Investigation of electrical and surface properties of spunbond nonwoven fabrics coated with graphene oxide and formed PVDF nano fibres via electrospinning on IT

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ABSTRACT – REZUMAT

Investigation of electrical and surface properties of spunbond nonwoven fabrics coated with graphene oxide and formed PVDF nano fibres via electrospinning on IT

Graphene oxide (GO) and Polyvinylidene fluoride (PVDF) are among the primary materials constituting the basis of conductivity and sensor research. In this study, PVDF and GO-filled PVDF nanofibers were formed by the electrospinning method on the polyester spunbond nonwoven fabric coated with aqueous graphene oxide dispersion via the dip coating method. The graphene oxide dip-coated spunbond nonwoven fabric as a substrate was used. Then, nanofiber surfaces with PVDF and GO-filled PVDF were formed by the electrospinning method onto GO-coated and reduced nonwoven fabrics. Polymer solutions were prepared as pure PVDF with 0.5 wt% – 1 wt% – 2 wt% GO. The chemical reduction operation by using Vitamin C and rosehip extract powder to nonwoven spunbond fabric coated with graphene oxide and forming GO-filled PVDF nanofibers on it, was processed. Characterization analyses of nonwoven spunbond fabric samples were performed by using XRD, FTIR, and SEM. To determine the functional properties, electrical resistance, water contact angle, and mechanical strength measurement results were evaluated. The use of nature- and human-friendly reducing agents in the present study is in alignment with the principle of sustainability.

Keywords: *graphene oxide, polyvinylidene fluoride, electrospinning, spunbond nonwoven fabric, sensor*

Investigarea proprietăților electrice și de suprafață ale nețesutelor consolidate la filare chimică acoperite cu oxid de grafen și nanofibre PVDF formate prin electrofilare pe IT

Oxidul de grafen (GO) și fluorura de poliviniliden (PVDF) se numără printre materialele primare care constituie baza cercetării conductivității și a senzorilor. În acest studiu, nanofibrele PVDF și PVDF umplute cu oxid de grafen au fost formate prin metoda de electrofilare pe materialul nețesut consolidat la filarea chimică din poliester acoperit cu dispersie apoasă de oxid de grafen prin metoda de acoperire prin imersie. Materialul nețesut consolidat la filarea chimică acoperit cu oxid de grafen prin imersie a fost utilizat ca substrat. Apoi, suprafețele de nanofibre cu PVDF și PVDF umplute cu oxid de grafen au fost formate prin electrofilare pe nețesute acoperite cu oxid de grafen și reduse. Soluțiile polimerice au fost preparate ca PVDF pur cu o greutate de 0,5% – 1% – 2% din greutatea oxidului de grafen. A fost prelucrată operația de reducere chimică prin utilizarea vitaminei C și a pulberii de extract de măceșe la materialul nețesut consolidat la filarea chimică acoperit cu oxid de grafen și s-au format nanofibre PVDF umplute cu oxid de grafen pe aceasta. Analizele de caracterizare a probelor nețesute consolidate la filarea chimică au fost efectuate prin utilizarea XRD, FTIR și SEM. Pentru a determina proprietățile funcționale, au fost evaluate rezultatele măsurătorilor privind rezistența electrică, unghiul de contact cu apa și rezistența mecanică. Utilizarea agenților de reducere prietenoși cu natura și omul în studiul de față este în concordanță cu principiul durabilității.

Cuvinte-cheie: *oxid de grafen, fluorură de poliviniliden, electrofilare, nețesut consolidat la filarea chimică, senzor*

INTRODUCTION

Smart textiles are defined as textile materials, unlike traditional textile materials, that can sense these stimuli coming from external sources such as temperature, pressure, elongation, moisture, radiation, light, pH or pressure change, electricity, vibration, noise, sound waves, magnetic field, mechanical action, chemical interaction, etc. and react to these warnings by generating a response [1]. Smart textiles that can sense, actuate, generate/store energy/power, and communicate have gained importance in the textile and clothing industry in recent years. Smart materials are classified into three categories such as passive, active, and very smart textiles. Passive smart textiles only sense the environmental conditions or the users. Active smart textiles can sense and react to stimuli coming from the environment. The very smart materials can sense, react to, and adapt to external conditions or stimuli [2]. In the production of smart textile materials, conductive fibers, shape memory fibers, photochromic fibers, temperature-sensitive fibers, pH-responsive gel fibers, healthy smart fibers, and piezo/tribo-electric materials have been used [3].

There are a lot of components in smart textile materials, like actuators, resistors, capacitors, inductors, antennas, interconnections, power supply, data processing, and sensors. Conductive materials are required to make these electrical parts or elements. Conductivity is a very crucial and desirable property of smart textile materials. Textile materials having conductive properties during polymerization, fiber spinning, and fabric production can be produced. The conductivity properties of any fabric with a coating or printing process can be achieved. Copper/silver wires, stainless steel fibers, silver-coated polyamide fibers, carbon-suffused nylon fibers, conductive bicomponent sheath/core type (conductive sheath) polyester fibers, and graphene are some of the conductive textile materials. In addition to these, carbon black, carbon nanotubes, graphene, and conductive polymers such as polyaniline and polyvinylidene fluoride (PVDF) can be included in the polymer melt during fiber spinning to manufacture electrically conductive composite fiber or yarn [4]. Among all conductive materials, graphene, which has a higher specific surface area, high electrical and thermal conductivity, and excellent mechanical properties, has special importance and great potential as a smart material component. Although graphene is a very expensive material, chemically modified graphene materials (CMG) such as graphene oxide (GO) and reduced graphene oxide (RGO) can be obtained cheaply on a large scale [5]. First, graphite is converted to graphene oxide, and then graphene oxide is reduced by a chemical reduction process, and graphene production is carried out. The chemical method of graphene synthesis stands out as the most favorable, being particularly suited for laboratory studies. In synthesis with the chemical method, first, new bonds are formed between the carbon atoms of the graphite via oxidation, and the carbon layers are separated. With the subsequent reduction process, the bonds between the distant carbon layers are broken down, and sheets of single or multiple layers of carbon are extracted. The resulting structure, known as graphene [6], is commonly obtained using the layer separation method, epitaxial growth, the silicon-carbon method, or Hummer's method [7]. When graphite is oxidized, graphene oxide (GO) results in a material with fewer electrical properties than graphite or graphene [6, 8]. To restore and enhance conductivity, GO sheets must be reduced chemically, thermally, or electrochemically [9]. The material obtained after undergoing the reduction process is called reduced graphene oxide. Concerning graphene and its derivatives in textiles, applications include flexible wearable electronic textiles (fibers, yarns, and fabrics) [10], information transfer, providing communication, heating, reacting to impact, protecting people and sensitive electronic devices against electromagnetic waves and electrostatic discharges, medical textiles [11], conductive nano textiles and nano-optoelectronics [12]. At the same time, graphene-based materials are also widely utilized in strain and pressure sensors due to their excellent flexibility and good electrical conductivity [13].

