Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

Cytotoxicity studies and antibacterial modification of poly(ethylene 2,5-furandicarboxylate) nonwoven

Mariia Svyntkivska [a,*], Tomasz Makowski [a,*], Roza Pawlowska [a], Dorota Kregiel [b], Ele L. de Boer [c], Ewa Piorkowska [a]

[a] Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
[b] Department of Environmental Biotechnology, Faculty of Biotechnology and Food Sciences, Lodz University of Technology, Wolczanska 171/173, 90-924 Lodz, Poland
[c] Avantium Renewable Polymers BV, Zekeringstraat 29, 1014 BV Amsterdam, the Netherlands

ARTICLE INFO

ABSTRACT

Novel poly(ethylene 2,5-furandicarboxylate) PEF nonwovens were produced by solution electrospinning and further modification. To improve the wettability of the hydrophobic nonwovens with water, they were treated with sodium hydroxide. Cytotoxicity tests carried out with human keratinocytes confirmed that the nonwovens did not have a toxic effect on healthy cells. The hydrophilicity of the sodium hydroxide treated nonwoven favored the adherence of the cells and their growth. In turn, the two-step modification of the nonwovens by reactions with (3-mercaptopropyl)methyldimethoxysilane and silver nitrate permitted to deposit silver particles on the fiber surfaces. The bacteria growth inhibition zones around the tested specimens were observed evidencing their antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*.

1. Introduction

The development of biobased polymeric materials is a subject of intensive research [1–6] as it plays an important role in struggling with carbon dioxide emissions and in diminishing the dependence on fossil resources. Besides natural polymers derived directly from biomass, like cellulose, starch, chitosan, etc., and bio-engineered polymers like polyhydroxyalkanoates of bacterial origin, the biobased polymer class includes also those synthesized from monomers obtained from renewable resources. Poly(ethylene 2,5-furandicarboxylate) (PEF), obtained from biomass-based 2,5-furandicarboxylic acid and ethylene glycol, can be viewed as a poly(ethylene terephthalate) (PET) analog, with a benzene ring replaced by a furan ring. PEF is a slowly crystallizing polymer, with a melting temperature in the range of 200–230 °C [7,8] and a glass transition temperature (T_g) around 85 °C [7,9]. PEF exhibits a higher elastic modulus and much better barrier properties to gases and liquids than PET [10–15]. It is a promising biobased alternative to polymers derived from petroleum hydrocarbons, especially PET [9,16–18], and potentially useful, for instance, for bottles, films, and fibers [16,19,20]. So far, most reports on PEF focused on its synthesis, crystallization, mechanical performance, and barrier properties [7–16,20–23]. Modification of PEF properties by copolymerization, filling, or blending, for

example with poly(propylene 2,5-furandicarboxylate) [24–29] was also reported.

A few published reports on producing PEF fibers concerned the melt spinning of PEF [30,31], fibers of poly(ethylene terephthalate-*co*-ethylene 2,5-furandicarboxylate) [32] and fibers of a copolymer obtained from ethylene glycol, 2,5-furandicarboxylic acid and poly(ethylene glycol) [33]. Previously [34], we described solution electrospinning of PEF nonwovens and their morphology, thermal and mechanical properties.

It should be emphasized that synthetic textiles are widely used in many applications. The preparation of fibers and nonwovens by solution electrospinning has numerous advantages. The solution electrospinning does not require a high temperature, which is especially important in the case of polymers susceptible to thermal degradation. It should be noted, that there are multi nozzle electrospinning systems, that allow the production of nonwovens on an industrial scale [35,36]. It is also worth noting that, in principle, solvents can be recovered if the process is conducted in a closed system. Fibers made of different polymers have been electrospun, and their modifications have been extensively studied to make them applicable in diverse fields, for instance, air and water filtration [37–39], food packaging [40,41], and biomedical applications [42,43], including regenerative medicine. It is worth noting that

---

* Corresponding authors.
 E-mail addresses: mariia.svyntkivska@cbmm.lodz.pl (M. Svyntkivska), tomasz.makowski@cbmm.lodz.pl (T. Makowski).

 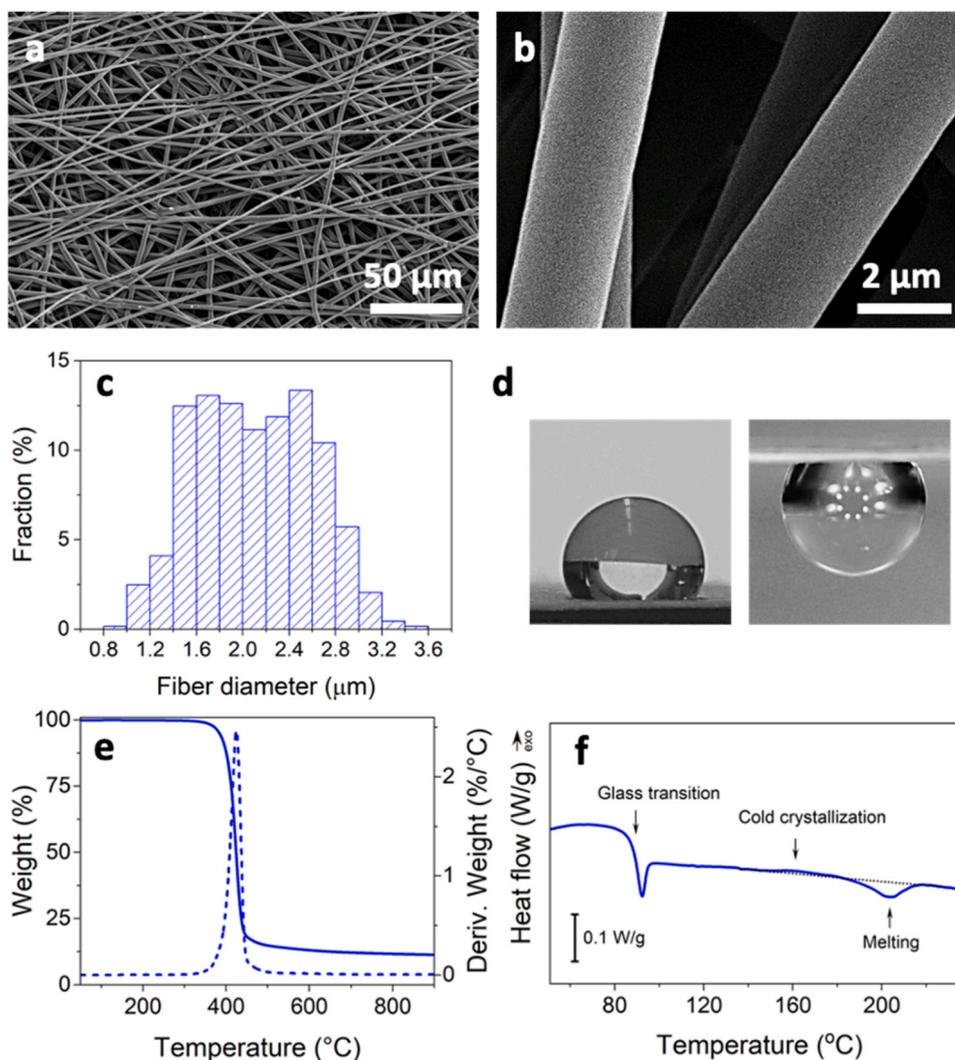
a
50 µm
b
2 µm
c
Fraction (%)
15
10
5
0
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
Fiber diameter (µm)
d
e
Weight (%)
100
75
50
25
0
200
400
600
800
Temperature (°C)
Deriv. Weight (%/°C)
2
1
0
f
Heat flow (W/g) exo
Glass transition
Cold crystallization
Melting
0.1 W/g
80
120
160
200
Temperature (°C)

Fig. 1. a, b) SEM micrographs of PEF nonwoven after drying, c) fiber diameter distribution, d) photograph of water droplet on nonwoven surface (left) and illustration of rose petal effect (right), e) TGA thermograms of PEF nonwoven, weight loss and derivative of weight loss with respect to temperature, recorded at rate of 20 °C/min, f) DSC heating thermogram recorded at rate of 10 °C/min.

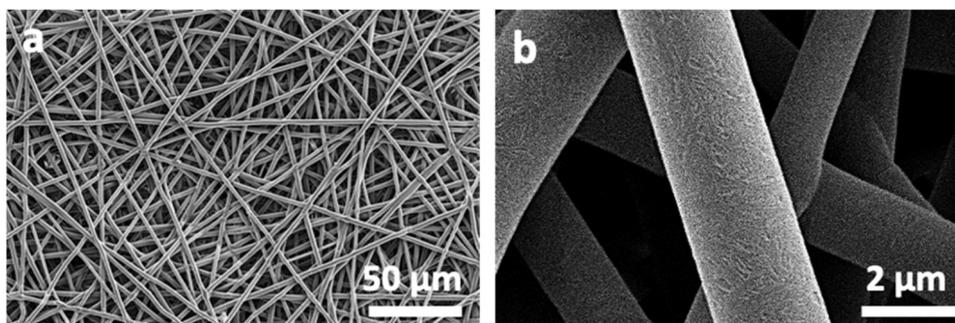

a
50 µm
b
2 µm

Fig. 2. SEM micrographs of NaOH-treated PEF nonwoven.

although biodegradability is usually desirable in the design of materials for regenerative medicine applications, in some circumstances it is necessary to use materials that do not degrade inside the body, for instance for bone adhesive and inserts, teeth and breast implants, dialysis membranes as well as heart valves and aortic grafts. The non-degradable materials may be used to replace or promote the regeneration of damaged tissues [44] and are also commonly used as surgical meshes which provide proper mechanical strength for abdominal and inguinal hernia application. The non-degradable nature, high tensile strength, and cell growth are beneficial for promoting tissue regeneration [45]. Moreover, it has also recently been indicated that non-degradability may paradoxically be an advantage, especially in the context of recent reports on the toxicity of some degradation products inside the body [46]. Thus, although biodegradable materials for biomedical applications appear on the market on an increasing scale, for some purposes non-degradable materials seem to be difficult to replace.
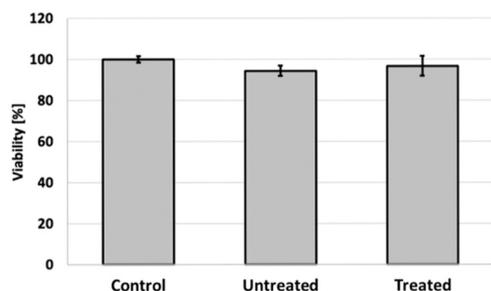
Fig. 3. Cytotoxicity of tested nonwovens, untreated and NaOH-treated, for human keratinocytes HaCaT after 72 h incubation. Relative cell viability (%) is presented as a percentage of living cells after treatment with nonwoven extracts compared to the control. Data represent the average value of at least three independent experiments (the mean viability $\pm$ standard error [%]).

