HYDROPHOBIC AND BIOCIDAL PROPERTIES OF ELECTROSPUN SiO_2 NANOFIBERS

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Abstract

The developing nanotechnology is getting increased attention through wide range of industries. A variety of nanofibers (mostly polymer-based) can be made for applications in many research and industrial branches as well as civil engineering. One of our aims is to find out more about application of nanofibers in civil engineering. The possible uses of these electrospun nanofibers are promising as the surface protective layers. In these sense, there is a great potential for utilizing of nanofibers in civil engineering. Since the silica compounds play a fundamental role in materials applied in civil engineering, we studied the basic properties of silica-based nanofibers. We measured their biocidal properties against fungi and contact angles between SiO_2 nanofibers and water. The biocidal properties of SiO_2 nanofibers against fungi were evaluated by laboratory test as a percentage of the surface coverage of the fibers by fungi. Aspergillus niger was used as a model organism.

Keywords: Silicon oxide nanofibers, hydrophobicity, biocidal properties

1. INTRODUCTION

The industrial use of nanotextiles in civil engineering is still in its infancy. Nanofibers have a nanometers size and are optimized in terms of their functional properties by nanotextile coatings, i.e. can be hydrophobic, dirt-repellent, abrasion proof, antibacterial or antifungal [1,2,3]. The construction industry (mainly reconstruction of historical buildings) has been seen as potential area where nanotextiles could be used [4,5]. Silicon oxide is a chemically stable material, which can effectively protect heritage from environmental damage. Water, fungi and dust can be isolated by the nanofiber structure while moistures content of materials can pass through the nanotextiles and materials can breathe [6]. These conditions can keep a favorable environment for the historical buildings. Choosing the most appropriate treatment for a historical building requires careful decision making about using of appropriate material for renovation. Using of nanotextiles should be minimal modifications to the historic appearance and protect from negative influences.

The roughness of the surface is related to the material's contact areas that interact with its environment. Decreasing the roughness of a surface in the micro or nano dimension can prevent dirty particles from catching. Application of nanotextiles on the surface of materials can improve the surface finish (i.e. decreasing of roughness, hydrophobicity). Hydrophobic surfaces have a contact angle of more than 90° and promote the formation of droplets, which can wash off dirty particles from surface [7,8]. Dirt-repellent and hydrophobic properties can even be created artificially by means of coatings or special structures (nanotextiles). The development of water repelling surface can markedly reduce and limit degradation processes of building construction. Water spreads over the surface and removes the dirty particles and dust.

Silicon oxide nanofibers were produced by a combination of an electrospinning technique and the so-gel method [9]. The polymer solution was prepared by the sol-gel method using tetraethoxysilane (TEOS), acid, H_2O and the isopropyl alcohol (solvent) [10]. Prepared polymer solution was used for the production of silicon oxide nanofibers by electrospinning used Nanospider device in TUL [11,12]. The electrospun samples afterwards were put in a furnace and were heat-stabilized at 180°C for 2 hours.

2. CONTACT ANGLES MEASUREMENTS

One of the most important parameters, required for nanotextiles in civil engineering applications, is their hydrophobicity. There are different methods to measure the hydrophobic properties of a material. The degree of wettability can be evaluated by a contact angle of a water droplet on the surface of the material.

Wetting angle reflects 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 [13]. Wettability studies usually comprise the measurement of contact angles as the primary data, which indicate the degree of wetting when a solid and liquid interact. Small contact angles (<90°) correspond to high wettability, while large contact angles (>90°) correspond to low wettability [14].

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 5 µl distilled water was dropped on the surface of a flat sample (thin film of silicon oxide nanofibers) 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 several times on samples S1 (11.9 gsm), S2 (19.8 gsm) and S3 (34.2 gsm). The web thickness is expressed in grams per square meter, or gms. Often referred to as basis weight, this measure indicates the thickness of the nanofiber web. The contact angles were measured optically using 3 different devices and then were calculated using 3 drop-shape analysis methods.