The word piezoelectric is derived from the ancient Greek words for "pressure" and "electric" [14]. In 1969, Kawai discovered very high piezo activity in polarized fluoropolymers [15]. Among fluoropolymers, polyvinylidene fluoride (PVDF) is one of the most widely known and used polymers, with one of the strongest piezoelectric effects [14]. Properties of the PVDF polymer include the possibility of functioning in a frequency range of 0.001 to 109 Hz and 10–8 to 106 psi (lb/in^2) pressure range, as well as high voltage, elasticity, dielectric resistance, and strength [14]. After PVDF polymers are polarized, they can maintain their polar structure at room temperature for an extended period; however, their polar structure and piezoelectric properties deteriorate with increasing temperature [16]. Piezoelectric materials produce electrical signals when subjected to load and strain. The amplitude and frequency of the generated signal are directly proportional to the mechanical deformation [13]. PVDF is used in the production of sensors thanks to its piezoelectric properties, creating a current when exposed to mechanical effects or undergoing mechanical change due to the effects of currents [17]. Abbasipour et al. [14] studied the piezoelectric effect by adding graphene oxide, graphene, and halloysite nanotube materials of various morphologies and concentrations to PVDF polymer. They reported that the β phase ratios of nanofiber PVDF mats prepared using the electrospinning method were up to 49% higher in GO-doped nanofibers compared to undoped mats. Abolhasani et al. [15] prepared graphene-PVDF composite nanofiber mats, employing the technique of electrospinning using different graphene contents. They observed that the addition of a small amount of graphene (0.1% by weight) significantly increased the β-phase formation and open circuit voltage of the nanofibers. However, increasing the graphene content reduced the electrical output voltage of randomly oriented nanofibers. They reported that the PVDF/graphene nanogenerator that was produced could fully synchronize finger movement and that the electricity generated could light a commercial LED for 30 seconds.

In the literature, it was seen that numerous studies have been performed on the coating of textile surfaces with GO. In most of these scientific studies, woven or knitted fabrics were coated with GO using various methods, after which the GO was reduced and its properties examined. Although most studies on PVDF have employed the electrospinning method, it was realized that, thus far, no study has been conducted in which both the GO coating and GO-doped PVDF polymer solution were used on a nonwoven fabric. In addition, many different reducing agents have been utilized in the literature. The important and remarkable side of our study is that the substances chosen and used as reducing agents were both natural and human & and environmentally friendly. Our study aimed to produce GO-filled PVDF nanofibers by the electrospinning method on GO-coated polyester spunbond nonwoven fabric, to examine their properties and to proffer suggestions regarding novel areas of use by the resulting functional properties of the nonwoven fabrics developed.

EXPERIMENTAL

Materials

All chemicals were of analytical reagent grade and used without further purification. Graphite flakes, acetone, dimethylformamide (DMF), and Vitamin C (L-ascorbic acid) were purchased from Sigma Aldrich (USD). Sulfuric acid (H_2SO_4, 95–98%), potassium permanganate ($KMnO_4$), and ethanol were purchased from Isolab (Türkiye). Hydrogen peroxide (H_2O_2, 35%), phosphoric acid (H_3PO_4), and hydrochloric acid (HCl, 37%) were purchased from Merck (Germany). Water-soluble rosehip extract powder (Rosa canina) was purchased from Naturalya Chemistry (Türkiye). Distilled water was used throughout the experiments. The polyester spunbond nonwoven fabric with a basis weight of 25 g/m^2 was used as the substrate fabric. PVDF (M_w = 244000, Solef® 1000 series) was provided by Solvay (Holland).

Synthesis of GO

Graphene oxide was synthesized from flake graphite by the improved Hummers' method according to the Gültekin et al. [18]. Briefly, a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (360:40 ml) was added to a mixture of graphite flakes (3 g) and $KMnO_4$ (18 g). The reaction was then heated to 50°C and stirred for 12 h. The reaction was then cooled to room temperature and poured onto ice (400 ml) with 35% H_2O_2 (6 ml). The resulting suspension was washed by repeated centrifugation (each at 8000 rpm for 30 min), first with 400 ml of 1 M HCl and 200 mL of ethanol (×2), then with distilled water until a pH of 4–5 was achieved. The obtained solid product was dried overnight in an oven at 60°C.

Coating of nonwoven fabric

2g/l GO aqueous dispersion was prepared with the obtained graphene oxide. As-obtained 100% polyester nonwoven fabrics were dip-coated with the prepared GO aqueous dispersion and became ready for the electrospinning process. The bath ratio for dip coating was determined as 1:20. The nonwoven fabric was dipped into GO dispersion for 30 min at ambient conditions. Then, the fabric was dried in an oven at 60°C.

Electrospinning

The pure polymer solution was prepared with 10 wt% PVDF in a 3:2 ratio (DMF/Acetone) by using a magnetic stirrer at 50°C. For the preparation of GO-doped PVDF solution, GO ratios were determined and prepared as 0.5 wt%, 1 wt%, and 2 wt%. The electrospinning parameters for the production of neat and GO-doped PVDF nanofibers were set as 12 cm collector-nozzle distance, 200 rpm collector rotation speed, 2 ml/h feeding rate, and 27 kV applied voltage.

