Wettability of SiO_x Nanofibrous Mats and Their Modification Using Cold Atmospheric Plasma Treatment

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In this paper, the wetting characteristics of silica-based (SiO_x) nanofibrous mats were studied. First, the contact angles of the nanofibrous mat surface were determined using optical tensiometry. Contact angles for two probe liquids (distilled water and diiodomethane) were measured using the static sessile drop method. Then, the initially hydrophobic SiO_x nanofibrous mat (water contact angle $\approx 136^\circ$) was changed to hydrophilic using plasma treatment. Surface modification with a cold atmospheric plasma device is a fast, dry, cost-effective, and environmentally friendly process. Contact angle measurement data were utilized to calculate the surface free energy of the mat based on the model of Owens, Wendt, Rabel, and Kaelble. Finally, the potential applications (e.g., filtration, separation) of SiO_x nanofibrous mats were briefly described.

topics: silica nanofibers, contact angle, surface energy, cold atmospheric plasma

1. Introduction

In recent decades, nanoscale fiber materials have been at the forefront of modern material science. They attracted attention due to their unique physicochemical properties, such as light weight, controllable porosity and fiber density, high specific surface area, and excellent mechanical properties [1–3]. Nanofibrous mats can be manufactured on a large scale with a relatively high production rate using electrospinning [4]. They are mostly synthesized from various organic polymers, for instance, silk fibroin, cellulose, gelatin, poly(lactic-acid), poly(lactic-co-glycolic acid). Apart from polymer fibers, inorganic fibers, especially those based on silica, have attracted attention due to their beneficial properties, such as low thermal conductivity, thermal stability, chemical inertness, and nontoxicity [5, 6].

2. Electrospun nanofibers

The most common method of producing the SiO_x nanofibers is electrospinning. Novel alternatives to the electrospinning fabrication method are centrifugal spinning and solution blowing with subsequent calcination. Centrifugal spinning results in thick, fluffy, homogeneous and defect-free structures with a higher fiber diameter. Solution blowing provides more compact structures with smaller pore size [5]. Several applications have been reported for inorganic nanofibrous mats including filtration, separation, catalysis, adsorption, purification, bio- and chemical sensors, fiber-reinforced composites, tissue engineering, drug delivery systems, wound dressings, energy conversion and storage, etc. [1, 2, 4, 7, 8]. Nowadays, tuneable wettability has attracted extensive interest in both fundamental research and industry. For this reason, the field of application of functionalized nanofibers with specific surface properties (e.g., hydrophobic/hydrophilic surfaces) has expanded [6, 8, 9].

2.1. Wettability and surface free energy

Contact angle (CA) measurement is one of the common ways to determine the degree of wetting of the material. A fluid droplet in contact with a solid surface and air creates a three-phase interface, which produces measurable conditions (Fig. 1). An optical tensiometer is the most commonly used equipment for CA measurements, which offers a quick evolution of photographs of the liquid interface. Contact angles are then calculated depending on the approximation chosen (e.g., spherical cap approximation, polynomial fitting, tangent line) [10].

Although the CA measurements provide valuable information about the wettability of a surface, many surface properties (adhesion, friction) are related to the surface free energy (SFE). This quantity expresses the amount of intermolecular force created at the surface of a material, and it determines the work necessary to increase the size of the

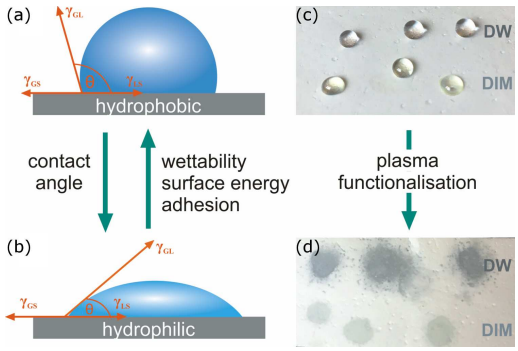

Fig. 1. Sessile water drop on (a) hydrophobic and (b) hydrophilic surfaces demonstrating the three-phase boundary (interaction between the liquid, solid, and air). Photographs of water and diiodomethane droplets placed on (c) hydrophobic and (d) hydrophylic SiO_x mats.