Silicone-based non-degradable materials are used in the applications like heart valves, microfluidic devices, 3D bioscaffolds for cellular therapies and soft tissue implants, like internal biliary stents for biliary reconstruction and breast implants [47,48]. By surface modification certain benefits, such as increasing cell adhesion, antibacterial effect, and reducing of the immune system response may be achieved [49–55]. It should be noted that nonwovens are good substrates for cell growth, hence electrospun mats can be used as scaffolds for tissue engineering [56]. The high porosity of the nonwoven scaffolds provides an optimal environment for cell growth with more space for the exchange of nutrients and metabolic waste. The hydrophilicity of surface is preferred for more effective cell adhesion and enhancement of cell migration. The hydrophilicity of hydrophobic nonwovens can be achieved by surface modification, such as alkaline etching or copolymerization with more hydrophilic monomers [57–59].

In many applications, including biomedical applications, the antibacterial activity of materials is important. Synthetic electrospun textiles with antibacterial properties can be used for food packaging [40,41, 60], water purification and disinfection [61,62], and wound dressing materials [63,64]. To obtain antibacterial electrospun nonwovens, appropriate functional agents are added to polymer solutions [40,65] or applied on ready mats by post-spinning chemical modification or coating [66–68]. Non-specific bacterial toxicity of silver (Ag) particles impedes the bacteria resistance development and also broadens the spectrum of antibacterial activity [69]. The main mechanisms of metal nanoparticles or ions include attraction to bacterial cell walls, disruption of the cell walls and cell functions [69–73]. Ag-containing compounds were used for the preparation of antibacterial materials with applications for wound dressing, food packaging materials, and protective clothing or masks [74]. Electrospun nonwovens with antibacterial activity were obtained through the addition of Ag-containing compounds to polymer solutions [75,76] or post-spinning deposition of Ag particles on fiber surfaces [62,67]. For example, the Ag particles were electrochemically deposited on surfaces of electrically conductive fibrous materials [77,78]. It is worth noting that the post-spinning modification led to the stronger antibacterial activity of polyacrylonitrile and polylactide (PLA) mats than that obtained by adding Ag or Ag-containing compounds to polymer solutions [79,80].

In this work, PEF nonwovens were electrospun from PEF solutions in 1,1,1,3,3,3-hexafluoro-2-propanol, and characterized. Taking into consideration that the cytotoxicity of PEF and PEF nonwovens has not been studied before, as well as to verify the potential usefulness of PEF nonwovens as scaffolds for tissue engineering, the cytotoxicity and cell growth on the surface of the nonwovens were investigated. The nonwovens were treated with NaOH to increase their hydrophilicity and reactivity by generating hydrophilic carboxyl and hydroxyl groups. Moreover, Ag particles were formed on the fiber surfaces by reactions with (3-mercaptopropyl)methyldimethoxysilane and silver nitrate, which resulted in antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*.

2. Experimental

2.1. Preparation of nonwovens

Poly(ethylene 2,5-furandicarboxylate) (PEF) grade of G90P was obtained from Avantium Renewable Polymers (the Netherlands). The PEF grade used was G90P with an intrinsic viscosity of 0.86 dL/g, as measured according to ASTM D4603, and weight average molar mass (M_w) of 128 kg/mol, as determined using gel permeation chromatography with 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as a solvent and a classical calibration with a poly(methylene methacrylate) standard. It is worth noting that the PEF polymer is biobased, and was synthesized from 2,5-furandicarboxylic acid obtained by catalytical conversion of plant-based sugars and from commercially available biobased mono ethylene glycol.

Before further use, PEF granulate was dried at 140 °C for 16 h under reduced pressure (0.1 bar). The nonwovens were prepared by electrospinning using a 12 wt % solution of PEF in HFIP (99 %, Apollo Scientific, Poland), according to the procedure described by us previously [34]. The nonwovens were electrospun in an environmental chamber at room temperature (RT) and controlled relative humidity of 30–35 %. To apply a voltage of 15 kV, a high voltage power supply CM5 Simco-Ion (the Netherlands) was used. The fibers were collected on a static square aluminum collector, 20 cm × 20 cm, at a 25 cm distance from the nozzle. The solution was dosed with a nozzle, which was a syringe and a needle with 18 gauge and a 0.83 mm inner diameter. The dosing rate of 1.5 mL/h was controlled by a stepper motor T-LLS105, Zaber Technologies (Canada).

To evaporate solvent residues, the nonwovens were dried stepwise: at 60 °C for 24 h, 100 °C for 24 h, and finally at 140 °C for 8 h. Such protocol permitted to avoid the damage of fiber surfaces due to too rapid evaporation. To prevent deformation and shrinkage of the nonwovens during drying above T_g, they were placed between perforated aluminum plates, pressed, and held under the stress of approx. 5 kPa [34].

To increase the wettability of the nonwovens with water by generating hydrophilic hydroxyl and carboxyl groups on fiber surfaces, the nonwovens were treated with sodium hydroxide, NaOH (98.8 %, Chempur, Poland). To this aim, the nonwovens were immersed in a 0.05 M solution of NaOH in a mixture of methanol (99.5 %, Chempur, Poland) and distilled water in a 2:3 volume ratio for 2 min, as was described by others for PLA [81]. Then, the nonwovens were rinsed in an ultrasonic bath with methanol/water mixture for one minute and dried at 50 °C in the air. The duration time of NaOH treatment was determined based on preliminary experiments, as the shortest time necessary to make the nonwovens hydrophilic. It is worth noting that the weight loss of nonwovens due to the short NaOH treatment, determined by weighing the nonwoven before and after the treatment, was below 0.5 %.

2.2. Characterization of nonwovens

To examine the surface morphology and structure of the nonwovens, they were vacuum sputtered with a 10 nm gold layer using a Quorum EMS150R ES (UK) coater and analyzed with a scanning electron microscope (SEM) JEOL 6010LA (Japan) with an energy dispersive spectroscopy (EDS) detector at an accelerating voltage of 10 kV. To determine a diameter distribution, diameters of approx. 600 fibers were measured in five SEM images of the nonwoven. The surface density of the nonwoven was determined based on its size and weight. The porosity was calculated according to Eq. (1) [82,83], assuming that the density of the amorphous PEF is 1.43 g/cm^3 [21]:

$$Porosity = \left(1 - \frac{fibers\ volume}{nonwoven\ volume}\right)100\% \tag{1}$$

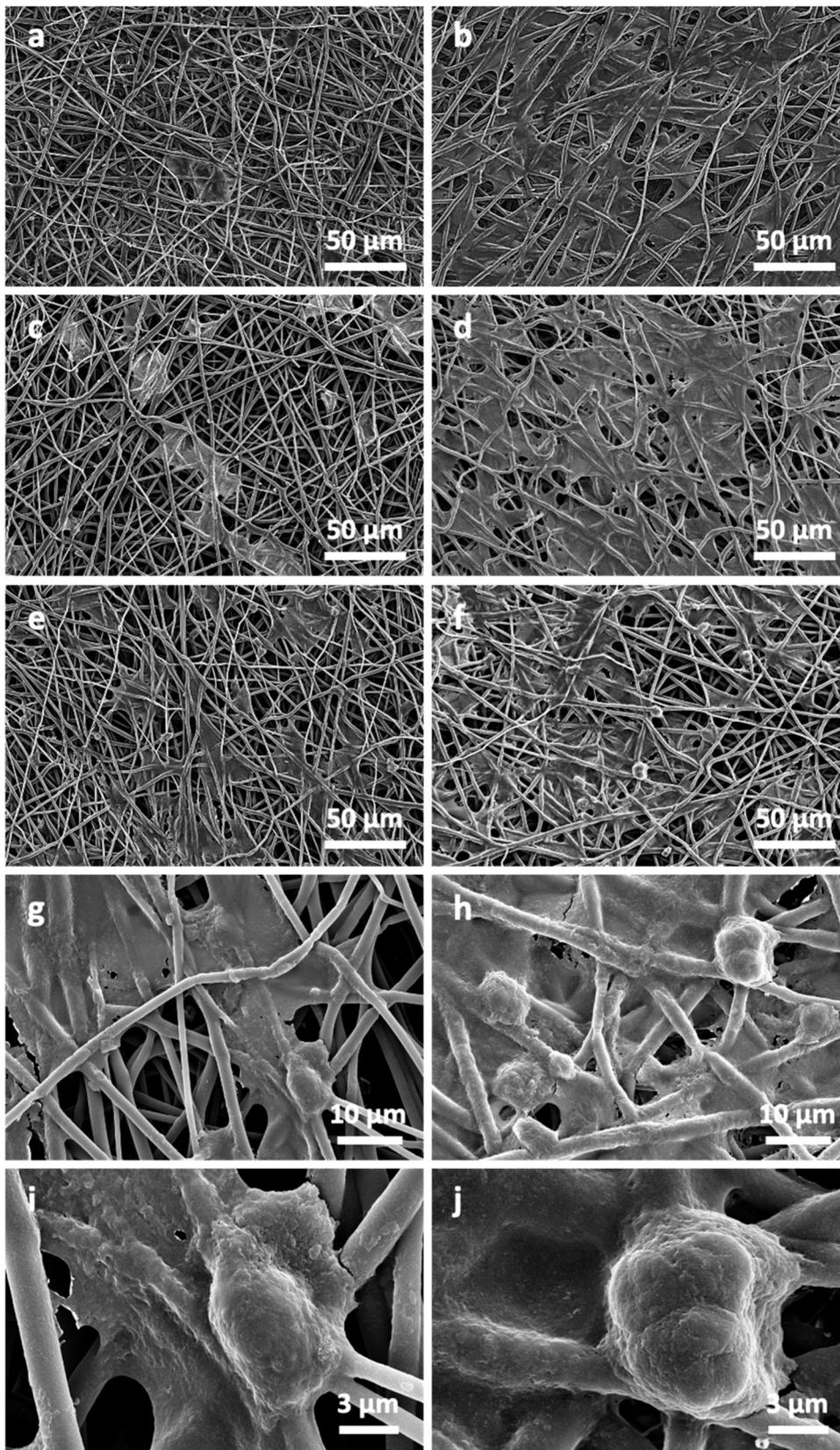The thermal properties of the nonwoven were studied by differential