2.1. Drop Shape Analysis System

The surface contact angles were firstly measured on a Drop Shape Analysis System (DSA30) (KRUSS, Germany). Droplets of the distilled water were automatically placed onto the sample with a syringe during the experiment. A picture of the drop was captured after the drop set onto the sample. The interface between drop and surface of the sample (base line) are manually determined for analysing contact angle and the software detects the drop shape. The contact angles were calculated by the software through analyse the shape of the drop. The contact angle θ was an average of 5 measurements.

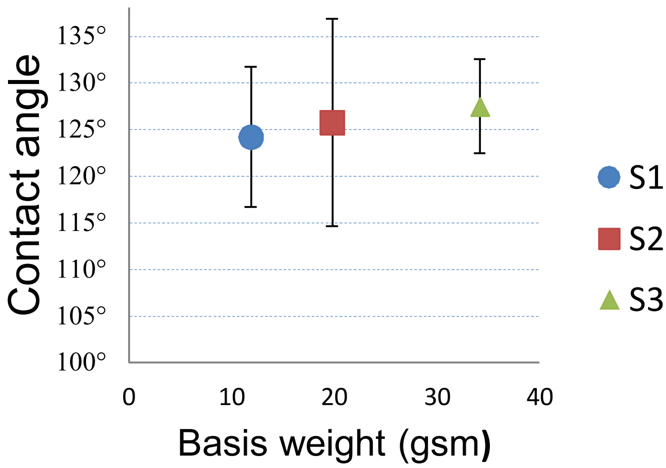

Figure 1 Contact angles as a function of web area weight of silicon oxide nanofibers measuring by DSA30

The surface wetting analysis using contact angle measurements demonstrated dependence of hydrophobicity on web area weight (gsm) of silicone oxide nanotextiles. The contact angle between the edge of a 5 µl droplet of distilled water and the surface of different thickness of silicone oxide nanotextiles was measured to be around 125° (**Figure 1**). Samples of silicon oxide nanotextiles are hydrophobic.

2.2. SEE System

The measurements of the contact angle of water were carried out applying device for evaluation of surface energy SEE SYSTEM - Surface Energy Evaluation System Instrumentation. The droplet application onto the planar solid sample was done using a micropipette. The droplet volume was equal to 5 µl. Deposited drop is recorded by camera immediately after its placing on the sample and it is displayed on the PC monitor. Further it is utilized using SEE software. Analysis of droplets was realized by detection of 2 points on interface liquid-solid matter and 1 point on drop outline. Contact angle is determined by circular interpolation. To obtain statistically relevant data, the contact angle was averaged from six independent measurements (**Figure 2**).

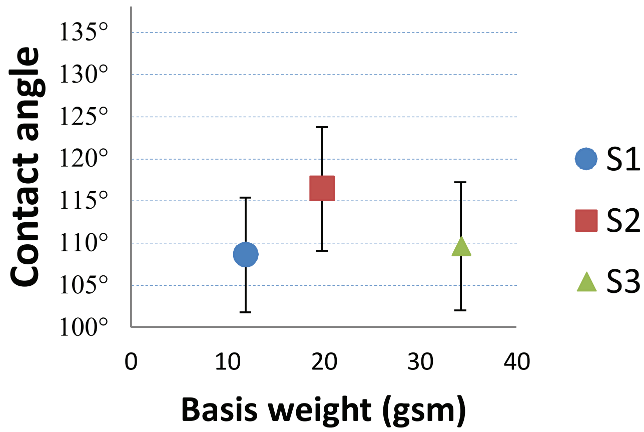

Figure 2 Contact angles as a function of web area weight of silicon oxide nanofibers measuring by See System

2.3. CAMTIA

In order to obtain mutual comparable results of the contact angles, we used a special optical set enabling the direct optical reading of the contact angle sizes. The principle of the method rests in photographing of the droplet outline illuminated by a backlight flow. The source of the flux was an optical reflector. To ensure satisfactory parameters of the flow, the light was restricted by a circular aperture and convex lens. The sample was placed in the middle of the set. Small droplets (5 µl) of the test liquid (distilled water) were manually placed using a micropipette on the surface of the samples. The digital single lens reflex camera (DSLR) was placed on the opposite side of the light source. The outline of the droplet illuminated by the backlight flush was recorded and then evaluated using SW CAMTIA (http://mech.fsv.cvut.cz/~nezerka/software.html). Six measurements were performed for each sample (**Figure 3**). The optical set is illustrated in the **Figure 4**.

