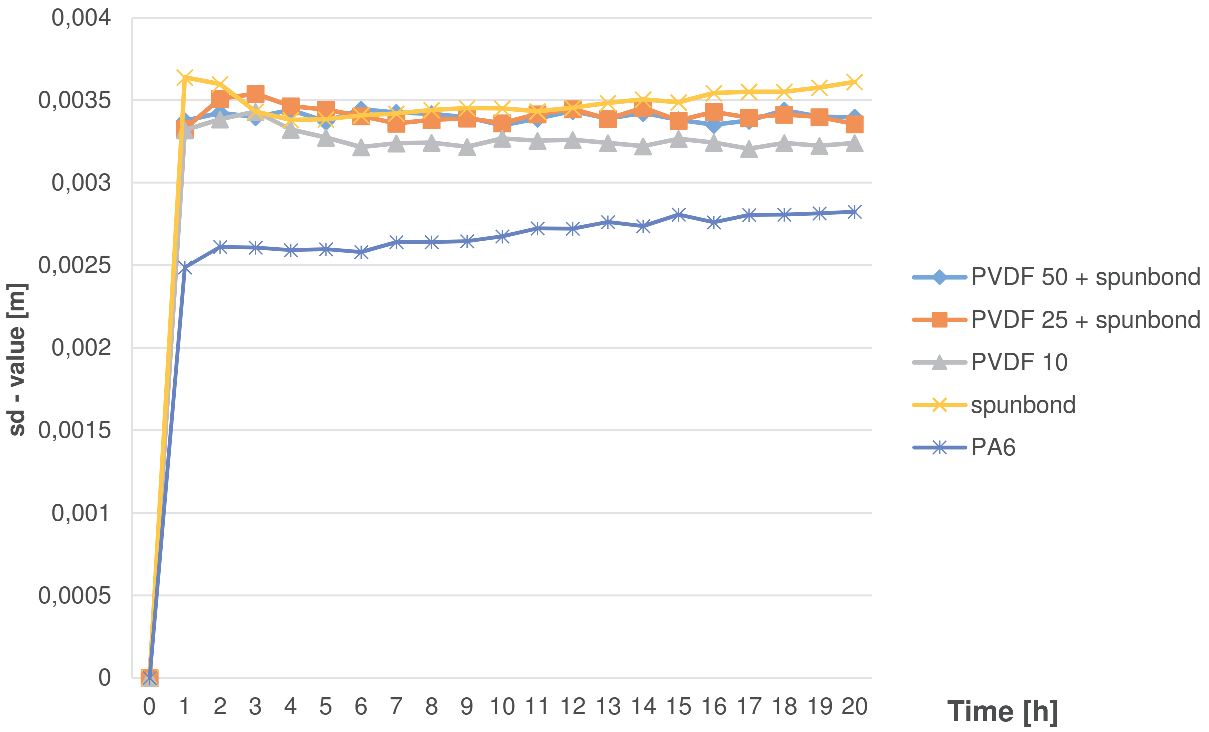

Figure 5 Water vapour diffusion equivalent air layer thickness s_d of PVDF nanotextiles and PA6 nanotextile calculated from the diffusion measurement as a function of time

6. CONCLUSION

The laboratory measurements were aimed at contact angle, watertightness, the water vapour diffusion equivalent air layer thickness s_d and morphology of PA6 and PVDF nanofibers. The results revealed an increase of the average pore size with increasing fibre diameter. PA6 and PVDF nanotextile are breathable. The hydrophobic nature of PVDF nanotextiles has an important role in surface protective applications through their effects on the diffusion. The thickness is an essential parameter that influences the watertightness of the PVDF nanotextiles. The surface wetting analysis using contact angle measurements demonstrated a hydrophobicity of PVDF and PA6 nanotextiles.

Applications of nanotextiles can provide many advantages in civil engineering. It is possible to design ductile, flexible, breathable, permeable properties of nanofibers.

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