Fig. 4. SEM micrographs illustrating cell growth after 24 h (a, b), 48 h (c, d) and 72 h (e, f, g, h, i, j) on untreated (left column) and NaOH-treated (right column) nonwovens.
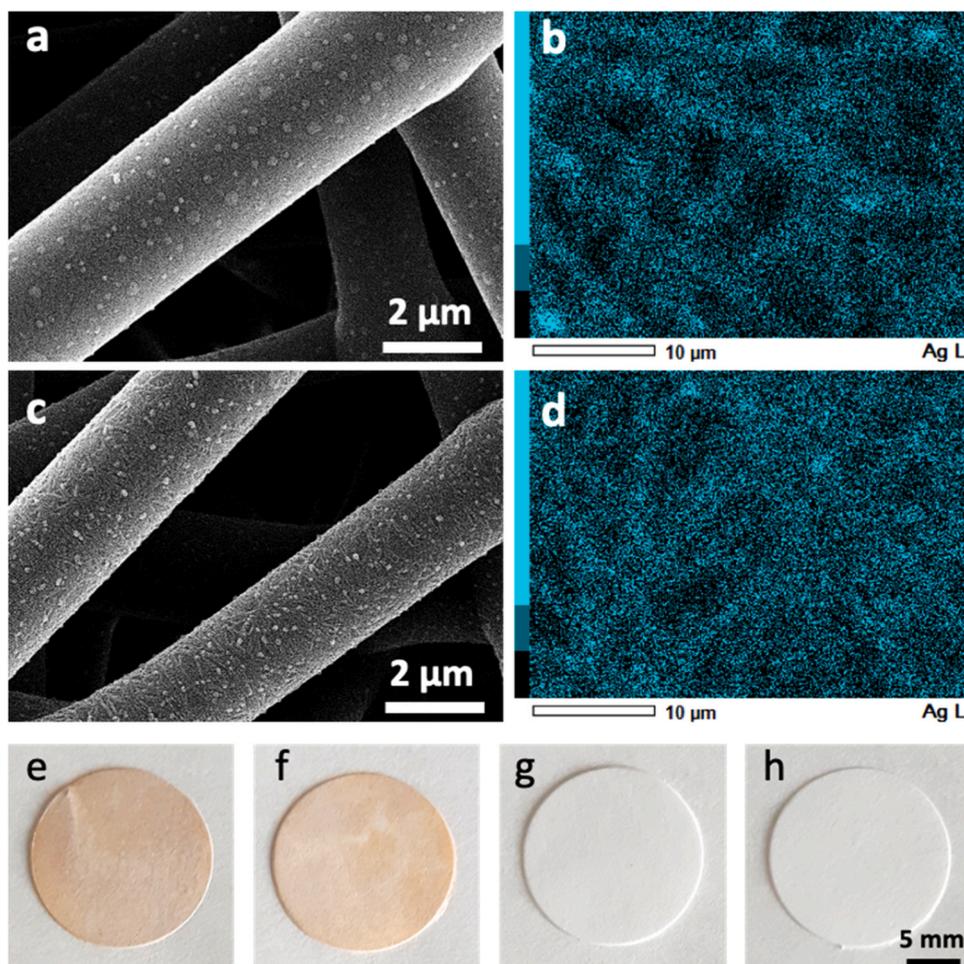
Fig. 5. SEM micrographs and Ag EDS mapping of Ag-modified untreated nonwoven (a, b) and NaOH-treated nonwoven (c, d), photographs of Ag-modified nonwovens untreated (e) and NaOH-treated (f), untreated (g) and NaOH-treated (h) nonwovens before modification with Ag.

scanning calorimetry (DSC), using DSC3 from Mettler Toledo (Switzerland) during heating at 10 °C/min to 250 °C. The thermal stability and the residual solvent content in the nonwoven were determined by thermogravimetry (TGA) using TGA 5500 from TA Instruments (USA) during heating at 20 °C/min under a nitrogen atmosphere.

To determine the wettability of the nonwovens with water, water contact angles (WCA) were measured by a drop method with 5 μL droplets, at RT, using a 100–00–230 NRL Rame Hart goniometer (USA) and ImageJ Drop Analysis program. In each case, the measurements were carried out five times and the results were averaged.

2.3. Examination of cytotoxicity

Human keratinocytes (HaCaT) were cultured in Dulbecco's modified Eagle's medium (DMEM) from Biological Industries (Izrael) with the addition of 10 % of fetal bovine serum (FBS) from Sigma-Aldrich (USA), 100 U/mL penicillin and 100 μg/mL streptomycin (Invitrogen) at 37 °C in an atmosphere of 5 % CO_2. The cytotoxicity of materials was estimated by MTT (3-(4, 5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay based on the measurements of mitochondrial dehydrogenase activity, which catalyzes the conversion of soluble yellow tetrazolium salt into purple insoluble formazan. The number of living cells was calculated based on the formazan concentration.

Before the experiment, the 10 mm nonwoven discs were soaked for 20 min in 70 % ethanol and then dried in a laminar chamber under sterile conditions. Then, the nonwovens were placed in DMEM culture medium and antibiotics (100 U/mL penicillin and 100 μg/mL