surface [10]. The SFE cannot be directly measured, it is calculated from the CA measurements. At least two probe liquids (e.g., distilled water (DW), diiodomethane (DIM), ethylene glycol, glycerol, etc.) with different polar and dispersive components have to be used to perform the CA measurements. These CA values then are converted to quantitative SFE data using various theories (e.g., Zisman; Wu; Acid-base; Fowkes; Owens, Wendt, Rabel, and Kaelble (OWRK); Schultz) [10, 11]. The theories, however, are not universal — proper combinations of test liquids and theory have to be chosen to achieve reasonable results for a given material.

Generally, a surface with a "high" SFE causes high wetting (the liquid droplet does not spread onto the surface), hence resulting in a CA of less than 90°. The opposite case is true for a "low" SFE that causes low wetting (the droplet spreads out on the surface), and the liquid creates a CA between 90° and 180° with the solid [10]. Based on water's CA, surfaces are classified into two categories, i.e., hydrophobic surfaces with low affinity to water, and hydrophilic surfaces with strong affinity to water (Fig. 1a, b).

2.2. Surface functionalization using atmospheric cold plasma

Controlled changes in wettability can be obtained by modifying the surface of the material [12]. Plasma technology has become widespread in material science because it has been recognized as an efficient approach to enhance various surface properties of materials (e.g., wettability, adhesion, and printability) [9, 13]. In the process of plasma functionalization, various gases are employed that dissociate and react with the surface of the material, introducing new functional groups to it. Other reactions (e.g., chain scission, cross-linking, etc.) can also occur.

Using appropriate plasma treatment, a broad range of control of surface wettability can be achieved from extreme hydrophilicity (e.g., plasma activation using oxygen-based gas) to significant hydrophobicity (e.g., plasma passivation using a fluorine-based gas). The efficiency of plasma treatment depends on the reactor type (various low pressure and atmospheric pressure plasma devices) and its operating parameters (such as duration, pressure, power, gas mixture, etc.). Therefore, cold atmospheric plasma (CAP) systems appear as one of the most successfully emerging plasma technologies due to their technological and economic advantages. Furthermore, CAP can be utilized for temperature sensitive materials. Surface treatment of different materials (such as polymer fibers, metal, wood, paper, glass, ceramic, etc.) using CAP has already been reported [14].

The main purpose of this paper was to study the wettability of electrospun SiO_x nanofibrous mats and their surface modification using cold atmospheric plasma. Relying on CA measurements, we calculated the surface free energy of the mats after the electrospinning and plasma treatment processes.

3. Experimental

3.1. Materials

Biodegradable inorganic silicon oxide (SiO_x) nonwoven three-dimensional nanofibrous mats (25.04 g/m^2) were made via sol–gel electrospinning. Four components were used for the preparation of the silica sol: tetraethoxysilane (TEOS), isopropyl alcohol (IPA), water (H_2O) and hydrochloric acid (HCl). The sol–gel method is based on hydrolysis and polycondensation reactions. First, 400 ml of TEOS and 330 ml of IPA were mixed and transformed into tetraalkoxysilane. Then H_2O and HCl were added to the solution (molar ratio of H_2O/tetraalkoxysilane = 2.0 and the molar ratio of HCl/tetraalkoxysilane = 0.01). The desired viscosity was achieved by controlled evaporation of the solvent to a final content of 40 wt% SiO_x. The electrospinning (process parameters: voltage of 70 kV and electrode–collector distance of 175 mm) was carried out using the Nanospider device (Elmarco, Technical University of Liberec). Finally, the mats were thermally stabilized at 180 °C for 2 h [15]. Their surface morphology was characterised using scanning electron microscopy.