Reduction of graphene oxide

The nature-friendly reducing agents determined for the reduction process of the nanofibrous structure obtained on the nonwoven fabric were Vitamin C (L-ascorbic acid) and Rosehip powder extract. For the reduction process with Vitamin C, a 0.2 M aqueous Vitamin C solution was prepared. For the reduction process with rosehip extract, 10 wt% aqueous rosehip extract solution was prepared with 0.5 wt% Vitamin C. After the electrospinning process, the nanofiber samples were reduced with Vitamin C for 90 minutes at 95°C and with rosehip extract solution for 5 hours at 95°C. After reduction, the samples were washed with gradual washing with distilled water and dried in the oven for 60 min.

Characterization

The X-ray diffraction (Shimadzu, LabX XRD 6100) spectra were performed with a Cu Kα (λ=1.5406 Å) radiation source with a θ-2θ range of 5° – 70°. Measurements were made at 40 kV voltage and 30 mA current values. An attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Perkin Elmer Spectrum Two) was used at 400–4000 cm^{-1}. Scanning electron microscopy (TESCAN, VEGA 3) was employed to observe the morphology of GO and RGO-filled PVDF nanofibers, GO, and RGO-coated nonwoven fabrics. The surfaces of the samples were coated with a gold/palladium mixture on the (Quarum, SC7620) for 165 seconds before analysis. Diameters of the electrospun nanofibers were analyzed from the SEM images using ImageJ software.

Tensile strength measurements of nanofiber surfaces were made with the Instron 4411 device. Tensile strength test conditions were set at 30 mm/min test speed and 10 mm to 50 mm sample dimensions. Measurements were performed and reported in both vertical and horizontal directions. The surface electrical resistivity of the samples was measured with a 4-point probe. The setup consists of a sourcemeter (Keithley 2450 Sourcemeter) and a four-point probe station (Everbeing Int'l Corp). The water contact angle measurement of nonwoven and nanofiber samples was measured by using a contact angle meter (CAM 100, KSV Instruments).

RESULT AND DISCUSSION

FTIR Analysis

The FTIR has been used to analyze the coating and reduction of GO nanosheets on the polyester nonwoven fabric surface, and also, to analyze the structural transformation of the crystalline phases within the PVDF nanofiber. Figure 1, *a* shows the FTIR analysis of GO, RGO-R, and RGO-C coated polyester nonwoven fabric. The peaks at 722 cm^{-1}, 871 cm^{-1}, and 1408 cm^{-1} are attributed to the C-H bond in the aromatic group, the peaks at 1711 cm^{-1} and 1238 cm^{-1} were assigned to C=O and C-O stretching vibrations of aromatic ester and ester, respectively [19, 20]. The

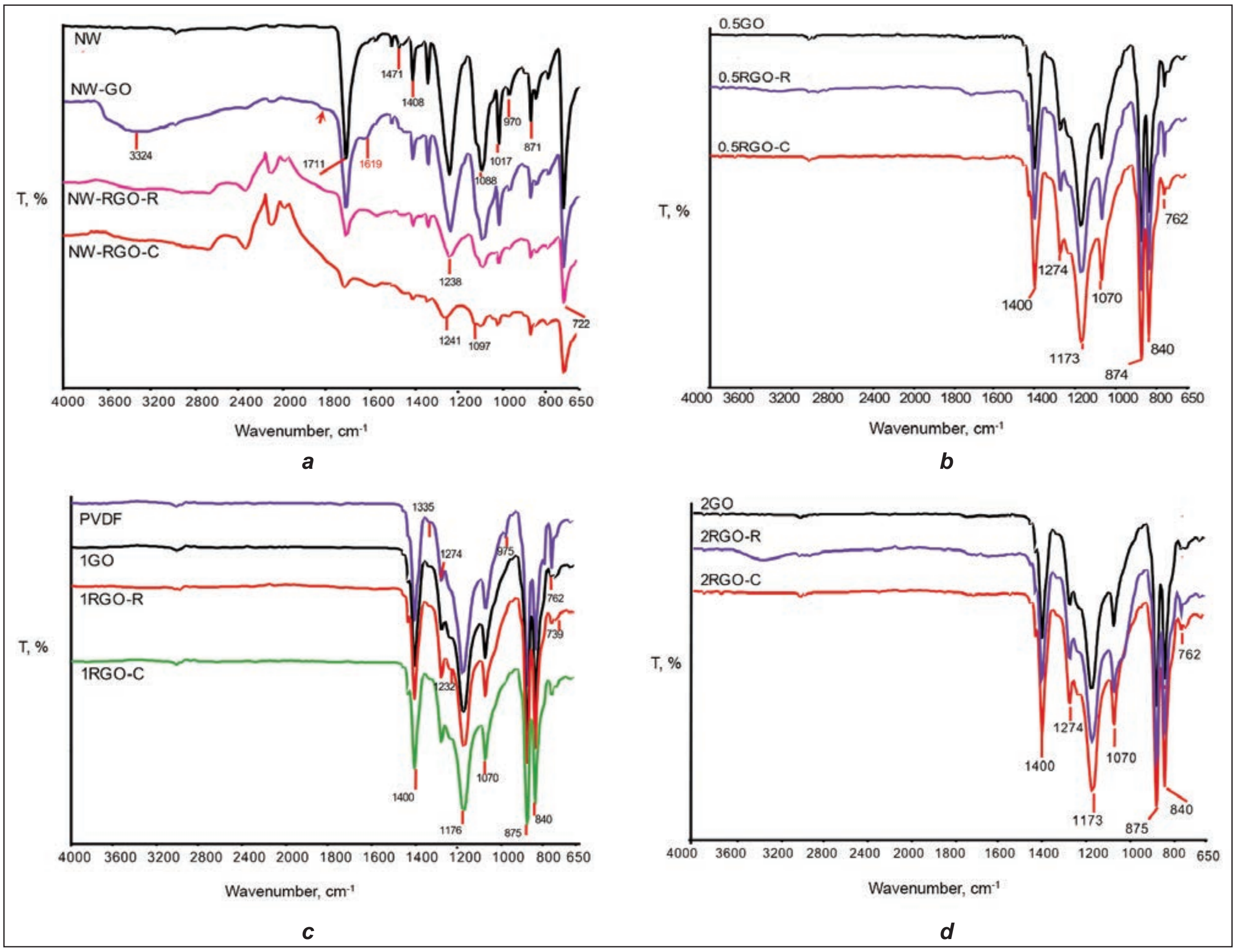


Fig. 1. FTIR spectra of: *a* – neat nonwoven fabric, GO-coated nonwoven fabric, reduced samples with rosehip and Vitamin C; *b* – electrospun neat PVDF nanofibers, 1 wt% GO-PVDF and reduced GO-PVDF composite nanofibers; *c* – electrospun neat PVDF nanofibers, 1 wt% GO-PVDF and reduced GO-PVDF composite nanofibers; *d* – electrospun neat PVDF nanofibers, 2 wt% GO-PVDF and reduced GO-PVDF composite nanofibers