streptomycin from Invitrogen) in the ratio of 1 disc (10 mm diameter) per 1 mL of medium. The tubes with tested materials were then incubated for 24 h in a cell culture incubator at 37 °C in an atmosphere of 5 % CO_2. Such prepared extracts were then administrated to cells. Prior to the extract treatment, HaCaT cells were detached from the surface of the culture vessel by Trypsin/EDTA solution from Biowest, counted using a ScepterTM 2.0 Cell Counter from Merck (USA), and seeded into 96-well plates (Nunc) at a concentration of 10^4 cells per well in 200 μL of appreciated culture medium. After overnight incubation at 37 °C and 5 % CO_2, the medium was removed and replaced by extracts from tested specimens. The medium containing 1 % of sodium dodecyl sulfate (SDS), as well as the medium without tested additives were used as a positive and negative control, respectively. After 72 h of incubation in the standard conditions (37 °C and 5 % CO_2), 20 μL of MTT reagent (5 mg/mL, Sigma-Aldrich, USA) was added to each well, and cells were incubated for the additional 2 h in 37 °C. After that time, the medium was removed and 100 μL of isopropanol was added into the wells, and plates were placed on the microplate shaker for 2 h. The absorbance at 570 nm and 630 nm (reference wavelength) was measured using Synergy HT 96-well plates microplate reader from Bio-Tek (USA). Cell viability was determined as a percentage of living cells in the tested sample relative to the non-treated control cells. All variants were performed in triplicate. For each nonwoven, at least three independent experiments were performed.
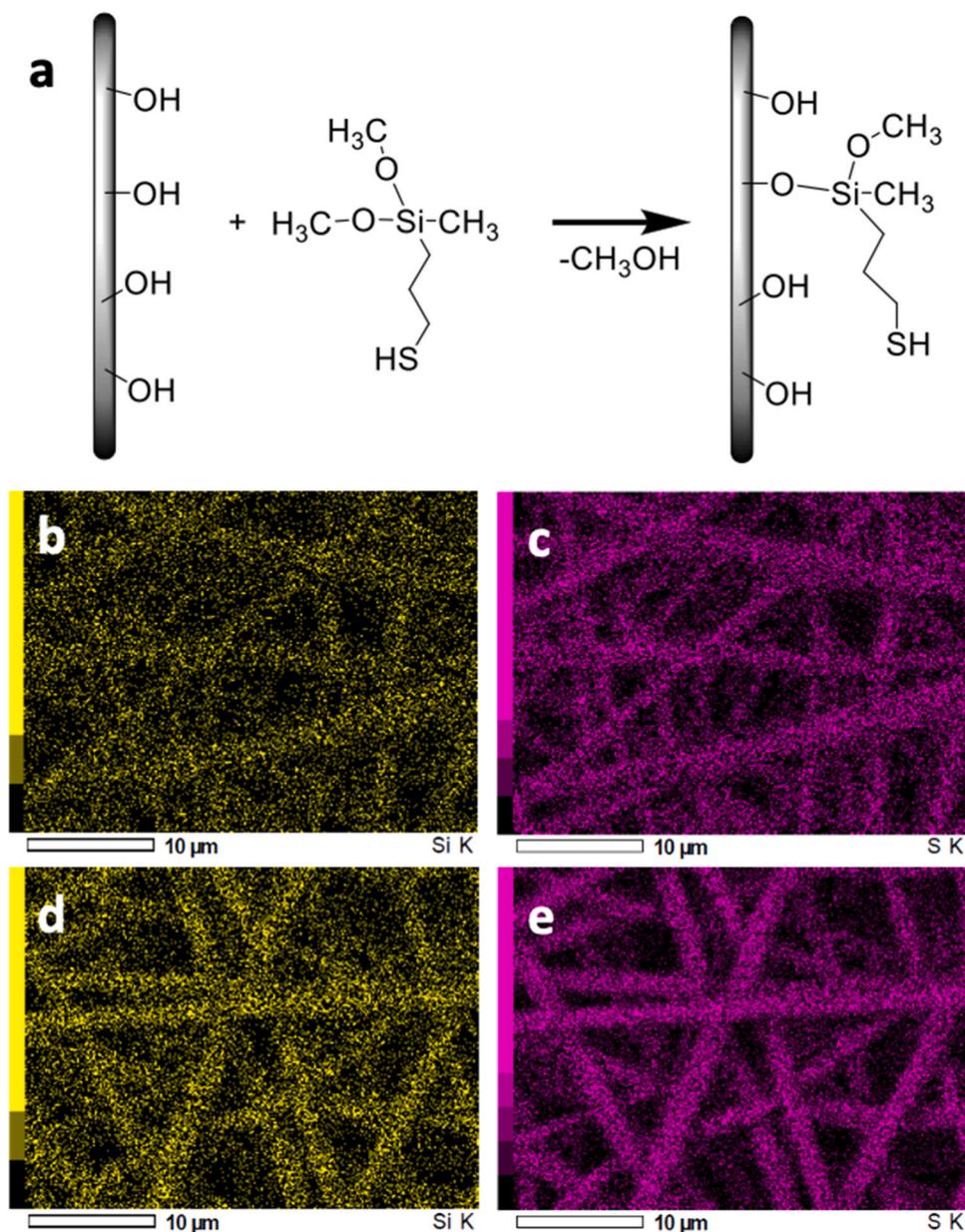
Fig. 6. Reaction of hydroxyl groups with (3-mercaptopropyl)methyldimethoxysilane (a), Si and S EDS mapping of untreated and NaOH-treated nonwovens after reaction with (3-mercaptopropyl)methyldimethoxysilane: untreated nonwoven, Si (b), and S (c) mapping, NaOH-treated nonwoven, Si (d) and S (e) mapping.
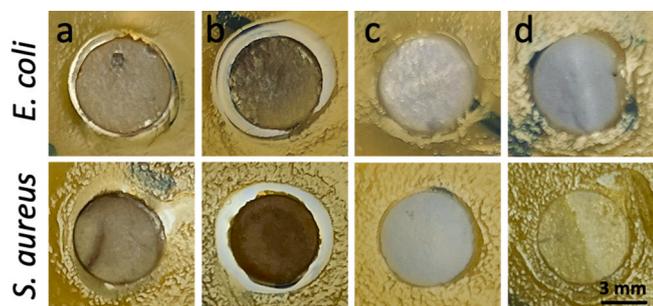

Fig. 7. Nonwoven disks with 6 mm diameters on *E. coli* and *S. aureus* inoculated agar after 24 h of incubation. Ag-modified nonwovens: a) untreated and b) NaOH-treated, and unmodified control nonwovens: c) untreated and d) NaOH-treated.

2.4. Cell growth

The nonwovens were tested for their usefulness as a scaffold for cell growth. For this purpose, 10 mm diameter discs were used. Before the experiments, the materials were treated for 20 min with 70 % ethanol and dried at RT in sterile conditions. The dry materials were placed into the sterile 24-well plates for cell cultures from Thermo Fisher Scientific (USA). To estimate the possibility of skin cell growth on the nonwoven surface, human keratinocytes (HaCaT) were used. Cells in the exponential growth phase were washed with Phosphate Buffered Saline (PBS) without Ca^{2+}, Mg^{2+} ions from Biowest, detached from the surface of the culture vessel by Trypsin/EDTA solution from Biowest, suspended in the cell culture medium and seeded into the plate with nonwoven discs. The 250,000 cells in 300 µL of DMEM with 100 U/mL penicillin and 100 µg/mL streptomycin from Invitrogen were used for each well containing tested nonwovens disc. Cell counting was performed using a ScepterTM 2.0 Cell Counter. For each experiment, positive control – cells seeded into an empty well (without tested material), as well as
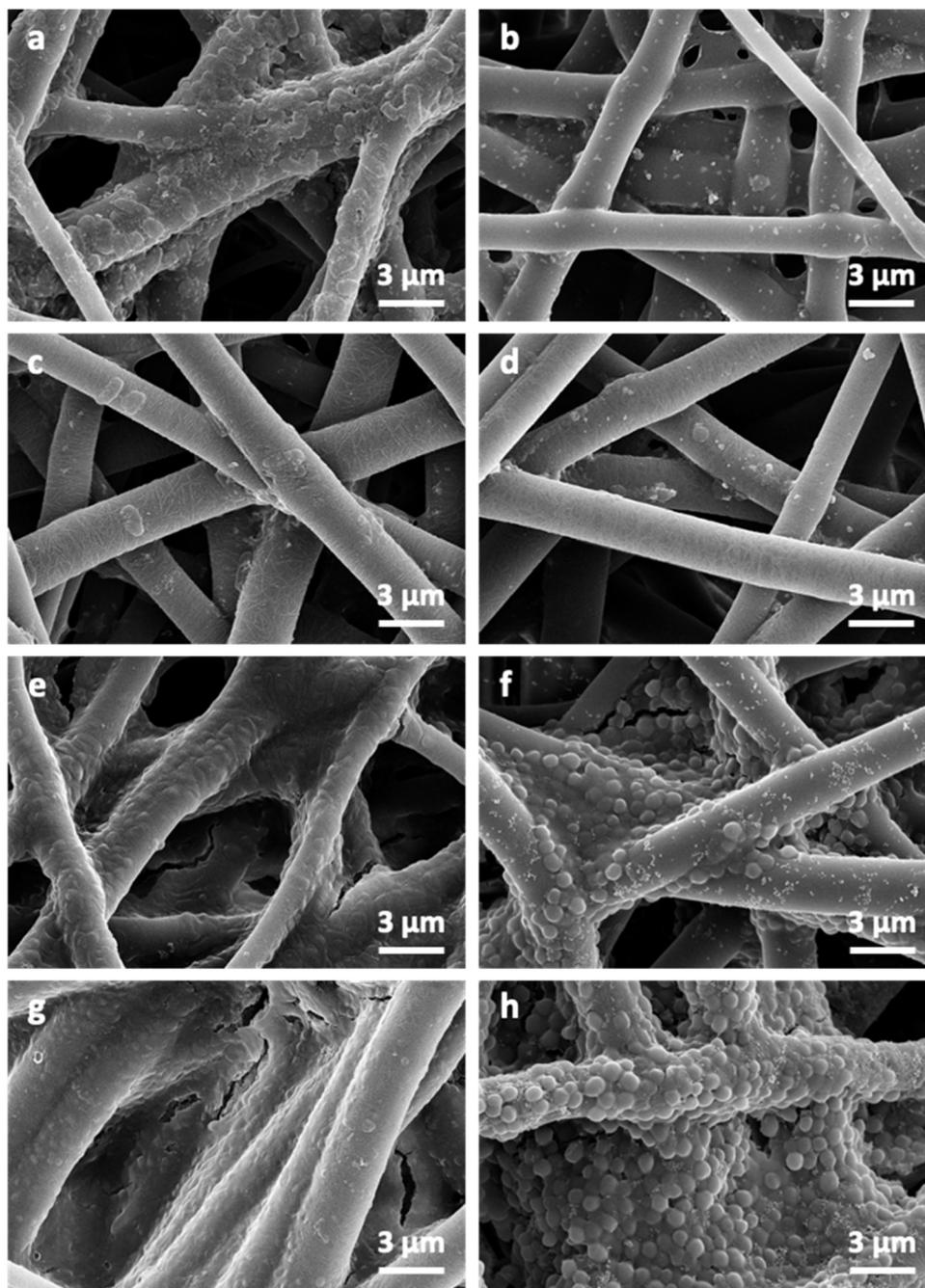
Fig. 8. SEM micrographs of bottom sides of Ag-modified nonwovens, untreated (a,b) and NaOH-treated before modification (c,d), and also unmodified control nonwovens, untreated (e,f) and NaOH-treated (g,h), removed from *E. coli* (left column) and *S. aureus* (right column) inoculated agar.

negative control – nonwoven discs incubated in the medium without cells were performed. The plates were incubated in a cell culture incubator from Binder in the standard conditions (37 °C and 5 % CO_2) for 24, 48, and 72 h. At the appropriate time points, the nonwovens were removed from the culture vessel, washed twice with PBS buffer, and placed into the 75 % ethanol solution. After 20 min incubation, the nonwovens were dried at RT and SEM analysis was performed.

