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THE HYDROPHOBIZATION OF A NANOFIBER LAYER USING LOW-VACUUM PLASMA

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Abstract:

Nanofiber materials offer a wide range of use in various production fields, e.g., different types of filtration, or areas requiring high hydrostatic resistance. They are made from different polymers, some of which are more hydrophobic than others, for instance some types of polyurethanes and polyvinylidene fluoride. However, even these polyurethanes cannot guarantee a high hydrophobicity of the final nanofiber material. To increase this desired property, we have to use the so-called hydrophobic substances like fluorocarbon. The nanofiber layer has to be prepared so that its pores do not get blocked, which would worsen its filtration capability and air permeability. This is why a roll-to-roll low-vacuum plasma was used in our case for creating a fabric with nanofiber layer for the clothing industry. The result is a nanofiber material with a hydrostatic resistance higher than a 15,000 mm water column. Under suitable conditions, we can produce a nanofiber membrane for clothing with thermophysiological properties similar to those of membranes produced with different principles, e.g., nanoporous membranes. The nanofiber membrane provides us desirable properties such as stability during repeated washing.

Keywords:

Fluorocarbon, hydrophobicity, membrane, nanofiber layer, plasma

1. Introduction

Hydrophobic treatment is a common procedure for textiles. It is carried out on those textile materials whose purpose is to resist water penetration such as raincoats, umbrellas, or tents. The treatment influences the liquid absorption and ascent property of the textile fabric.

The highest hydrophilicity is observed in natural fibers, especially when their natural fat or wax has been removed. Synthetic textiles on the other hand show much lower water absorption properties, and when used to make dense thread-count fabrics, they can even be hydrophobic. The criterion of hydrophobicity is the contact angle between water and the flat fabric. If the contact angle is greater than 90°, the surface tension of the textile is lower and the material is more hydrophobic. Therefore, if the textile should be more hydrophobic, it must have a lower surface tension. This lower surface tension can be achieved by hydrophobicity-increasing agents [1, 2].

1.1 Current state of increase of hydrophobicity for nanofiber layers

Ma and Hill [3] created a basic overview of making superhydrophobic textile surfaces. The research into superhydrophobic surfaces intensified in the early 90s. At that time, many ways of roughening the surface for making it superhydrophobic were investigated. Most of these studies took the lotus flower surface as their model. In their work, Ma and Hill reached a contact angle higher than 160° by using paraffin crystals that contain mostly -CH_2 groups. In the case of lotus leaves, the lower surface energy of -CH_3 groups or fluorocarbohydrates is not required to get a superhydrophobic surface. This proves that very low surface energy is not necessary for achieving the non-wettability of a surface. The ability to control the morphology of a surface on the level of micrometers and nanometers might be of more significance. Superhydrophobic properties were achieved not only with the use of silicones or fluorocarbons (FCs) but also with other materials, which can be organic. There is a variety of materials and a variety of methods and ways to create a superhydrophobic surface. The surface of a material with a low surface energy is usually roughened. These methods are mostly just one-step processes, whose simplicity is an advantage. However, these methods are limited to a small number of materials. Han and Steckl [4] used coaxial spinning to create superhydrophobic nanofibers. Teflon AF was used as a sheath and polycaprolactone (PCL) as a core material. By using coaxial electrospinning and these core/sheath fibers, superhydrophobic membranes have been successfully produced even though Teflon is normally not spinnable because its low dielectric constant prevents sufficient charging. Yoon, Park and Kim [5] created superhydrophobic surface using electrospinning and nanofibers; caprolactone was used as the starting polymer. The method achieved a 150° contact angle. Liao et al [6] created a nanomembrane from polyvinylidene fluoride (PVDF), together with dimethylformamide and acetone. The solution was stirred for 24 hours at 60°C. The fibers were

spun using a nozzle, a voltage of 25–30 kV, and a distance of 12–15 cm between the needle and the collector . The resulting material had a contact angle of 136°–142°, and a higher hydrophobicity was achieved, thanks to the rough surface. This work also hints at the possible influence of humidity during spinning on the final hydrophobic properties. Lower humidity seems to increase the surface hydrophobicity of the created nanofibers. The same author studied, as in the abovementioned work, the modification of a PVDF membrane surface. Using the same solution and nozzles, the spinning was carried out at a voltage of 28 kV and with the distance between the nozzle and collector as 12 cm. To increase adhesion between the fibers and the silver nanoparticles, the nanofiber membranes were first coated by polydopamine (PDA). In the next step, the membrane was coated with silver nanoparticles to optimize its morphology and to roughen its surface. According to this study, the method of membrane modification using PDA should be universal as its use is suitable for many types of materials and complicated shapes.