3.2. Contact angle measurement, surface free energy calculation

The CA measurements were performed at ambient temperature using an Attension Theta Optical Tensiometer (Biolin Scientific, Finland). Static CAs were measured by the sessile drop method. The automatic dispenser created a liquid droplet (2–4 μl), which was placed on the surface of the sample. The analysis and evaluation of the resting drop was performed from the high-resolution camera data (maximum image resolution of 1280 × 1024 pixels,

TABLE I

Surface tension components (total, dispersive, polar) of the selected probe liquids (for 20 °C) [11].

Probe liquid	Distilled water (DW)	Diiodomethane (DIM)
character	polar	dispersive
γ_L [mN/m]	72.8	50.8
γ_L^d [mN/m]	21.8	50.8
γ_L^p [mN/m]	51.0	0

maximum measuring speed of 2068 fps). The tensiometer recorded drop images, which were analysed using the OneAttension software. The CAs were evaluated by fitting a mathematical expression to the outline of the drop and determining the tangent of the CA at the three-phase point (Fig. 1a, b). Each droplet was recorded for 15 s. Ten measurements were made for each liquid, and the mean values with standard deviation were calculated.

The CA is directly related to the surface free energy of the material, and for this reason the measurement data were used to mathematically calculate the SFE of the SiO_x mat. The Owens–Wendt–Rabel–Kaelble model was used, which is one of the most common methods for SFE calculations [11]. The equation called OWRK can be written as

$$\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p} = 0.5\gamma_L\big(1+\cos(\theta)\big), \qquad (1)$$

where γ_S^d, γ_S^p are the dispersive and polar components of the solid, and γ_L^d, γ_L^p are the dispersive and polar components of the liquid. There are two unknown parameters in (1) — γ_S^d, γ_S^p. The total SFE is the sum of the polar and dispersive components [10, 11].

To determine the SFE, the CA measurements with at least two probe liquids were necessary, which were selected with respect to the following aspects:

- the liquid should be pure and homogeneous;
- the fibrous mat should be chemically inert to the probe liquid;
- the sample should be tested with at least one dispersive and one polar liquid of known dispersive and polar parts of the surface tension;
- the surface tension of the probe liquid has to be higher than the SFE of the mat.

Distilled water was chosen as the polar liquid, and diiodomethane (methylene iodide) was used as the nonpolar probe liquid (see Table I).

3.3. Atmospheric cold plasma treatment

The SiO_x nanofibrous mats were subjected to plasma treatment in order to achieve hydrophilic surfaces. The plasma functionalization was performed in a diffuse coplanar surface barrier discharge (DCSBD) type plasma reactor (RPS 400, Roplass, Czech Republic). It generates low-temperature (<40 °C) uniform plasma (of the volume of $20 \times 8 \times 0.03$ cm^3) in the surrounding air at atmospheric pressure. Both sides of the mat (5×3 cm^2) were treated at 200 W power with treatment durations of 30 s–2 min.

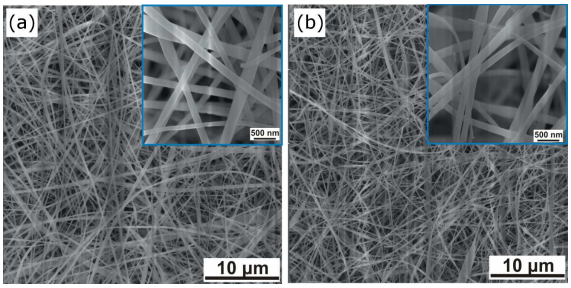

Fig. 2. Surface morphology of (a) hydrophobic and (b) plasma-treated hydrophilic SiO_x nanofibrous mat.

4. Results and discussion

4.1. Nanofibrous mat structure

The electrospun SiO_x mats are composed of randomly oriented smooth beadless fibers with a circular cross-sectional shape. Nanofibers with a diameter of 200–300 nm created a three-dimensional porous network (Fig. 2). The mats were produced without the need for a carrier polymer, and despite this fact, they were very flexible. The prepared mats can be folded without any damage and impairment of their original shape.