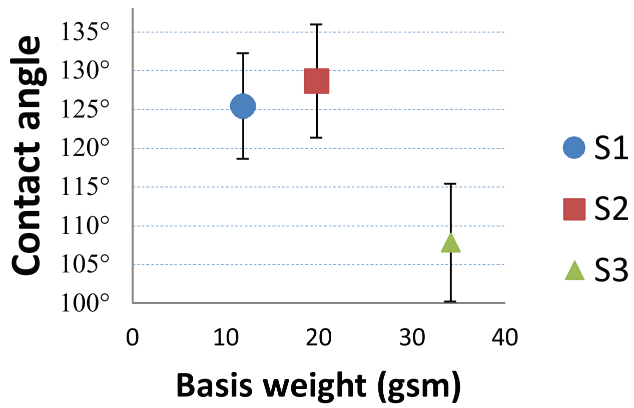

Figure 3 Contact angles as a function of web area weight of silicon oxide nanofibers measuring by Camtia

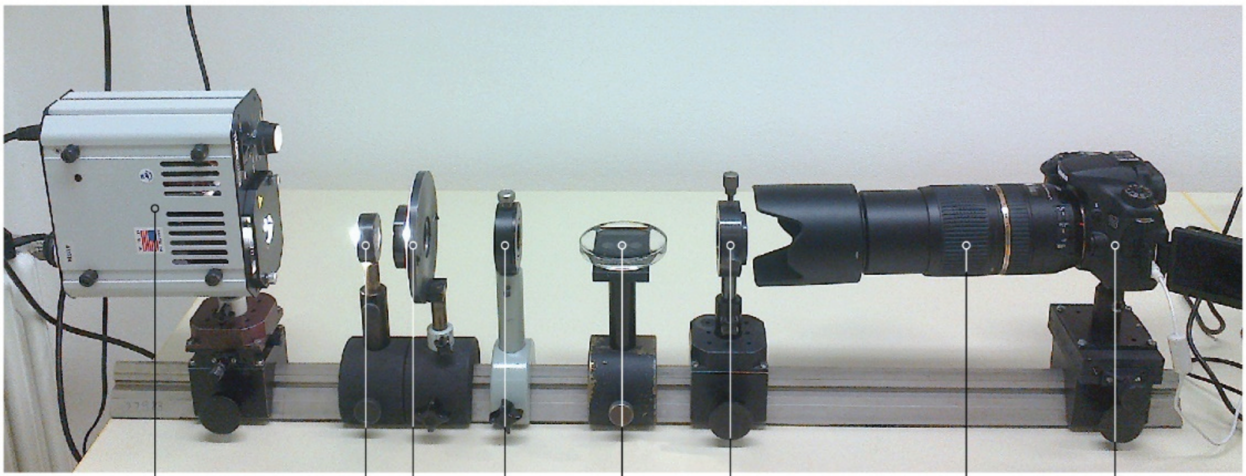

Figure 4 Experimental device for measuring contact angle

The measurement results are summarized in **Table 1**, the contact angles are averaged. Samples of silicon oxide nanotextiles measured by three different methods are hydrophobic.