Another possibility to utilize low surface energy is the application of a block copolymer like polystyrene-*b*-dimethylsiloxane (PS–PDMS). For example, Ma et al [7] created superhydrophobic nanofiber membranes using electrostatic spinning. A contact angle of 163° was achieved through a combination of applying PS–PDMS on the fiber surface and the roughness of the surface due to the small diameters of the fibers (150 –400 nm). This method might find its use in the textile industry as well as biomedicine. Jonoobi et al [8] created cellulose nanofibers with hydrophobic properties. They submitted cellulose nanofibers to acetylation. This process changed the surface properties of the fibers from hydrophilic to more hydrophobic. Gautam et al [9] created a polyamide nanofiber membrane for microfiltration. In comparison with commercial PET (polyester) and PVDF membranes, whose contact angle is about 41, this nanomembrane reached the smallest contact angle of 86° and therefore the best results.

Hsieh and Fan [10] created fluorinated carbon fibers by catalytic chemical vapor deposition and subsequent fluorination by perfluorohexane. By this way, they decreased the surface tension of carbon nanofiber (CNF) and achieved a contact angle of 166°. Lee et al [11] used atmospheric plasma to increase the hydrophobicity of silk fibers for medical applications. They used fluorocarbon CF_4 and managed a contact angle of 99.7°–131°. Balu, Breedveld and Hess [12] improved the hydrophobicity of cellulose, which is biodegradable. Amorphous cellulose was selectively etched in atmospheric plasma and subsequently coated with a thin FC film also using plasma. This modification resulted in a contact angle of 166.7°. Lejeune et al [13] also used etching in atmospheric plasma to improve hydrophobicity. In their work, they increased the roughness of the silicon surface. Thorvaldsson et al [14] achieved higher hydrophobicity by coating a textile cellulose microfiber with electrospun cellulose nanofibers (using NaOH), creating a large and rough surface area that is further plasma treated with a fluorine plasma.

Panagiotis and Evangelos [15] studied superhydrophobicity using atmospheric plasma. Atmospheric plasma was used mainly for the low cost of the necessary equipment and also

the for the possibility of continuous production in the case of one-step processes like creating low surface tension. For multistep processes, the production process is discontinuous, such as when low-vacuum plasma is used. Yang et al [16] created a hydrophobic surface on cellulose (cotton)-based natural materials. Hexamethyldisiloxane polymer and atmospheric plasma were used for this environmentally friendly surface finish. Novák et al [17] studied the increase in surface hydrophobicity of a polyester/cotton fabric using atmospheric plasma. The fabric was subsequently modified by a sol–gel process using organofunctional silanes to further enhance its hydrophobicity. The contact angle was higher than 150°. This method could be used on an industrial scale. Ryu et al [18] increased the hydrophobicity of a polytetrafluoroethylene sheet using plasma treatment with argon and oxygen gases. This one-step plasma etching of the surface created nano-sized spherical tips and increased the contact angle from the pretreatment angle of 111° to 179°. The contact angle stayed unchanged even after an air-aging test of 80 days, i.e., no degradation was observed.

1.2. Agents used for surface hydrophobization

According to a patent from 1856 [19], aluminum soaps are used for the hydrophobization of flat textiles. Since that time, many types of agents have occurred in the field of textile hydrophobization. Currently, the following agents are among the most used paraffin wax emulsions: aluminum or zirconium salts, higher fatty acids derivates, silicones, and perfluoroalkanes. More details can be found in [2].

1.3. FC finishing

FCs are formed by adding perfluoroalkyl groups to acryl or urethane monomers, which polymerize directly on the treated surface, in our case a fiber. Maximum hydrophobicity is achieved when the final polymer has a -CF_3 group at its end. The FC chain can contain up to 10 carbon atoms. After applying the FCs, the textile material must be thermally treated to obtain the desired parameters. The heat treatment causes increased orientation of the FC chains, which improves repellency. This process, sometimes called as activation, is especially necessary after washing or dry cleaning and occurs during ironing or tumble drying of the textile. These days there are some FCs in which the reorientation of their chains occurs at ambient temperature during free drying. However, their efficiency and durability are not very high. They are mostly used in the field of furniture and home textiles.