2.5. Antibacterial modification

To deposit Ag particles on PEF fiber surfaces the following reagents and solvents were used: silver nitrate $AgNO_3$ (99 % purity), anhydrous ethanol (99.8 % purity), toluene (99.5 % purity), all three from POCH (Poland), and (3-mercaptopropyl)methyldimethoxysilane $HS(CH_2)_3Si$

$(OCH_3)_2CH_3$ (95 % purity) from ABCR (Germany).

The nonwovens were modified through reactions with (3-mercaptopropyl)methyldimethoxysilane and $AgNO_3$ similarly to the modification of polysiloxane microspheres described in [84]. The nonwovens were immersed in a mixture of 5 mL of (3-mercaptopropyl)methyldimethoxysilane and 15 mL of toluene and kept there for 2 h. After removal from the mixture, the nonwovens were dried in the air at 50 °C, washed with toluene, and dried again to evaporate toluene. Then, they were immersed in a saturated solution of $AgNO_3$ in ethanol (0.26 M), kept there for 1 h, and after removal from the solution, dried as described above, washed with ethanol, and dried again.

After the modifications, all samples were washed several times with distilled water and ethanol to remove excess reaction products. Before the examination of their antibacterial activity, the nonwovens were

additionally dried at 60 °C under reduced pressure for 16 h.

2.6. Antibacterial activity testing

Antibacterial activity of the Ag-modified PEF nonwovens against Gram-positive *Staphylococcus aureus* ATCC 6538 (*S. aureus*) and Gram-negative *Escherichia coli* ATCC 8739 (*E. coli*) bacterial strains was examined according to ISO 20645:2004 "Textile fabrics – Determination of antibacterial activity – Agar diffusion plate test". At first, 15 mL of nutritive agar medium, Tripticase Soy Agar from Merck-Poland was poured on sterile Petri dishes. The inoculums of a bacterial culture tested of $1–5 \times 10^8$ CFU/mL (0.2 mL) were then spread onto the agar medium. In the next step, discs with 6 mm diameters cut out of the nonwovens were placed on the agar surface. The unmodified nonwovens were tested as control specimens. It should be noted that before the tests, all samples were sterilized with UV light (wavelength of 265 nm) for 30 min on each side. The level of antibacterial activity was assessed by the presence and extent of the inhibition zones around the disk specimens. Measurements of inhibition zone diameters were carried out after 24 h of incubation samples at 37 °C on the agar plates. To evaluate the colonization of bacteria in the contact zone between the agar and the specimens, the specimens removed from the agar were also analyzed by SEM.

3. Results and discussion

3.1. Characterization of nonwovens

Fig. 1a, b show SEM micrographs and the fiber diameter distribution of the PEF nonwoven. The nonwoven consisted of randomly oriented smooth and defect-free fibers with diameters ranging from 0.8 to 3.6 μm and an average diameter of 2.1 μm. Thickness, surface density, and porosity, the latter calculated according to Eq. (1), of the nonwoven were 0.24 mm, 9.7 mg/cm^2, and 71.6 %, respectively.

TGA thermogram of the nonwoven, recorded during heating at 20 °C/min in a nitrogen atmosphere, shown in Fig. 1e, evidenced that the weight loss at 220 °C was only 0.1 wt %, which confirmed the absence of solvent after drying. The temperature of peak rate of weight loss, 425 °C, close to that of PEF granulate [34], showed the lack of adverse effect of the processing on the thermal stability of the nonwoven.

The DSC first heating thermogram recorded at 10 °C/min, shown in Fig. 1f, exhibited a glass transition, with T_g at 88 °C, a trace of cold crystallization exotherm at about 163 °C, and a small melting endotherm with a peak at 204 °C. The cold crystallization enthalpy of 0.6 J/g was smaller than the melting enthalpy ΔH_m of about 3 J/g, indicating that only weak crystallization could occur during drying.

The water droplet deposited on the untreated nonwoven surface is shown in Fig. 1d. The WCA angle was 140°. Moreover, the nonwoven exhibited the rose petal effect as reported and discussed previously [34]. The hydrophobicity of polymer nonwovens was observed also by others, even for those made of hydrophilic polymers, due to nonwoven porosity, and the air trapped between fibers resulting in the Cassie-Baxter hydrophobicity regime [85,86].

The NaOH treatment made the PEF nonwoven hydrophilic, most possibly because of the formation of hydroxyl and carboxyl groups on fiber surfaces, as on PLA surface [87,88]. Moreover, the treatment caused the fiber surface roughness on a nanoscale, as shown in Fig. 2, most probably due to etching. The nano-roughness increased the surface contact area between the hydrophilic polymer surface and water droplets thus additionally improving the wettability. The hydrophilicity of the fibers became a dominant effect and water droplets completely soaked into the NaOH treated nonwoven. It is worth noting that NaOH solutions were used for the surface etching of PLA [88–91] and PET [92].

3.2. Cytotoxicity of nonwovens and adhesion of cells to their surface

Tests carried out on HaCaT confirmed that the untreated and NaOH-treated nonwovens did not have a toxic effect on healthy cells, as shown in Fig. 3. No decrease in survival rate was observed for any of the samples after 72 h of cell culture in DMEM medium with antibiotics. The number of viable cells in the tested samples was comparable to the control and in all cases was above 90 %. The obtained results indicated that due to the lack of cytotoxicity, the tested nonwovens can be potentially used for biomedical applications requiring contact with the skin.

In addition, the cell growth and its adhesion to the surface of the nonwovens were studied. The performed research showed that human keratinocytes (HaCaT) could attach to both types of tested materials and grow on their surfaces. In both cases, an increasing covered surface of nonwovens was observed with the extension of the culture time. Fig. 4 shows the cell growth on the surface of untreated and NaOH-treated PEF nonwovens at intervals of 24, 48, and 72 h. The hydrophobicity of the untreated nonwovens complicated adhesion and the growth of cells on the surface because the surface was not wetted with the cell growth medium, so cells could not easily attach to the fibers. Only some small areas covered with cells are visible on the surface of untreated nonwovens after 24 h of culture (Fig. 4a). The amount and area of zones coated by cells are increased with increasing time of incubation. The surface of NaOH-treated nonwovens was much more accommodated for the growth and adhesion of cells, and this is visible in the SEM micrographs (Fig. 4b, d, f). The hydrophilicity of the treated nonwovens favoured the adherence of the cells, and in its particular growth, the surface of the nonwovens was almost completely covered by cells. Additionally, the nanoscale pattering of the NaOH-treated fiber surfaces could improve the adhesion of cells to the surface due to the increasing surface roughness. SO$_2$ plasma treated PET foil also showed improved human umbilical vein endothelial cells adhesion and viability with increasing surface roughness and wettability in comparison to the untreated sample [93]. In both cases, cells had grown into a free space between fibers and were flattened. The flattened and stretched morphology with an increased nonwoven surface area coated by cells showed good cell-to-cell and cell-to-fiber interactions. Some globular morphology could be seen in the SEM micrographs taken after 72 h of incubation in both cases, but much more so for NaOH-treated nonwovens. SEM micrographs of the globules with higher magnification are presented in Fig. 4g, h, i, j. Furthermore, the large expansion of keratinocytes by migration both, on the surface of nonwovens and in-depth, between the fibers, was observed during culture. The lack of cytotoxicity combined with the observed cell adhesion to the surface and penetration into the nonwovens allows these materials to be considered as potential scaffolds for cell growth in large skin defects associated with burns, chronic diseases, surgical procedures, transplants, chronic ulcers, or other disturbances.

3.3. Antibacterial properties of silver modified nonwovens

SEM micrographs of the Ag-modified nonwovens in Fig. 5a, c, show that Ag particles formed on the PEF fibers through a reaction with (3-mercaptopropyl)methyldimethoxysilane and AgNO$_3$. The hydroxyl end-groups of PEF chains, and those generated on the fiber surfaces by NaOH treatment allowed the introduction of organosulfhydryl (organothiol) groups, as schematically shown in Fig. 6a. The presence of silicon (Si) and sulfur (S) on the fiber surfaces in NaOH-treated and untreated nonwovens after the reaction with (3-mercaptopropyl)methyldimethoxysilane was evidenced by EDS mapping, as shown in Fig. 6b, c, d, e.

Then, Ag particles were formed on the fibers due to the substitution of Ag$^+$ for the proton in the organosulfhydryl groups, as was described and discussed in [84]. Silver thiolates are prone to form complex associates [84,94], in which a partial reduction of Ag$^+$ to Ag$^\circ$ occurs. This

leads to the formation of Ag nanoparticles, which subsequently may produce larger particles through aggregation. The sizes of particles on the untreated and NaOH-treated fibers were in the range of 80–240 nm and 60–200 nm, respectively. EDS Ag mapping also shown in Fig. 5b, d confirmed the presence of Ag particles on the fibers. The nonwovens after the reaction changed their colors to light brown, as illustrated in Fig. 5e, f. It is worth noting, that the results of Si and S EDS mapping of the fibers after the reaction with AgNO₃ (not shown) were similar to those presented in Fig. 6.

Bacteria growth inhibition zones were observed for the Ag-modified nonwovens, as shown in Fig. 7.

Diameters of the zones in *E. coli* and *S. aureus* inoculated agar around the untreated nonwoven samples were 7 and 8 mm, respectively, whereas those around the NaOH-treated samples were 8 and 9 mm, respectively. The stronger activity of the NaOH-treated nonwovens could originate from a larger number of hydroxyl groups on the fiber surfaces formed during NaOH treatment, which resulted in a larger Ag content.