After the electrospinning process, the fibrous mat had very poor wetting, the probe liquids did not wet the solid (Fig. 1c). Cold atmospheric plasma was successfully applied, which induced changes in the surface wettability. The water spread on the surface of the mat even after the shortest plasma treatment (Fig. 1d). Increasing the duration of the plasma treatment was not necessary (prolonged treatment did not result in further improvement). The plasma treatment occurred homogeneously over the whole sample. The mat remained intact without color (Fig. 1d) or morphology changes (smooth surface fibers without diameter reduction, Fig. 2b) due to the cold character of the plasma device. The non-thermal atmospheric plasma treatment affects only the surface of the material, while the bulk properties of the material remain unchanged [14].

4.2. Contact angle measurement

The sessile drop CA measurements provided quick quantitative data about the wettability of the surface of the SiO_x mats. Screenshots from the software (Fig. 3) show representative droplet profiles,

TABLE II

Mean values and standard deviation of contact angles and surface energies of the SiO_x nanofibrous mat.

Sample	Contact angle [°]		Components of the surface free energy [mJ m^{-2}]			Polar ratio [%]
	DW	DIM	Dispersive part γ_P^d	Polar part γ_P^p	Total γ_P	
electrospun SiO_x mat	136 ± 2.5	123 ± 3.0	2.63	0.14	2.77	5.05
plasma treated SiO_x mat	8 ± 1.5	5 ± 2.0	50.61	30.18	80.79	37.35

which were used for the CAs evaluation. The baseline of the measurements is the horizontal green line representing the contact between the liquid and the mat surface. This line was set manually for each droplet before the analysis process. The drop edge is marked with the blue outline (computer-drawn ellipse). The measured CAs (left and right) are displayed next to the droplets.

Results for the two probe liquids (distilled water and diiodomethane) are summarised in Table II.

The CA measurements proved that the electrospun SiO_x nanofibrous mat exhibited a highly hydrophobic character, which prevents the penetration of the liquid drop into the material. The mean water CA was 136° with a standard deviation smaller than 2.5°, while the DIM contact angle was 123° with a standard deviation smaller than 3°. After the plasma treatment, the mats become absorbing, the contact angle values of both water and DIM decreased to $< 10°$. The polar ratio of the SiO_x mat was calculated as a ratio of the polar component to the total surface free energy.

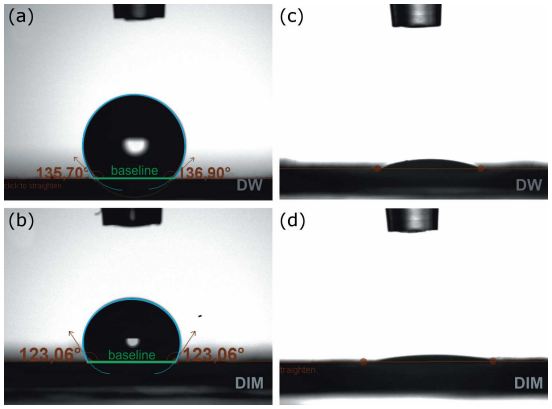

Fig. 3. Screenshots from the contact angle evaluation OneAttension software: (a), (b) hydrophobic and (c), (d) hydrophilic SiO_x fibrous mat with water (DW) and diiodomethane (DIM) droplets.

4.3. Surface free energy calculation

The CA measurements data were used to calculate the SFE of the samples using the OneAttension software. The selection of the test liquid was essential to achieve reliable values. Distilled water was an obvious choice as a polar liquid due to its nontoxicity and availability. The selection of other liquids (e.g., a suitable nonpolar liquid) was more cumbersome. When the surface tension of the liquid is lower than the SFE, the liquid wets the surface completely (i.e., no liquid droplets), thus the determination of the dispersive component becomes impossible. For example, ethylene glycol, glycerol, alfabromonaphtalene, and formamide have been tried for the CA measurements, but the droplets immediately absorbed into the samples. For that reason, diiodomethane was chosen as the nonpolar probe liquid.