To lower their environmental impact and to avoid any possible health risks, current legislation allows the use of FCs with C6 or less, even though their negative effect on health and environment has not been proven yet.

1.4. Low-vacuum plasma

Langmuir was the first scientist who started working with plasma in 1928 [20]. His goal was to develop tubes that would conduct high-level currents at a low pressure. These tubes had to be filled with ionized gas. Discharge in gases occurs

in mercury rectifiers, hydrogen thyratrons, sparkover gaps in surge protection, arc welding, fluorescent and neon tubes and also in lighting.

Low-vacuum plasma technology uses gas under very low pressure in a vacuum, which is activated by electromagnetic energy. By using high vacuum pumps, a pressure of 10^{-2} to 10^{-3} mbar is reached in the vacuum container. Under these conditions, energetically rich ions and other reactive particles create a plasma.

2. Experimental part

The samples used in the experiment were prepared in two steps:

(1)   preparation of nanofiber layers and

(2)   modification of some samples using low-vacuum plasma of roll-to-roll type.

The detailed preparation of samples is described in sections 2.1 and 2.2.

2.1. Creating a nanofiber layer

The nanofiber layer was made from polyurethane because of its easy spinnability and also high speed of spinning. A nonwoven fabric of the spunbond type with an areal weight of 30 g/m^2 was used as the support material. The production was performed in a laboratory using the Nanospider machine. The polymer solution was added to a basin with a rotating roller. This solution was exposed to an electric field of U = 76.1 kV voltage. A collector was placed above the basin at a distance of 175 mm. The speed at which the support textile material was moving was set at v = 0.1 m/min. The relative humidity in the spinning chamber was regulated at 21%. The humidity sensor was not placed directly in the spinning chamber but in the tube,

bringing the air to the chamber to ensure proper sealing. The turning of the roller (driven by a rotor) in the basin created a thin polymer solution layer on its surface from which in turn nanofibers were formed due to the high voltage and collected on the support textile material.

Nanofiber layers with the following areal weight were created: 1 g/m^2, 2.5 g/m^2, and 5 g/m^2 (samples marked WT1, WT2, and WT5, respectively). The parts of the samples were subsequently plasma modified – hydrophobized by FC C6. These modified samples were marked as AT1, AT2 and AT5, respectively. The hydrophobization process is described in the following paragraph.

2.2. Low-vacuum plasma of roll-to-roll type

In all experiments, low-vacuum plasma roll-to-roll type was used from the Belgian company Europlasma. During this type of surface modification, such a small amount of hydrophobic agent is applied that there is basically no chance of blocking the interfiber pores of the polymeric nanofiber layer. By creating a plasma hydrophobic coating on the surface of the polymeric nanofiber, the hydrostatic resistance of the whole nanofiber layer increases while time keeping its original excellent water vapor permeability due to the free interfiber spaces. The practical properties of a polymeric nanofiber layer with this kind of surface modification are much higher than with other hydrophobic treatments. Low-vacuum plasma was used as it allows to treat the material that is wound up on a plastic roller. The width of woundup material is about 0.5 m with a diameter of about 0.3 m. The device comprises a feed roll, a collector roll, and a plasma. This type of device is much more complicated than systems with individual cassettes as it requires control of the winding-over process of the fabric. The vacuum chamber itself comprises several electrodes that are placed between the feed and the collector rolls. The scheme of the hydrophobization using low-vacuum plasma is presented in Figure 1.
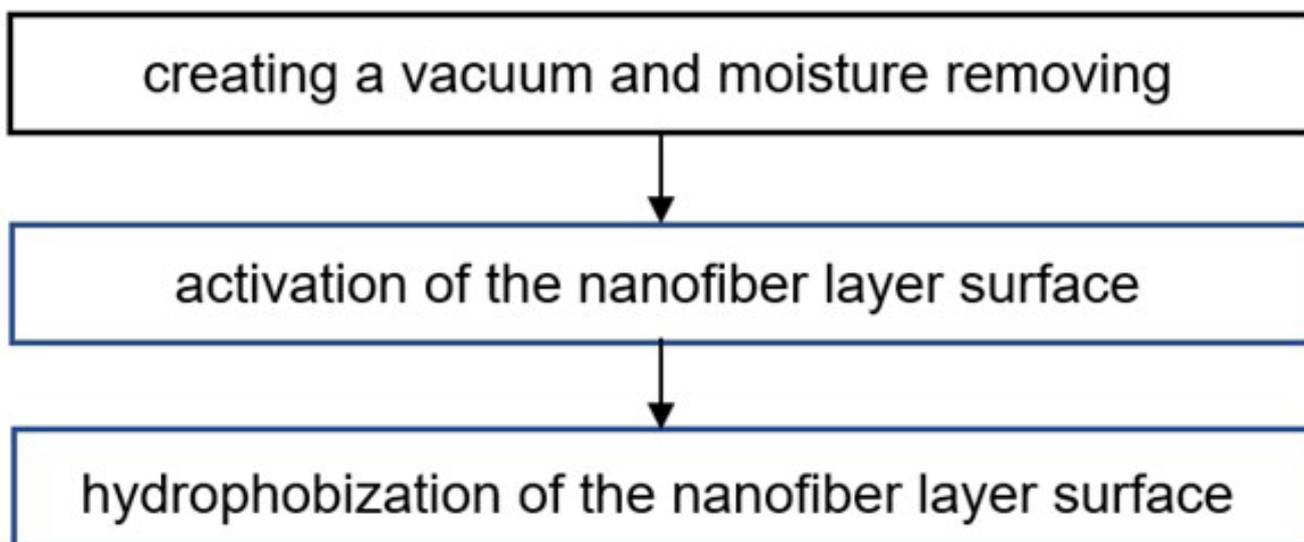
Figure 1. Low-vacuum plasma scheme.