The SEM images of the bottom side of the samples are shown in Fig. 8. On the Ag-modified NaOH-treated nonwoven only a few bacteria were visible. The same applies to the untreated nonwoven kept previously on *S. aureus* inoculated agar. In turn, *E. coli* bacteria on this nonwoven were more numerous. However, in each case, the visible bacteria lost their shapes and flattened, which was attributed by others to bacteria damage and death caused by contact with antimicrobial agents [95–98].

On the contrary, no bacteria growth inhibition zones were found around the control samples, without Ag particles, as shown in Fig. 7. Moreover, SEM micrographs in Fig. 8 evidenced that these samples were colonized by the bacteria, which formed thick biofilms on the fiber surfaces and between the fibers. *S. aureus* bacteria also grew on top of the NaOH-treated nonwoven, most possibly due to its hydrophilicity, which facilitated the bacteria colonization too.

4. Conclusions

Biobased PEF nonwovens were obtained by electrospinning from PEF solution in HFIP. To make them hydrophilic, the nonwovens were treated with NaOH. Tests carried out on HaCaT confirmed that both the untreated and NaOH-treated nonwovens did not have a toxic effect on healthy cells. No decrease in survival rate was observed for any of the samples after 72 h of cell culture in DMEM medium with antibiotics. The obtained results indicated that due to the lack of cytotoxicity, the tested nonwovens can be potentially used for biomedical applications requiring contact with the skin.

Furthermore, the good cell adhesion to the surface of the nonwovens, as well as their visible migration and penetration within the nonwovens suggested that this type of materials could be tested not only as potential dressing materials but also as a potential scaffold in regenerative medicine. The hydrophilicity of the NaOH nonwovens favoured the adherence of the cells and their growth. Additionally, the nanoscale pattering of the NaOH-treated fiber surfaces could improve the adhesion of cells to the surface due to the increasing surface roughness. The large expansion of keratinocytes both, on the surface of nonwovens and in-depth, between the fibers, observed during culture allows these materials to be considered as potential scaffolds for cell growth in large skin defects associated with burns, chronic diseases, surgical procedures, transplants, chronic ulcers, or other disturbances. It also seems reasonable to expand research in this area and to further assess the suitability of this type of materials for regenerative medicine in a wider range of applications.

The reactions with (3-mercaptopropyl)methyldimethoxysilane and silver nitrate resulted in the formation of silver (Ag) particles on the fiber surfaces. The presence of the particles on the fiber surfaces was confirmed by SEM analysis and EDS mapping. Growth inhibition zones of Gram-negative *E. coli* and Gram-positive *S. aureus* were observed for

the Ag-modified nonwovens. Diameters of the zones in *E. coli* and *S. aureus* inoculated agar around the untreated nonwoven 6 mm disk samples were 7 and 8 mm, respectively, whereas those around the NaOH-treated samples were 8 and 9 mm, respectively. The antibacterial activity of the Ag-modified nonwovens was confirmed by SEM analysis of the specimens removed from the agar. The stronger activity of the NaOH-treated nonwovens could originate from a larger number of hydroxyl groups on the fiber surfaces formed during NaOH treatment resulting in a larger Ag content. The antibacterial properties of the obtained nonwovens combined with the lack of cytotoxicity of the fibers to human skin cells make these materials good candidates for medical purposes, especially to support wound healing and other applications requiring direct contact with human skin.

CRediT authorship contribution statement

M. Svyntkivska: Conceptualization, Methodology, Investigation, Analysis of results, Writing – original draft; **T. Makowski:** Conceptualization, Writing – review and editing; **R. Pawlowska**: Investigation, Analysis of results, Writing – review and editing; **D. Kregiel:** Investigation, **E. L. de Boer:** Writing – review and editing; **E. Piorkowska:** Conceptualization, Supervision, Writing – review and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

References

[1] H. Nakajima, P. Dijkstra, K. Loos, The recent developments in biobased polymers toward general and engineering applications: polymers that are upgraded from biodegradable polymers, Analog. Pet. - Deriv. Polym. New. Dev. Polym. 9 (2017) 523.

[2] Y. Jiang, K. Loos, Enzymatic synthesis of biobased polyesters and polyamides, Polymers 8 (2016) 243.

[3] R.P. Babu, K. O'Connor, R. Seeram, Current progress on bio-based polymers and their future trends, Prog. Biomater. 2 (2013) 8.

[4] A.A. Wroblewska, S. Lingier, J. Noordijk, F.E. Du Prez, S.M.A. De Wildeman, K. V. Bernaerts, Polyamides based on a partially bio-based spirodiamine, Eur. Polym. J. 96 (2017) 221–231.

[5] V. Zargar, M. Asghari, A. Dashti, A review on chitin and chitosan polymers: structure, chemistry, solubility, derivatives, and applications, ChemBioEng Rev. 2 (2015) 204–226.

[6] A. Llevot, E. Grau, S. Carlotti, S. Grelier, H. Cramail, From lignin-derived aromatic compounds to novel biobased polymers, Macromol. Rapid Commun. 37 (2016) 9–28.

[7] M. Jiang, Q. Liu, Q. Zhang, C. Ye, G. Zhou, A series of furan-aromatic polyesters synthesized via direct esterification method based on renewable resources, J. Polym. Sci. Part A: Polym. Chem. 50 (2012) 1026–1036.

[8] J.G. van Berkel, N. Guigo, J.J. Kolstad, L. Sipos, B. Wang, M.A. Dam, N. Sbirrazzuoli, Isothermal crystallization kinetics of poly (ethylene 2,5-furandicarboxylate), Macromol. Mater. Eng. 300 (2015) 466–474.

[9] N. Guigo, E. Forestier, N. Sbirrazzuoli, Thermal properties of biobased polymers: furandicarboxylic acid (FDCA)-based polyesters, Adv. Polym. Sci. 283 (2019) 189–217.

[10] R.J.I. Knoop, W. Vogelzang, J. van Haveren, D.S. van Es, High molecular weight poly(ethylene-2,5-furanoate); critical aspects in synthesis and mechanical property determination, J. Polym. Sci. Part A: Polym. Chem. 51 (2013) 4191–4199.

[11] S.K. Burgess, O. Karvan, J.R. Johnson, R.M. Kriegel, W.J. Koros, Oxygen sorption and transport in amorphous poly(ethylene furanoate), Polymer 55 (2014) 4748–4756.

[12] S.K. Burgess, D.S. Mikkilineni, D.B. Yu, D.J. Kim, C.R. Mubarak, R.M. Kriegel, W. J. Koros, Water sorption in poly(ethylene furanoate) compared to poly(ethylene terephthalate). Part 1: equilibrium sorption, Polymer 55 (2014) 6861–6869.

[13] S.K. Burgess, D.S. Mikkilineni, D.B. Yu, D.J. Kim, C.R. Mubarak, R.M. Kriegel, W. J. Koros, Water sorption in poly(ethylene furanoate) compared to poly(ethylene terephthalate). Part 2: kinetic sorption, Polymer 55 (2014) 6870–6882.

[14] S.K. Burgess, R.M. Kriegel, W.J. Koros, Carbon dioxide sorption and transport in amorphous poly(ethylene furanoate), Macromolecules 48 (2015) 2184–2193.

[15] S.K. Burgess, G.B. Wenz, R.M. Kriegel, W.J. Koros, Penetrant transport in semicrystalline poly(ethylene furanoate), Polymer 98 (2016) 305–310.

[16] J.G. Rosenboom, D.K. Hohl, P. Fleckenstein, G. Storti, M. Morbidelli, Bottle-grade polyethylene furanoate from ring-opening polymerisation of cyclic oligomers, Nat. Commun. 9 (2018) 2701.

[17] X. Fei, J. Wang, J. Zhu, X. Wang, X. Liu, Biobased poly(ethylene 2,5-furancoate): no longer an alternative, but an irreplaceable polyester in the polymer industry, ACS Sustain. Chem. Eng. 8 (2020) 8471–8485.

[18] A. Eerhart, A.P.C. Faaij, M.K. Patel, Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance, Energy Environ. Sci. 5 (2012) 6407–6422.

[19] J.J. Kolstad, G.J.M. Gruter, Process for the preparation of a fiber, a fiber and a yarn made from such a fiber, 2018.

[20] M.B. Banella, J. Bonucci, M. Vannini, P. Marchese, C. Lorenzetti, A. Celli, Insights into the synthesis of poly(ethylene 2,5-Furandicarboxylate) from 2,5-furandicar-boxylic acid: steps toward environmental and food safety excellence in packaging applications, Ind. Eng. Chem. Res. 58 (2019) 8955–8962.

[21] S.K. Burgess, J.E. Leisen, B.E. Kraftschik, C.R. Mubarak, R.M. Kriegel, W.J. Koros, Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate), Macromolecules 47 (2014) 1383–1391.

[22] G. Stoclet, G.G. du Sart, B. Yeniad, S. de Vos, J.M. Lefebvre, Isothermal crystallization and structural characterization of poly(ethylene-2,5-furanoate), Polymer 72 (2015) 165–176.

[23] Y.M. Mao, D.G. Bucknall, R.M. Kriegel, Simultaneous WAXS/SAXS study on semi-crystalline Poly(ethylene furanoate) under uniaxial stretching, Polymer 143 (2018) 228–236.

[24] Z. Terzopoulou, L. Papadopoulos, A. Zamboulis, D.G. Papageorgiou, G. Z. Papageorgiou, D.N. Bikiaris, Tuning the properties of furandicarboxylic acid-based polyesters with copolymerization: a review, Polymers 12 (2020) 1209.