C-O stretching of glycol was seen at 1017 cm$^{-1,}$ and benzene in-plane vibrations were found at 970 cm^{-1}. The peak at 1088 cm^{-1} represents the ester C=O stretching vibration [21]. After the GO coating process, a broad peak between 3600–2800 cm^{-1} shows O-H stretching vibrations of carboxylic acid can be attributed to the water molecules and alcohol groups in GO. The new peak appeared at 1619 cm$^{-1,}$ corresponding to the C°C stretches from the unoxidized graphitic domain [22]. After the reduction of GO, the broad peak between 3600–2800 cm^{-1} disappeared, and the intensity of the sharp peaks decreased

The FT-IR spectra of electrospun neat PVDF nanofibers, 1 wt% GO-PVDF, and reduced GO-PVDF composite nanofibers are shown in figure 1, *b*. For the neat PVDF nanofibers, the characteristic vibrational peaks are observed at 764 cm^{-1}, 796 cm^{-1}, and 975 cm^{-1}, which correspond to the nonpolar α-phase. The peaks at 1274 and 1232 cm^{-1} confirm the nucleation of the polar β-phase and the semipolar γ-phase, respectively. For the 1GO nanofiber, all α-peaks disappeared, and the peaks corresponding to the electroactive β- and γ-phases became stronger. The peak at 840 cm^{-1} for the 1GO nanofibers is more intense than neat PVDF, which indicates the specific electrostatic interaction between the π- π-π-electron cloud and the oxygen-containing functional groups (carbonyl and carboxylic groups) in GO and the $-CH_2/-CF_2$ dipoles of PVDF [23]. Among the five crystalline phases (a, b, g, d, and e) of the PVDF, the stable non-polar phase is the most common crystalline phase, which can be easily obtained from melting crystallization and has no electroactivity. The polar b phase and g phase PVDF crystal have higher electroactivity than the a phase and different methods are used to convert the a phase to the b phase or g phase and enhance the piezoelectricity of PVDF [24]. The piezoelectric property is dependent on the β-phase's amount of the PVDF polymer or its total crystallinity [14]. FTIR is commonly used to identify the b crystalline phases in a polymer by the following equation:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} \qquad (1)$$

where K_α and K_β are the absorption coefficients at the particular wavenumber. K_α is 6.1×10^4 cm^2/mol and K_β is 7.7×10^4 cm^2/mol. X_α and X_β are mass

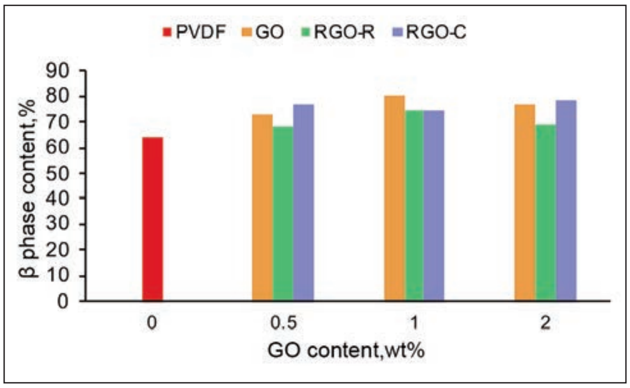


Fig. 2. The calculated b phase content of the electrospun PVDF nanofibers as a function of GO filler amount

fractions of α and β crystalline phases. A_β and A_β are the area of absorption bands at 762 and 840 cm^{-1} [25]. The values of F_β for the electrospun PVDF nanofibers are given in figure 2. The β-phase fraction for the neat PVDF nanofiber is obtained as 64%. The β-phase content increased with the addition of GO nanosheets. The highest β-phase content is obtained with the 1GO sample as 80%. According to the result, it can be said that the amount of β phase was increased by about 25% by the incorporation of GO to PVDF nanofibers. Moreover, the amount of the β phase showed a slight decrease after the reduction of GO with rosehip powder extract and Vitamin C. Although the reduction process of GO decreases the amount of β phase, it is still more than the neat PVDF nanofiber. The highest β-phase content for the reduced samples is obtained at 2RGO-C as 79% which is higher than that of the neat PVDF nanofiber about 23%. The use of GO as a nanofiller in the PVDF nanofibers provided effective dipole polarization and facilitated the nucleation of β phase crystals due to the enhanced dipole-dipole forces. The attachment of PVDF chains to the GO sheets was caused by the interaction between CF_2 in PVDF and the –C=O and COOH groups of the GO (hydrophilic interaction) [14]. The peaks at 840 and 762 cm^{-1} are used to investigate the improved β-phase development and α-phase suppression. The relative ratio of the peak intensities of these two absorption bands for neat PVDF is 2.2, while the highest value of 5.0 was obtained for the composite nanofiber with 1 wt.% of GO. The higher value of the 1GO sample confirms the development β-crystalline phase because of strong Van der Waals interactions between the highly electronegative fluorine on the PVDF chains and the free electron pairs on the GO oxygen atoms. [26]. The relative ratio of the peak intensities for 1RGO-R and 1RGO-C nanofibers is 3.85 and 3.81, respectively. The decrease in the amount of β phase and the relatithe ve ratio of relative intensities after the reduction of GO can be explained by the removal of the oxygen-containing functional groups which provide the interaction between PVDF and GO. The disruption of hydrophilic interaction caused the less amount of β phase.