The conditions of using the low-vacuum plasma in the individual steps were as follows:

(1)   vacuum creation and humidity removal – speed 1 m/min, pressure 25 mTorr, a chamber filled with argon (without the use of electrodes), argon consumption 200 sccm (standard cubic centimeters per minute);

(2)   activation of the nanofiber layer surface – argon at a speed of 1 m/min, pressure 100 mTorr, electrode output 2400 W, and argon consumption 700 sccm; and

(3)   hydrophobization of the nanofiber layer surface – using monomer at a speed of 1 m/min, pressure 10 mTorr, and electrode output 270 W; monomer consumption 200 sccm; and operational temperature of the chamber +40°C.

3. Results and discussion

Table 1 shows the individual samples and their nominal areal weights and produced areal weights including standard deviations (in brackets). The areal weight results are based on five measurements.

The module analysis of variance (ANOVA) from statistical software QCExpert was used for data analysis.

Other properties connected to thermophysiological comfort were also measured – air permeability (AP) was measured using the instrument Textest 3300 (standard ISO 9237). To measure air permeability, an air-pressure difference must be created between the two surfaces of the tested textile causing an air flow, which can be then measured. The pressure gradient was 100 Pa, and the area of the tested sample was 20 cm^2.

Water vapor permeability (*Ret*) was measured using the instrument Permetest (ISO 11902). During this test, the sample was put on the measuring head with a porous membrane and fastened between the head and the body of the instrument. Attention was paid not to damage the membrane. The resistance to water vapor was showed on the connected computer monitor after a relatively short time in *Ret* [Pa×m^2×W^{-1}]. Hydrostatic resistance (*H*) was measured using the instrument HydroPro Hydrostatic Head Tester (ISO 811). During the hydrostatic test, a grid (100% polyester warp-knit fabric with an areal weight of 25 g×m^{-2}) was placed on the membrane at 60 cm/min pressure and the water pressure was exerted from the side of the membrane; the tested area was 100 cm^2. The measurements were carried out three times for each sample. The results are shown in Table 2. The table shows arithmetic means with the relevant standard deviations in brackets. For measuring the contact angle *AW* (°), a method was chosen where the sample is placed on a metal plate and scanned by a microscope with a camcorder connected to a computer. A 10 μl drop of water was placed on the sample using a micropipette. For the evaluation of this experiment, the picture analysis software Lucia G was used. This system enables communication between the scanning instrument (camcorder), the scanning card, and the computer. When using a camcorder for scanning the picture of the water droplet and a computer for its digitalization and evaluation, the accuracy of determining the contact angle increases up to an accuracy of 1°.

The contact angle *AW* using modification arose approximately two times – from approximately 68° at all samples marked as *WT* to approximately 120° at all samples *AT*. The contact so significantly exceeds the angle 90°, which is considered as the borderline between wettable and non-wettable surfaces. We can therefore state that the procedure used in our work leads to hydrophobization.