[25] J.G. Wang, X.Q. Liu, Y.J. Zhang, F. Liu, J. Zhu, Modification of poly(ethylene 2,5-furandicarboxylate) with 1,4-cyclohexanedimethylene: Influence of composition on mechanical and barrier properties, Polymer 103 (2016) 1–8.

[26] A. Codou, N. Guigo, J.G. van Berkel, E. de Jong, N. Sbirrazzuoli, Preparation and characterization of poly(ethylene 2,5-furandicarboxylate)/nanocrystalline cellulose composites via solvent casting, J. Polym. Eng. 37 (2017) 869–878.

[27] A. Codou, N. Guigo, J.G. van Berkel, E. de Jong, N. Sbirrazzuoli, Preparation and crystallization behavior of poly(ethylene 2,5-furandicarboxylate)/cellulose composites by twin screw extrusion, Carbohydr. Polym. 174 (2017) 1026–1033.

[28] A. Koltsakidou, Z. Terzopoulou, G.Z. Kyzas, D.N. Bikiaris, D.A. Lambropoulou, Biobased poly(ethylene furanoate) polyester/TiO2 supported nanocomposites as effective photocatalysts for anti-inflammatory/analgesic drugs, Molecules 24 (2019) 564.

[29] N. Poulopoulou, A. Pipertzis, N. Kasmi, D.N. Bikiaris, D.G. Papageorgiou, G. Floudas, G.Z. Papageorgiou, Green polymeric materials: on the dynamic homogeneity and miscibility of furan-based polyester blends, Polymer 174 (2019) 187–199.

[30] T. Hohnemann, M. Steinmann, S. Schindler, M. Hoss, S. Konig, A. Ota, M. Dauner, M.R. Buchmeiser, Poly(ethylene furanoate) along its life-cycle from a polycondensation approach to high-performance yarn and its recyclate, Materials 14 (2021) 1044.

[31] W. Takarada, K. Sugimoto, H. Nakajima, H.A. Visser, G.J.M. Gruter, T. Kikutani, Melt-spun fibers from bio-based polyester-fiber structure development in high-speed melt spinning of poly(ethylene 2,5-furandicarboxylate) (PEF), Materials 14 (2021) 1172.

[32] P. Wang, W. Huang, Y. Zhang, J. Lin, P. Chen, An evoluted bio-based 2,5-furan-dicarboxylate copolyester fiber from poly(ethylene terephthalate), J. Polym. Sci. 58 (2020) 320–329.

[33] P. Ji, D.P. Lu, S.M. Zhang, W.Y. Zhang, C.S. Wang, H.P. Wang, Modification of poly (ethylene 2,5-furandicarboxylate) with poly(ethylene glycol) for biodegradable copolyesters with good mechanical properties and spinnability, Polymers 11 (2019) 2105.

[34] M. Svyntkivska, T. Makowski, E.L. de Boer, E. Piorkowska, Solution electrospinning and properties of poly(ethylene 2,5-furandicarboxylate) fibers, Polym. Test. 113 (2022) 107677.

[35] L. Persano, A. Camposeo, C. Tekmen, D. Pisignano, Industrial upscaling of electrospinning and applications of polymer nanofibers: a review, Macromol. Mater. Eng. 298 (2013) 504–520.

[36] S. Omer, L. Forgách, R. Zelkó, I. Sebe, Scale-up of electrospinning: market overview of products and devices for pharmaceutical and biomedical purposes, Pharmaceutics 13 (2021) 286.

[37] Z.-M. Zhang, Z.-Q. Gan, R.-Y. Bao, K. Ke, Z.-Y. Liu, M.-B. Yang, W. Yang, Green and robust superhydrophilic electrospun stereocomplex polylactide membranes:

[38] X. Qin, S. Subianto, Electrospun nanofibers for filtration applications, Electro Nanofibers (2017) 449–466.

[39] I.A. Borojeni, G. Gajewski, R.A. Riahi, Application of electrospun nonwoven fibers in air filters, Fibers 10 (2022) 15.

[40] S. Ataei, P. Azari, A. Hassan, B. Pingguan-Murphy, R. Yahya, F. Muhamad, Essential oils-loaded electrospun biopolymers: a future perspective for active food packaging, Adv. Polym. Technol. 2020 (2020) 9040535.

[41] L.Y. Zhao, G.G. Duan, G.Y. Zhang, H.Q. Yang, S.J. He, S.H. Jiang, Electrospun functional materials toward food packaging applications: a review, Nanomaterials 10 (2020) 150.

[42] H.L. Cheng, X.Y. Yang, X. Che, M.S. Yang, G.X. Zhai, Biomedical application and controlled drug release of electrospun fibrous materials, Mater. Sci. Eng. C. - Mater. Biol. Appl. 90 (2018) 750–763.

[43] R. Contreras-Caceres, L. Cabeza, G. Perazzoli, A. Diaz, J.M. Lopez-Romero, C. Melguizo, J. Prados, Electrospun nanofibers: recent applications in drug delivery and cancer therapy, Nanomaterials 9 (2019) 656.

[44] A. Subramaniam, S. Sethuraman, Biomedical applications of nondegradable polymers, in: S.G. Kumbar, C.T. Laurencin, M. Deng (Eds.), Natural and Synthetic Biomedical Polymers, Elsevier, Oxford, 2014, pp. 301–308.

[45] M. Cevasco, K.M.F. Itani, Ventral hernia repair with synthetic, composite, and biologic mesh: characteristics, indications, and infection profile, Surg. Infect. 13 (2012) 209–215.

[46] T. Khodaei, E. Schmitzer, A.P. Suresh, A.P. Acharya, Immune response differences in degradable and non-degradable alloy implants, Bioact. Mater. 24 (2023) 153–170.

[47] M. Razavi, R. Primavera, A. Vykunta, A.S. Thakor, Silicone-based bioscaffolds for cellular therapies, Mater. Sci. Eng. C 119 (2021) 111615.

[48] F.T. Foroushani, K. Dzobo, N.P. Khumalo, V.Z. Mora, R. de Mezerville, A. Bayat, Advances in surface modifications of the silicone breast implant and impact on its biocompatibility and biointegration, Biomater. Res. 26 (2022) 80.

[49] D.M. Faulk, R. Londono, M.T. Wolf, C.A. Ranallo, C.A. Carruthers, J.D. Wildemann, C.L. Dearth, S.F. Badylak, ECM hydrogel coating mitigates the chronic inflammatory response to polypropylene mesh, Biomaterials 35 (2014) 8585–8595.

[50] M.T. Wolf, C.L. Dearth, C.A. Ranallo, S.T. LoPresti, L.E. Carey, K.A. Daly, B. N. Brown, S.F. Badylak, Macrophage polarization in response to ECM coated polypropylene mesh, Biomaterials 35 (2014) 6838–6849.

[51] N. Sanbhal, X. Saitaer, Y. Li, Y. Mao, T. Zou, G. Sun, L. Wang, Controlled levofloxacin release and antibacterial properties of β-cyclodextrins-grafted polypropylene mesh devices for hernia repair, Polymers 10 (2018) 493.

[52] M. Ackermann, X. Wang, S. Wang, M. Neufurth, H.C. Schröder, F.-E. Isemer, W.E. G. Müller, Collagen-inducing biologization of prosthetic material for hernia repair: Polypropylene meshes coated with polyP/collagen, J. Biomed. Mater. Res. Part B Appl. Biomater. 106 (2018) 2109–2121.

[53] E. Kulaga, L. Ploux, L. Balan, G. Schrodj, V. Roucoules, Mechanically responsive antibacterial plasma polymer coatings for textile biomaterials, Plasma Process Polym. 11 (2014) 63–79.

[54] C. Labay, J.M. Canal, M. Modic, U. Cvelbar, M. Quiles, M. Armengol, M.A. Arbos, F. J. Gil, C. Canal, Antibiotic-loaded polypropylene surgical meshes with suitable biological behaviour by plasma functionalization and polymerization, Biomaterials 71 (2015) 132–144.

[55] S. Mirel, A. Pusta, M. Moldovan, S. Moldovan, Antimicrobial meshes for hernia repair: current progress and perspectives, J. Clin. Med. 11 (2022) 883.

[56] E. Tanzli, A. Ehrmann, Electrospun nanofibrous membranes for tissue engineering and cell growth, Appl. Sci. - Basel 11 (2021) 6929.

[57] C.-S. Ha, J.A. Gardella, Surface chemistry of biodegradable polymers for drug delivery systems, Chem. Rev. 105 (2005) 4205–4232.

[58] Z. Ma, Z. Mao, C. Gao, Surface modification and property analysis of biomedical polymers used for tissue engineering, Colloids Surf. B 60 (2007) 137–157.

[59] M.M. Lim, T. Sun, N. Sultana, In vitro biological evaluation of electrospun polycaprolactone/gelatine nanofibrous scaffold for tissue engineering, J. Nanomater. 2015 (2015), 303426.

[60] Z. Zhou, Y. Liu, Z. Liu, L. Fan, T. Dong, Y. Jin, M.D.A. Saldaña, W. Sun, Sustained-release antibacterial pads based on nonwovens polyethylene terephthalate modified by β-cyclodextrin embedded with cinnamaldehyde for cold fresh pork preservation, Food Packag. Shelf Life 26 (2020), 100554.

[61] S. Fahimirad, Z. Fahimirad, M. Sillanpaa, Efficient removal of water bacteria and viruses using electrospun nanofibers, Sci. Total Environ. 751 (2021), 141673.

[62] L.J. Liu, W.Z. Yuan, A hierarchical functionalized biodegradable PLA electrospun nanofibrous membrane with superhydrophobicity and antibacterial properties for oil/water separation, N. J. Chem. 42 (2018) 17615–17624.