XRD Analysis

The crystalline structure of electrospun PVDF nanofibers was characterized by XRD patterns. Figure 3 presents the XRD patterns of PVDF, 1GO, 1RGO-R, and 1RGO-C nanofibers. PVDF electrospun nanofiber shows characteristic peaks at 2θ = 18.6° and 20.2° associated with the reflections of α (020) and β ((200), (110)) polymorphs, respectively. The molecular chains of PVDF are uniaxially stretched by the high electrical forces during the electrospinning process, and the electroactive phase formation in the pure PVDF nanofibers takes place. It can be observed that in the sample containing 1 wt% GO, the α peak at 2θ = 18.6° changed to a β characteristic shoulder peak at 20.6°. The characteristic peak of the α phase diminishes, while a new crystallization peak corresponding to the (020) and (110) reflections of the β phase appears at 20.6°, indicating the existence of the β phase. The transformation from α to β phase in the fibers electrospun with GO benefits from the stretching and in situ poling during electrospinning. The incorporation of GO as a nanofiller improves the β-phase crystallinity. Also, a slight increase in the intensity of the β-phase is attributed to the interaction between the carbonyl groups present in the GO and the CF_2 segments in PVDF [27]. After the reduction process with rosehip extract powder and Vitamin C, the characteristic α phase appeared. This is possibly caused by an insufficient amount of carbonyl groups of RGO to nucleate enough PVDF chains into the required trans-trans (TT) conformation of the β-phase [28]. However, it can be seen that after the reduction process, the PVDF nanofibers are still enriched with β-phase compared to the neat PVDF nanofibers. As a result, the analysis of the XRD spectra of the electrospun nanofibers is in line with the analysis of the FTIR spectra.

SEM Analysis

Surface morphology of polyester nonwoven fabric with and without GO and after reduction of GO was characterized by scanning electron microscopy. SEM images of polyester nonwoven fabric coated with GO and RGO are given in figure 4. In figure 4, *a*, the presence of GO nanosheets between and around the polyester fibers confirms the coating process of GO nanosheets from the aqueous dispersion. In figures 4, *b* and *c*, the presence of nanosheets after the reduction of GO with rosehip powder extract and Vitamin C, respectively, can be observed.

The surface morphologies of the neat PVDF and the GO-filled PVDF nanofibrous structures were examined by scanning electron microscopy and are given in figure 5. In figure 5, *a*, the surface of the PVDF nanofibers is smooth and uniform. However, it can also be seen that the beaded nanofibers were

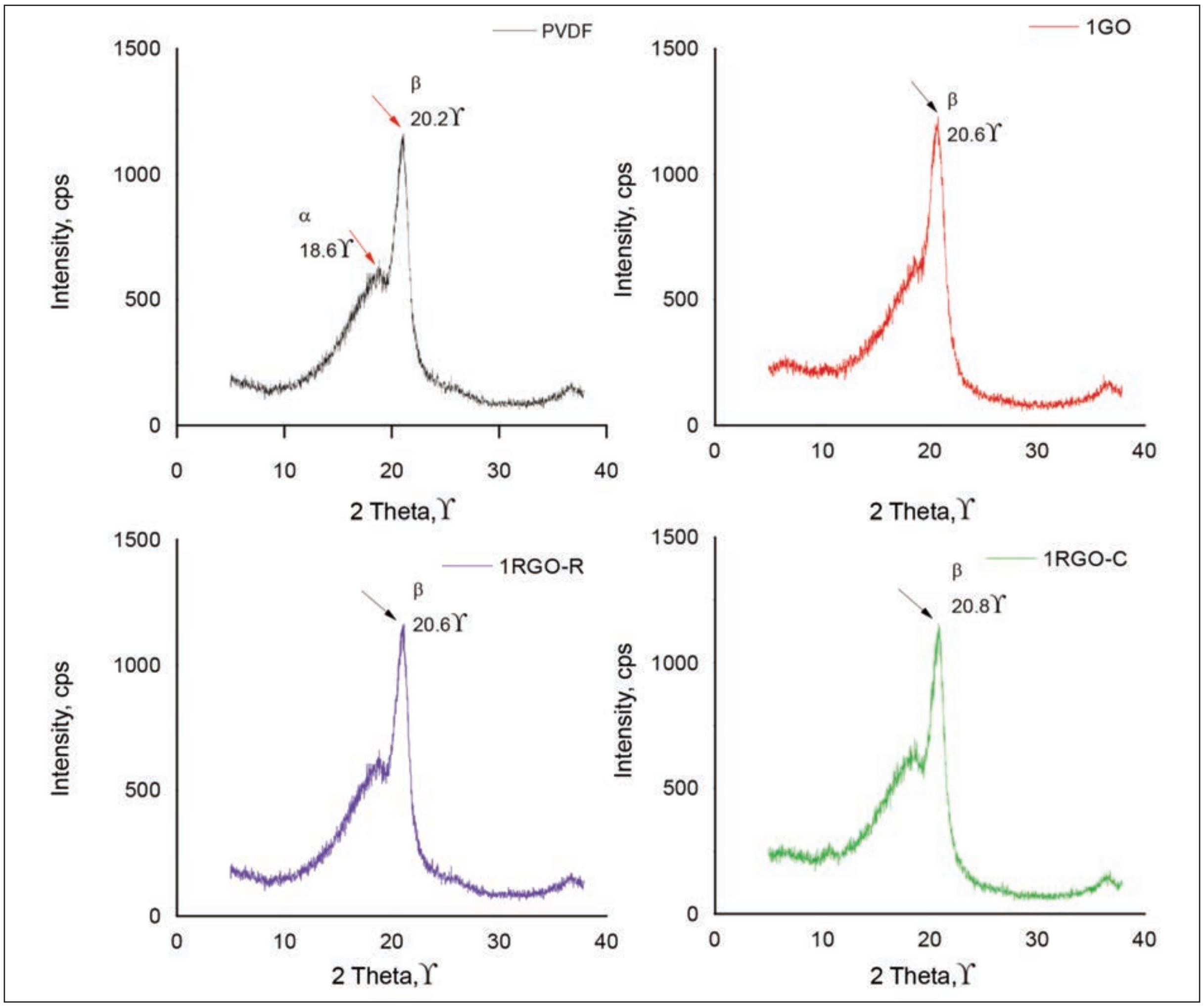


Fig. 3. XRD spectra of electrospun PVDF nanofibers with/without GO and after the chemical reduction process by rosehip extract powder and Vitamin C