Surface free energies calculated using the OWRK model are shown in Table II. The total SFE is the sum of the polar and dispersive components. As it can be seen, after the plasma treatment, the total SFE increased to 80.79 mJ/m^2 due to the plasma activation process. Attachment of the oxygen (containing functional groups such as carbonyl, carboxylic acid, hydroxyl, peroxyl, etc.) to a low energy surface turned it into a higher energy surface [14]. Plasma treatment also yields a higher ratio of a polar component to the SFE, increased from 5.05% (untreated samples) to 37.35% (plasma-treated samples). The fibrous mats remained hydrophilic even after a few weeks (stored under ambient conditions).

Taking into account these results, it can be concluded that plasma treatment is a very effective and low-cost method for increasing the wettability of nanofibrous mats. The hydrophilic SiO_x mats are obtainable using short plasma functionalization. The CAP device enables rapid treatment of large areas (or multiple mats can be treated simultaneously). These facts are very useful from an economic point of view (e.g., it is not necessary to create new materials, atmospheric plasma can be generated without using vacuum systems or expensive gases, etc.). Furthermore, the CAP is an environmentally benign approach, which does not involve toxic chemicals [14].

4.4. Potential applications

The nanofibrous SiO_x mats have potential applications in many fields, such as oil–water separation [7], dentistry [16], filtration [17], and water-absorption [6]. Dai et al. [4] fabricated SiO_2 mats showing good flexibility (without cracking after 180° bending) using a conjugate electrospinning process and calcination. Tepekiran et al. [17]

demonstrated that centrifugally spun silica-based nanofibers exhibit high particle capture performance, enabling their use in industrial hot air filtration applications. In the paper of Wang et al. [16], it was shown that the SiO_2 nanofibers are effective in improving the overall performance of dental resin composites. The composite properties were improved because the one-dimensional fibers created an overlapped fibrous network which was able to shield particular fillers from being abraded off (i.e., high wear resistance). Furthermore, excellent mechanical properties and low polymerization shrinkage were achieved — also crucial in ensuring the long-term durability of dental restorations [16].

Surface functionalization of the nanofibers expands the area of possible applications. Nanofibrous mats can be considered as potential candidates for tissue engineering applications. The optimal surface properties of electrospun plasma-functionalized nanofibrous mats allow favorable cell–surface interactions (e.g., increased cell adhesion, enhanced protein adsorption), as shown by Asadian et al. [9]. Electrospun nanofibrous mats with specific wetting properties have excellent separation efficiency. For example, Jiang et al. [7] showed that superhydrophobic electrospun PVDF-SiO_2 fiber membranes have high oil/water separation efficiency (99.4%), good chemical stability and multicycle performance. Hromádko et al. [6] reported that due to the favorable combination of properties, including hydrophilicity (high number of OH groups on the surface), and textural properties (e.g., ultrahigh surface area, pore size distribution), SiO_2 fibers have excellent H_2O adsorption performance.

5. Conclusion

In this paper, the wetting characteristics of silica (SiO_x) nanofibrous mats were studied. The inorganic silica mats were produced using electrospinning, which is considered to be a versatile and cost-effective fabrication method for manufacturing nanofibrous materials with controllable composition and structure. The initial mat had a highly hydrophobic surface with high water contact angle ($> 135°$), and low surface energy. The cold atmospheric plasma treatment led to a strong reduction in the contact angle ($< 10°$), thereby the wettability of the initial fabric was greatly improved. New oxygen-containing polar moieties were formed on the surface which led to improved surface hydrophilicity. The treated mat also possessed higher surface free energy (according to the OWRK method, 80.79 mJ/m^2), as compared to the untreated sample. It can be concluded that SiO_x nanofibrous mats have unique properties, e.g., a large surface to volume ratio, good mechanical properties, flexibility, biocompatibility, etc., and they have an easy-to-tune wettability using an effective, short, one-step plasma treatment.

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