[63] B. Azimi, H. Maleki, L. Zavagna, J.G. De la Ossa, S. Linari, A. Lazzeri, S. Danti, Bio-based electrospun fibers for wound healing, J. Func. Biomater. 11 (2020) 67.

[64] H.S. Sofi, A. Abdal-hay, S. Ivanovski, Y.S. Zhang, F.A. Sheikh, Electrospun nanofibers for the delivery of active drugs through nasal, oral and vaginal mucosa: Current status and future perspectives, Mater. Sci. Eng. C - Mater. Biol. Appl. 111 (2020), 110756.

[65] S. Amjadi, H. Almasi, M. Ghorbani, S. Ramazani, Reinforced ZnONPs/rosemary essential oil-incorporated zein electrospun nanofibers by kappa-carrageenan, Carbohydr. Polym. 232 (2020), 115800.

[66] I. Maliszewska, T. Czapka, Electrospun polymer nanofibers with antimicrobial activity, Polymers 14 (2022) 1661.

[67] X. Deng, A. Yu Nikiforov, T. Coenye, P. Cools, G. Aziz, R. Morent, N. De Geyter, C. Leys, Antimicrobial nano-silver non-woven polyethylene terephthalate fabric via an atmospheric pressure plasma deposition process, Sci. Rep. 5 (2015) 10138.

[68] H.-W. Chien, Y.-Y. Chen, Y.-L. Chen, C.-H. Cheng, J.-C. Lin, Studies of PET nonwovens modified by novel antimicrobials configured with both N-halamine and dual quaternary ammonium with different alkyl chain length, RSC Adv. 9 (2019) 7257–7265.

[69] M.C. Stensberg, Q. Wei, E.S. McLamore, D.M. Porterfield, A. Wei, M.S. Sepúlveda, Toxicological studies on silver nanoparticles: challenges and opportunities in assessment, monitoring and imaging, Nanomedicine 6 (2011) 879–898.

[70] E. Sánchez-López, D. Gomes, G. Esteruelas, L. Bonilla, A.L. Lopez-Machado, R. Galindo, A. Cano, M. Espina, M. Ettcheto, A. Camins, A.M. Silva, A. Durazzo, A. Santini, M.L. Garcia, E.B. Souto, Metal-based nanoparticles as antimicrobial agents: an overview, Nanomaterials 10 (2020) 292.

[71] S.A. Anuj, H.P. Gajera, D.G. Hirpara, B.A. Golakiya, Bacterial membrane destabilization with cationic particles of nano-silver to combat efflux-mediated antibiotic resistance in Gram-negative bacteria, Life Sci. 230 (2019) 178–187.

[72] S.A. Anuj, H.P. Gajera, D.G. Hirpara, B.A. Golakiya, Interruption in membrane permeability of drug-resistant Staphylococcus aureus with cationic particles of nano-silver, Eur. J. Pharm. Sci. 127 (2019) 208–216.

[73] B. Le Ouay, F. Stellacci, Antibacterial activity of silver nanoparticles: a surface science insight, Nano Today 10 (2015) 339–354.

[74] I. Shahid ul, B.S. Butola, F. Mohammad, Silver nanomaterials as future colorants and potential antimicrobial agents for natural and synthetic textile materials, RSC Adv. 6 (2016) 44232–44247.

[75] A. Mahapatra, N. Garg, B.P. Nayak, B.G. Mishra, G. Hota, Studies on the synthesis of electrospun PAN-Ag composite nanofibers for antibacterial application, J. Appl. Polym. Sci. 124 (2012) 1178–1185.

[76] J.C. Ge, J.Y. Kim, S.K. Yoon, N.J. Choi, Fabrication of low-cost and high-performance coal fly ash nanofibrous membranes via electrospinning for the control of harmful substances, Fuel 237 (2019) 236–244.

[77] T. Makowski, M. Svyntkivska, E. Piorkowska, D. Kregiel, Multifunctional polylactide nonwovens with 3D network of multiwall carbon nanotubes, Appl. Surf. Sci. 527 (2020), 146898.

[78] T. Makowski, C. Zhang, A. Olah, E. Piorkowska, E. Baer, D. Kregiel, Modification of dual-component fibrous materials with carbon nanotubes and methyltrichlorosilane, Mater. Des. 162 (2019) 219–228.

[79] S. Ullah, M. Hashmi, D. Kharaghani, M.Q. Khan, Y. Saito, T. Yamamoto, J. Lee, I. S. Kim, Antibacterial properties of in situ and surface functionalized impregnation of silver sulfadiazine in polyacrylonitrile nanofiber mats, Int. J. Nanomed. 14 (2019) 2693–2703.

[80] M.K. Selatile, V. Ojijo, R. Sadiku, S.S. Ray, Development of bacterial-resistant electrospun polylactide membrane for air filtration application: effects of reduction methods and their loadings, Polym. Degrad. Stabil. 178 (2020), 109205.

[81] C. Cummins, P. Mokarian-Tabari, J.D. Holmes, M.A. Morris, Selective etching of polylactic acid in poly(styrene)-block-poly(d,l)lactide diblock copolymer for nanoscale patterning, J. Appl. Polym. Sci. 131 (2014) 40798.

[82] M.M. Kareem, K.E. Tanner, Optimising micro-hydroxyapatite reinforced poly (lactide acid) electrospun scaffolds for bone tissue engineering, J. Mater. Sci. Mater. Med 31 (2020) 38.

[83] M.K. Selatile, S.S. Ray, V. Ojijo, R. Sadiku, Correlations between fibre diameter, physical parameters, and the mechanical properties of randomly oriented biobased polylactide nanofibres, Fibers Polym. 20 (2019) 100–112.

[84] U. Mizerska, R. Halasa, K. Turecka, J. Chojnowski, P. Pospiech, W. Fortuniak, S. Slomkowski, T. Makowski, W. Machnowski, P. Sowinski, Bacterial cell killing properties of silver-loaded polysiloxane microspheres, J. Mater. Sci. 53 (2018) 7125–7137.

[85] A.B.D. Cassie, Contact angles, Discuss. Faraday Soc. 3 (1948) 11–16.

[86] P.K. Szewczyk, D.P. Ura, S. Metwally, J. Knapczyk-Korczak, M. Gajek, M. M. Marzec, A. Bernasik, U. Stachewicz, Roughness and fiber fraction dominated wetting of electrospun fiber-based porous meshes, Polymers 11 (2019) 34.

[87] Z.A. Abdul Hamid, C.Y. Tham, Z. Ahmad, Preparation and optimization of surface-engineered poly(lactic acid) microspheres as a drug delivery device, J. Mater. Sci. 53 (2018) 4745–4758.

[88] M. Schneider, N. Fritzsche, A. Puciul-Malinowska, A. Baliś, A. Mostafa, I. Bald, S. Zapotoczny, A. Taubert, Surface etching of 3D printed poly(lactic acid) with NaOH: a systematic approach, Polymers 12 (2020) 1711.

[89] M. Sabee, N.A. Kamalaldin, B.H. Yahaya, Z.A.A. Hamid, Characterization and in vitro study of surface modified PLA microspheres treated with NaOH, J. Polym. Mater. 33 (2016) 191–200.

[90] M. Pluta, J. Bojda, T. Makowski, E. Piorkowska, M. Murariu, L. Bonnaud, P. Dubois, Significant modification of the surface morphology of polylactide (PLA) and PLA-halloysite nanocomposites in the presence of N,N '-ethylenebis (stearamide) upon thermal treatment, Express Polym. Lett. 14 (2020) 1155–1168.

[91] M. Svyntkivska, T. Makowski, I. Shkyliuk, E. Piorkowska, Electrically conductive crystalline polylactide nonwovens obtained by electrospinning and modification with multiwall carbon nanotubes, Int. J. Biol. Macromol. (2023), 124730.

[92] R. Ng, X.D. Zhang, N. Liu, S.T. Yang, Modifications of nonwoven polyethylene terephthalate fibrous matrices via NaOH hydrolysis: effects on pore size, fiber diameter, cell seeding and proliferation, Process Biochem. 44 (2009) 992–998.

[93] A. Vesel, N. Recek, H. Motaln, M. Mozetic, Endothelialization of polyethylene terephthalate treated in SO2 plasma determined by the degree of material cytotoxicity, Plasma 1 (2018) 12–22.

[94] J. Liu, D.A. Sonshine, S. Shervani, R.H. Hurt, Controlled release of biologically active silver from nanosilver surfaces, ACS Nano 4 (2010) 6903–6913.

[95] U. Mizerska, W. Fortuniak, T. Makowski, M. Svyntkivska, E. Piorkowska, D. Kowalczyk, S. Brzezinski, D. Kregiel, Antibacterial electroconductive rGO modified cotton fabric, Polym. Adv. Technol. 32 (2021) 3975–3981.

[96] L. Mei, X. Zhang, Y. Wang, W. Zhang, Z. Lu, Y. Luo, Y. Zhao, C. Li, Multivalent polymer–Au nanocomposites with cationic surfaces displaying enhanced antimicrobial activity, Polym. Chem. 5 (2014) 3038–3044.

[97] R.-b Chen, K. Zhang, H. Zhang, C.-y Gao, C.-l Li, Analysis of the antimicrobial mechanism of porcine beta defensin 2 against E. coli by electron microscopy and differentially expressed genes, Sci. Rep. 8 (2018) 14711.

[98] J. Shen, Y. Tian, Y. Li, R. Ma, Q. Zhang, J. Zhang, J. Fang, Bactericidal effects against S. aureus and physicochemical properties of plasma activated water stored at different temperatures, Sci. Rep. 6 (2016) 28505.