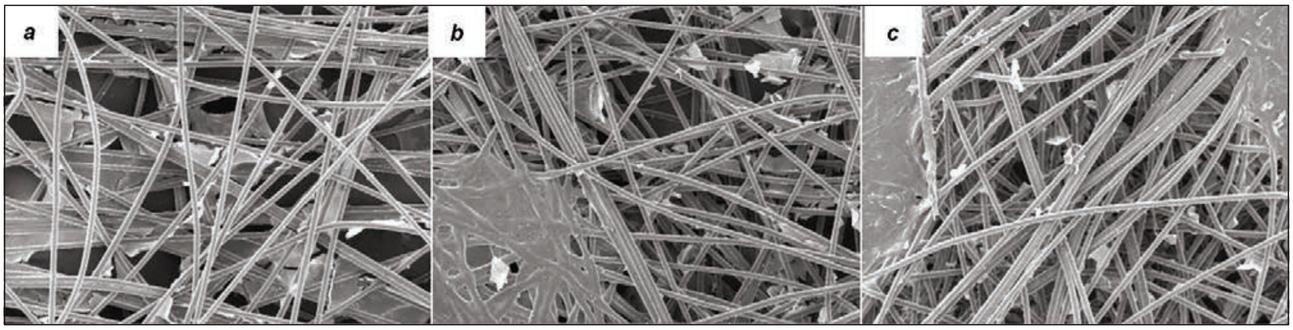


Fig. 4. SEM images (200x) of nonwoven fabric: *a* – coated with GO; *b* – reduced with rosehip powder extract; *c* – reduced with Vitamin C

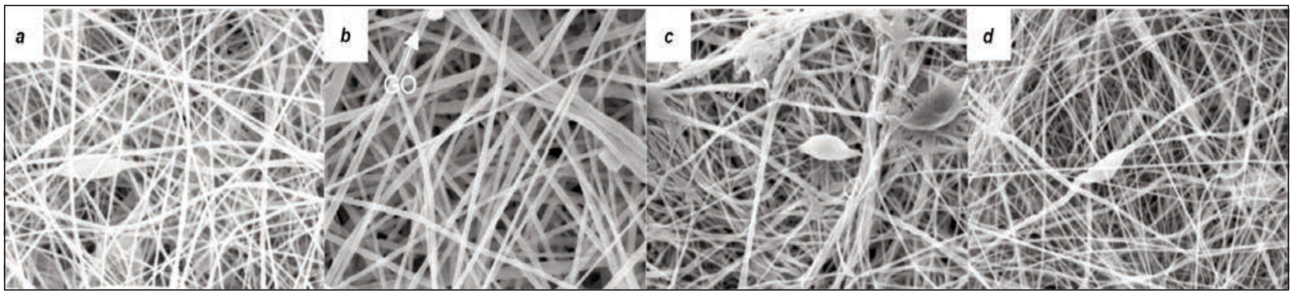


Fig. 5. SEM images (10kx) of: *a* – electrospun PVDF nanofibers: *b* – with GO; *c* – reduced with rosehip powder extract; *d* – reduced with Vitamin C

formed. With the addition of 1 wt% GO to the PVDF polymer solution, the nanofibers were obtained without bead formation. After the chemical reduction process of the GO-filled PVDF nanofibers by using Vitamin C and rosehip extract, the nanofibers maintained the original fibrous morphology, with the partial destruction of uniformity, resulting in the nanofibers sticking together, caused by the applied heat during the reduction process. Also, some defects, such as large beads or agglomerated GO/RGO nanosheets, can be seen in the images. Moreover, the results show the stability of the PVDF nanofibrous structure in aqueous solution at 95°C for a certain time.

The average diameter of nanofibers was measured and given in figure 6. It is seen that the diameter of the neat PVDF nanofibers was obtained as 230±26 nm. At the same time, the 1 wt% GO added PVDF nanofibers were obtained as 251±21 nm. The result suggests that the GO-added PVDF nanofibers have larger diameters than the neat PVDF nanofibers. However, the diameter of the nanofibers showed a dramatic decrease after the reduction process with Vitamin C and rosehip extract powder. The reason for the decrease in the diameter of the nanofibers after the chemical reduction process could be the removal of oxygen-containing functionalities located on the surface and the edges of the GO nanosheets, thus, the decrease in the interplanar distance of the nanosheets results in the finer nanofibrous structure.

The surface morphologies of neat PVDF and GO-filled PVDF nanofibrous structures were examined by scanning electron microscopy and are given in figure 4. In figure 4, *a*, the surface of the PVDF nanofibers is smooth and uniform. However, it can also be seen that the beaded nanofibers were formed. With the addition of 1 wt% GO to the PVDF polymer solution, the nanofibers were obtained without bead formation. After the chemical reduction process of GO-filled PVDF nanofibers by using Vitamin C and rosehip extract, the uniformity of nanofibers was destroyed and the applied heat during the reduction process caused the nanofibers to stick together. Also, some defects, such as large beads or agglomerated GO/RGO nanosheets, can be seen from the images. The average diameter of nanofibers was measured and given in figure 5. It is seen that the diameter of neat PVDF nanofibers was obtained as 230±0.026 nm, while the 1 wt% GO added PVDF nanofibers were obtained as 386±0.047 nm. The result suggests that the GO added PVDF nanofibers have larger diameters than the neat PVDF nanofibers. However, the diameter of the nanofibers showed a dramatic decrease after the reduction process with Vitamin C and rosehip extract powder.

Tensile strength measurements

The mechanical performance of neat PVDF, before and after reduction of GO-filled PVDF nanofiber surfaces, was analyzed using a universal tensile tester, and the results are presented in figure 7. The tensile strength properties of nanofiber samples were tested both in the machine direction and the cross direction. The results were evaluated in terms of elongation and tensile strength.