Table 1. The areal weights of samples – before and after treatment

Sample	Before treatment Arithmetic mean (standard deviation)			After treatment Arithmetic mean (standard deviation)		
	WT1	WT2	WT5	AT1	AT2	AT5
Nominal weight (g×m^{-2})	1	2.5	5	1	2.5	5
Produced areal weight, *W* (g×m^{-2})	1.03 (0.05)	2.52 (0.03)	5.01 (0.09)	1.03 (0.05)	2.51 (0.01)	5.03 (0.02)

Table 2. The results of thermophysiological comfort properties

Sample	WT1	WT2	WT5	AT1	AT2	AT5
Contact angle *AW* (°)	67.4	67.8	68.1	119.7 (1.5)	120.7 (1.2)	120.0 (1.0)
Air permeability – *AP* (l×m^{-2}×s)	8.60 (0.065)	7.22 (0.026)	4.70 (0.049)	8.45 (0.112)	7.09 (0.081)	4.67 (0.151)
Water vapor permeability – *Ret* (Pa×m^2×W^{-1})	<0.1 (–)	<0.1 (–)	0.25 (–)	<0.1 (–)	0.15 (–)	0.2 (–)
Hydrostatic resistance – *H* (mm×H$_2$O)	156.7 (11.5)	176.7 (30.6)	186.6 (15.3)	806.7 (40.4)	7967 (152.6)	12,030 (152.7)

The air permeability of samples with hydrophobic treatment stayed almost the same as one of the nontreated samples. This hydrophobic treatment has therefore no influence on the material's air permeability. Water vapor permeability *Ret* is below the minimum limit of the range of our measuring device (0.5). It proves that if a nanofiber layer with this treatment was used in a textile composite for outdoor clothing, this layer would have minimum influence on the overall water vapor permeability of the clothing. Its water vapor permeability would be determined only by the face material or lining material used. The hydrostatic resistance measurements show that the hydrophobic treatment caused sharp growth of hydrostatic resistance. Untreated samples had a hydrostatic resistance of approximately 150–200 mm of water column. The sample of areal weight of 1 g×m^{-2} showed an increase in hydrostatic resistance of about five times (sample *AT1* where the mean of *H* is more than 800 mm of water column). Heavier samples *WT2* and *WT5* saw hydrostatic resistance grow even more significantly after treatment (samples *AT2* and *AT5*) – in sample *AT2*, almost 8000 mm of water column and in sample *AT5*, approximately 12,000 mm of water column. The recognized hydrostatic resistance limit for the suitability of a textile material for outdoor use is 10,000 mm of water column. The results of sample *WT5* show that nanofiber layers with an areal weight higher than 5 g×m^{-2} and plasma FC treatment can be used as membranes for outdoor textiles.

4. Conclusions

In this paper, hydrophobization of a nanofiber layer using plasma and FC treatment is introduced. The goal was to create a procedure for a nanofiber layer with a hydrophobic finish, which could be used as a membrane in clothing for outdoor activities.

To verify the effectivity of such treatment, thermophysiological comfort properties were measured – air permeability, contact angle, hydrostatic resistance, and water vapor permeability. Nonwoven nanofiber textiles with areal weights of 1 g×m^{-2}, 2 g×m^{-2}, and 5 g×m^{-2} were produced. The results of the experiments show that the air permeability of the nanofiber layers was not influenced by the plasma treatment. The water vapor permeability is so low that it will have no effect on the water vapor permeability of the final composite outdoor textile where the nanofiber layer would be used as a membrane. The plasma treatment led to a sharp increase in hydrostatic resistance. The untreated samples had a hydrostatic resistance in the order of hundreds of millimeter of water column. The treated sample with an areal weight of 5 g×m^{-2} reached the mean value of hydrostatic resistance of more than 12,000 mm of water column. A nanofiber layer with a plasma FC finish can be used as a membrane in composite textiles meant for the production of outdoor clothing. As in this experiment the parameters of a nanofiber layer on its own were measured, it was not possible to wash this membrane and compare its surface hydrophobicity and hydrostatic resistance before and after the washing. The washing cycle would have damaged the nanofiber layer. Most papers on the hydrophobization of textile materials focus on atmospheric plasma treatment.

However, this study looks exclusively at low-vacuum plasma treatment used to increase the hydrophobicity of a surface and, as the results show, a simultaneous increase in hydrostatic resistance. The low-vacuum plasma equipment is significantly more complicated and also expensive, but as the results show, it has a great potential. It was proven that after low-vacuum plasma treatment of a nanofiber layer, not only the hydrophobicity of its surface but also its hydrostatic resistance increased substantially.

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