Table 1 Results of different tools for direct measurements of contact angles on sessile drops

Sample	Basis weight (gsm)	Contact angles (°) (standart deviation)		
		DSA 30	See System	Camtia
S1	11.9	124.2±7.5	125.4±3.9	108.6±6.8
S2	19.8	125.7±11.1	128.6±3.3	116.4±7.3
S3	34.2	127.5±5.1	107.8±2.2	109.6±7.6

3. ANTIFUNGAL ACTIVITY

The resistance of building materials to micro-organisms is one of their monitored properties. It is used to be tested the resistance to bacteria, mould and fungi. This paper deals with the resistance of the SiO_2 nanofibers to fungi. Fungi are complex organisms with slow growth rate. The antifungal activity of silicone oxide nanotextiles was tested against a model organism (Aspergillus niger) under laboratory conditions. Czapek-dox agar (20ml) was inoculated with Aspergillus niger (300 µl) and poured in petri dishes. The fungal spore suspension was grown in the dish for 24 hours. Afterwards, the round samples (diameter 25 mm) of nanotextiles were placed over the inoculated agar in petri dishes. Each sample was prepared in five replicates of samples S1 (11.9 gsm), S2 (19.8 gsm) and S3 (34.2 gsm). Samples were cultivated at temperature 23 ± 3 °C in dark. The experiment was evaluated as antifungal activity nanofibers visually after 14 days. The growth and development of mould mycelium on the dish and surface of samples of silicone oxide nanotextiles was monitored during the time of experiment. An example of the obtained results of dish with and without the sample of SiO_2 nanofibers is shown in the **Figure 5**. The fungal presence and growth were visible to the naked eyes. Experimental results indicated that the pure silicon oxide nanofibers have no antifungal activity.

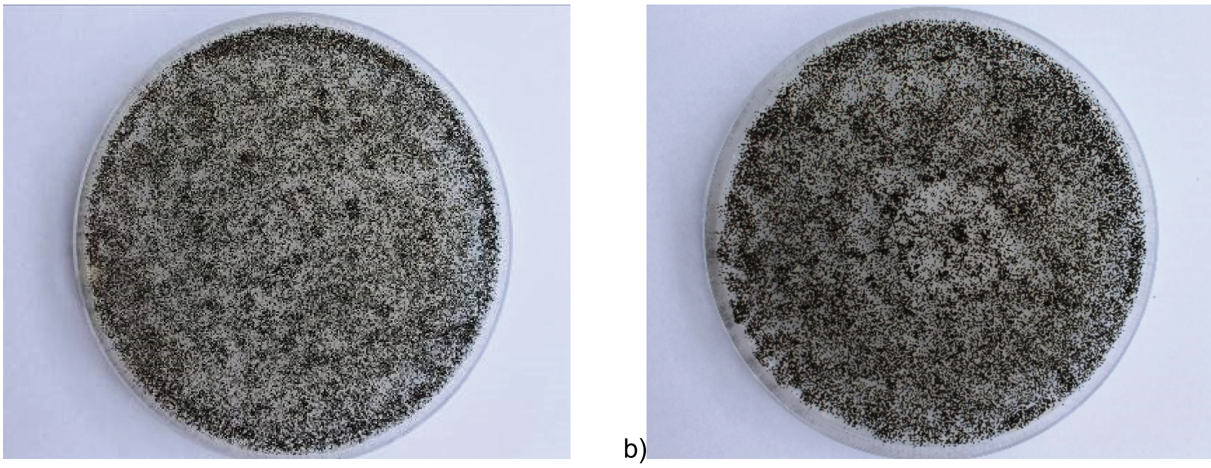
a) b)

Figure 5 Resulting image of fungi growth on nanotextile sample estimated after 14 days of incubation; a) sample without silicone oxide nanotextiles, b) sample with silicone oxide nanotextiles (sample S3; circle with diameter 25 mm placed into the centre of dish)

4. CONCLUSION

The aim of the presented research was to determine the antifungal activity and hydrophobicity of silicon oxide nanofibers. Experimental results of fungi growth on silicon oxide nanotextiles demonstrated no influence on the antifungal properties of the tested samples. The contact angle results of the three methods show the same hydrophobic behavior of the samples. Nanofibers provided good water protection without significant change in moisture vapor transport properties [15]. These preliminary results indicate that silicone oxide nanofibers could potentially be used as protective layer of construction materials. Hydrophobicity of construction materials can be improved with silicon oxide nanofibers. To obtain also antifungal properties, the protected layers using silicon oxide nanofibers have to be modified using more sophisticated procedures.

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