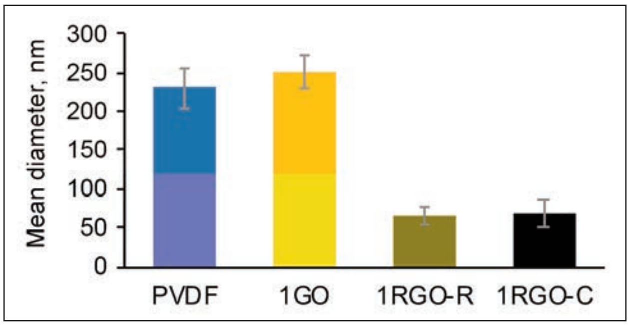


Fig. 6. Average nanofiber diameter of electrospun neat PVDF, GO, and RGO-filled PVDF nanofibers

The elongation and tensile strength of neat PVDF nanofibers were higher in the machine direction than in the cross direction. The elongation and tensile strength values of the neat PVDF nanofiber in the machine and cross directions were obtained as 107%, 1.5 MPa, and 92%, 1.4 MPa, respectively. With the addition of 0.5 wt.% of GO to the PVDF polymer solution, the mechanical performance of the nanofibrous structure increased prominently. When the GO filler content was increased to 1 wt.%, the highest mechanical performance in both directions was recorded. The elongation and tensile strength of the nanofiber containing 1 wt% GO increased by approximately 107% and 333% in the machine direction, and 139% and 436% in the cross direction, respectively, compared to those of the neat PVDF nanofiber. The results indicated the enhancement of the mechanical properties of GO-filled PVDF nanofibers. Besides, when the 2 wt% GO filler content was achieved, the mechanical performance of the nanofiber decreased, except for the tensile strength in both directions, compared to that of the neat PVDF nanofiber. Therefore, it can be inferred that the strength of the nanofibers increased without reducing the stretchability of the nanofibers at a certain amount of GO filler loading.

After the reduction of GO-filled PVDF nanofibers by using two different nature-based reducing agents, namely Vitamin C and rosehip extract powder, the mechanical performance of the RGO-filled PVDF nanofibers decreased compared to the GO-filled PVDF nanofibers. The reduction of GO-filled PVDF nanofibers with Vitamin C aqueous solution resulted in lower elongation values in both directions compared to those of the neat PVDF and GO-filled PVDF nanofibers. The elongation and tensile strength of Vitamin C-reduced nanofiber (RGO-C) samples increased with the increasing amount of GO nanosheets. The highest results were obtained with 2 wt% GO-filled PVDF nanofiber samples reduced with Vitamin C in both directions. The tensile strength of Vitamin C-reduced nanofiber samples was

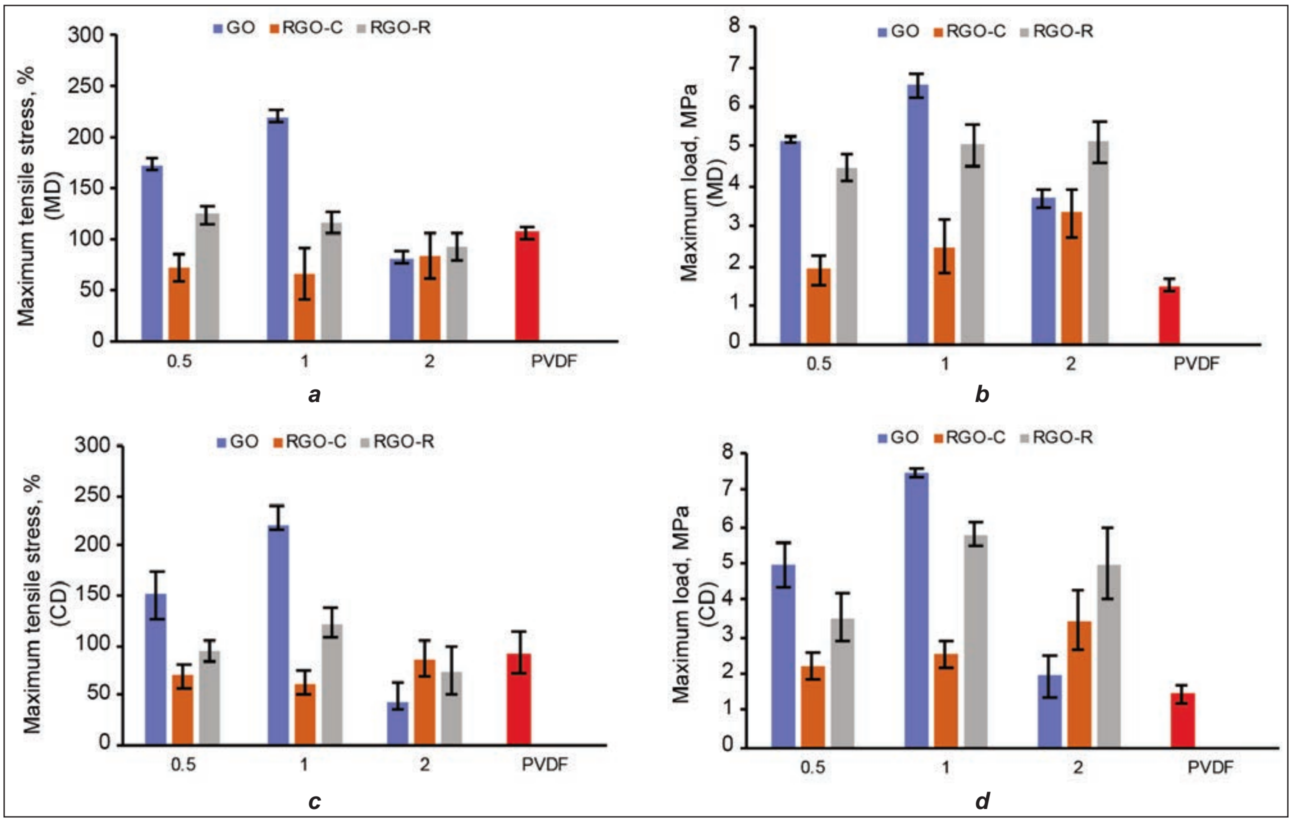


Fig. 7. Mechanical properties of PVDF nanofibers as a function of filler content, elongation (%) and tensile strength values of samples in the: *a* and *b* – machine direction; *c* and *d* – cross direction

obtained as 3.3 MPa and 3.4 MPa in the machine direction and the cross direction, respectively, which was higher than that of the neat PVDF nanofibers in both directions by about 120% and 143%, respectively. The reduction of GO-filled PVDF nanofibers with the aqueous solution of rosehip extract powder resulted in higher elongation and tensile strength values compared to those of Vitamin C-reduced (RGO-C) samples. The tensile strength of the rosehip extract-reduced (RGO-R) nanofibers increased with the increasing amount of GO nanosheets. The highest tensile strength was obtained as 5.1 MPa with a 2 wt% GO-filled PVDF nanofiber sample reduced with rosehip extract in the machine direction. On the other hand, the highest tensile strength was obtained as 5.8 MPa with a 1 wt% GO-filled PVDF nanofiber sample reduced with rosehip extract in the cross direction.

Electrical resistivity

The electrical surface resistivity of the polyester spunbond nonwoven fabric coated with GO and the GO-coated nonwoven fabrics after reduction by using Vitamin C and rosehip extract powder was measured. The obtained results are given in table 1. The electrical surface resistivity of polyester nonwoven fabric was obtained as $1.94 \cdot 10^6$ kW, indicating the electrical insulating property. The GO coating of polyester nonwoven fabric did not change the electrical surface resistivity value. The GO nanosheets present an electrically insulating character because of the presence of oxygenated functional groups. On the other hand, the reduced samples show relatively lower electrical resistivity. The reduction of GO-coated polyester nonwoven fabric with rosehip extract powder decreased the electrical surface resistivity to $7.06 \cdot 10^3$ kW. Moreover, the lowest value was obtained with Vitamin C-reduced GO-coated nonwoven fabric as $5.57 \cdot 10^2$ kW. It can be understood that the reduction of GO with Vitamin C and rosehip extract powder turned the electrically insulating GO into the electrically conductive RGO.

Table 1

SURFACE ELECTRICAL RESISTIVITY MEASUREMENTS OF NONWOVEN SAMPLES

Sample	Surface electrical resistivity (kW)
NW	$1.94 \cdot 10^6$
NW-GO	$1.70 \cdot 10^6$
NW-RGO-R	$7.06 \cdot 10^3$
NW-RGO-C	$5.57 \cdot 10^2$

The electrical resistivity of the PVDF, GO, RGO-R, and RGO-C nanofibers was measured as $1.70 \cdot 10^6$ kΩ. The results did not show any change with the change of the filler content and the reducing agent.

Water Contact Angle

The water contact angle measurements were made separately for all samples and given in tables 2 and 3 along with corresponding droplet images, for

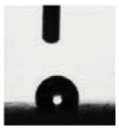
Table 2

WATER CONTACT ANGLE MEASUREMENT RESULTS AND DROPLET IMAGES OF ELECTROSPUN NANOFIBERS

Water contact angle (°) and droplet images									
PVDF	0.5%			1%			2%		
	GO	RGO-C	RGO-R	GO	RGO-C	RGO-R	GO	RGO-C	RGO-R
121.1 	129.8 	124.2 	61.2 	128.8 	124.5 	28.2 	124.1 	119.3 	26.8 

Table 3

WATER CONTACT ANGLE RESULTS (°) AND DROPLET IMAGES OF GO-COATED AND RGO-COATED NONWOVEN FABRICS

Water contact angle (°) and droplet images			
NW	NW-GO	NW-RGO-C	NW-RGO-R
108.6 	90.6 	94.1 	48.1 

nanofibers and nonwoven fabrics, respectively. From table 2, it can be understood that the neat PVDF nanofiber was hydrophobic due to having a water contact angle higher than 90°. With the addition of a small amount of GO to the nanofibrous structure, the water contact angle shows a slight increase. The increase in GO concentration in the PVDF polymer matrix does not affect the water contact angle of the nanofibers. The highest water contact angle was obtained as 129.8° with the GO-filled PVDF nanofiber containing 0.5 wt% filler. Although the water contact angle values of the nanofibers tend to decrease with the increase of GO content, the resulting values still indicate hydrophobicity. The reduction of GO-filled PVDF nanofibers with Vitamin C (RGO-C) retained the hydrophobicity. On the contrary, the water contact angle of the RGO-R samples decreased dramatically to values lower than 90°, indicating hydrophilicity.

Water contact angle results and corresponding droplet images of GO and RGO-coated nonwoven fabric samples are given in table 3. Since all nonwoven fabrics are coated in the same way, one measurement is taken as a reference measurement for all GO-coated nonwoven fabrics. The water contact angle of the polyester nonwoven fabric was measured as 108.6°. When the water contact angle values of nonwoven surfaces are examined, it is seen that the GO-coated nonwoven fabric can be considered hydrophobic due to the water contact angle obtained as 90°. However, a slight decrease in the water contact angle of GO-coated nonwoven fabric was obtained when compared to neat nonwoven fabric. After the reduction with Vitamin C, the water contact angle increased to a value of 94°.

Nevertheless, the water contact angle of the reduced sample by using rosehip extract powder decreased dramatically, and the surface of the sample became hydrophilic.

CONCLUSIONS

In this study, the GO-dip-coated polyester spunbond nonwoven fabric is used as a substrate to fabricate electrospun GO-filled PVDF nanofibers. The GO coating concentration remained constant, and the amount added to the PVDF polymer solution was changed. Moreover, the GO-filled PVDF nanofibers were post-processed by chemical reduction with Vitamin C and rosehip extract powder. The electrospun PVDF nanofibers with different amounts of GO were characterized by FTIR, XRD, and SEM. The mechanical properties, electrical surface resistivity, and water contact angle of the samples were analyzed. FTIR and XRD results revealed an increase in the b phase by the addition of GO. After the reduction of GO-filled PVDF nanofibers, the crystalline b phase was obtained higher level than the neat PVDF nanofibers. The morphological study obtained by SEM images confirmed both the dip-coating of GO nanosheets between the polyester fibers and the formation of PVDF nanofibers with uniform structures. The mechanical performance of the electrospun nanofibers in terms of tensile strength was obtained highest at the 1 wt% GO-filled sample in both directions. The tensile strength and elongation results revealed the increase of mechanical properties by the addition of different amounts of GO and the application of the chemical reduction process compared to that of the neat PVDF nanofibers. The surface electrical resistivity of the reduced GO-coated nonwoven fabric was found as $7.06 \cdot 10^3$ kΩ and $5.57 \cdot 10^2$ kΩ for the samples NW-RGO-R and NW-RGO-C, respectively. A slight decrease in hydrophobicity was observed after the GO coating of the polyester nonwoven fabric coated. The hydrophobic structure of the neat PVDF nanofiber decreases after reduction both with Vitamin C and rosehip extract powder. However, after reduction with rosehip extract powder, both the nanofibers and the nonwoven fabric turned into a hydrophilic state.

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