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Antibacterial and Antifungal Properties of Polyester and PLA Nonwovens (And PES and Cotton Fabrics), Functionalized with Aquous Dispersions Containing Copper Silicate, Titanium Dioxide, Zinc Oxide, or Hybrid Composite Oxide ZnO·SiO_2

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Abstract: Many stable water dispersions of various chemical compositions containing bioactive chemical compounds: copper silicate, titanium dioxide and zinc oxide (and other auxiliary substances) were developed and fabricated - they were used for preparation of thin hybrid coatings having very good antimicrobial properties against gram negative bacteria (*Escherichia coli*), gram positive bacteria (*Staphylococcus aureus*) and yeast fungus (*Candida albicans*). Polyester (PES) nonwovens were modified by dip-coating, and PES and cotton fabrics - by dip-coating and coating methods.

Keywords: antimicrobial modification of textile materials; antibacterial and antifungal properties; biofunctionalization; polyester; poly(lactic acid) (PLA); nonwovens; PES and cotton fabrics; copper silicate hydrate; $CuSiO_3$; titanium dioxide; TiO_2; zinc oxide; hybrid composite oxide ZnO·SiO_2

1. Introduction

In a literature, for a very long time, have been known properties of silver [1] and zinc [2] ions, as well copper microparticles (MPs), nanoparticles (NPs), and its surfaces [3,4], showing a strong inhibitory effect on a growth of different bacteria. The antimicrobial properties of silver MPs and NPs have great application potential in the textile industry and in medicine [5–12]. Silica nanofibers containing Ag NPs [13] and PLA-chitosan composite fibers [14] also exhibited excellent antibacterial properties.

Copper (II) oxide CuO also has antibacterial, antifungal and even antiviral properties [15–20]. Although, for most microorganisms low concentrations of copper are sufficient, usually much higher doses of Cu (even in the amount of 3-10 weight %) were used to inhibit the growth of some microorganisms and provide antimicrobial features [21,22]. Research studies on modifying the properties of polymeric and textile materials, in order to obtain more effective and economical methods of antimicrobial protection, have been continued in the recent two decades. The constant development of research on the antibacterial properties of materials containing Cu NPs has been observed [4,22–26].

From the publication of C.C. Trapalis *et al*. [27], the method of obtaining thin composite silicate coatings containing copper particles (CuPs) deposited on glass plates by a sol-gel method [Cu/silica (SiO_2)] was also known. The fabricated coatings showed high antibacterial activity against *Escherichia Coli* bacteria, which was increasing with the increase of the metal content, and decreasing with the

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increase of the thermal treatment temperature in a deposition process of metal nanoparticles on different surfaces. The CuPs incorporated onto nanosilica also showed the inhibitory effect on the growth of microorganisms. They were also used to remove the odor of mercaptans [28]. The CuPs immobilized onto the surface of SiO_2 spheres did not aggregate and showed good antimicrobial properties against colonies of *Escherichia coli*, *Staphylococcus aureus* and *Candida albicans*, when the concentration of SiO_2@Cu was higher than 500 μg/ml [29]. Silica NPs with a "core-shell" structure (nucleus-shell), containing the addition of approximately 0.1 μg of Cu (in the form of insoluble copper hydroxide) had much better antibacterial properties against *Escherichia coli* and *Bacillus subtilis* than it was observed against $Cu(OH)_2$ alone, and the *Minimum Inhibitory Concentration* (MIC) of these bacteria was 2.4 μg Cu/ml in the case of SiO_2@Cu having the "core-shell" structure [30].

Very good antibacterial properties against numerous pathogens occurring in hospital conditions (*Acinetobacter baumannii, Klebsiella pneumoniae, Stenotrophomonas maltophilia, Enterococcus faecium, Staphylococcus aureus and Pseudomonas aeruginosa*) showed thin layers of Cu-SiO_2 nanocomposites (NCs) obtained by the chemical vapor deposition (CVD). These coatings with microbiological properties can be used for protection of metal and ceramic surfaces [31]. It has also been observed that copper and zinc alginates and their composites with silica had the stronger antibacterial effect against *Enterococcus faecalis* bacteria, than in the case of ordinary solutions of Cu and Zn salts [32].

High stability in the air atmosphere (over 3 months) and excellent microbiological activity against various colonies of bacteria: *Escherichia coli* [33], *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Enterococcus faecalis* showed Cu NPs deposited on the surface of sodium aluminosilicate (sodium montmorillonite, MMT) or intercalated inside its layered structure, causing the disappearance of >90% of bacteria after 12 h. Cytotoxicity studies have shown a minimal adverse effect of this nanocomposite on human cells when the MIC of these microorganisms was exceeded. Nevertheless, promising prospects for the use of the MMT-Cu nanocomposite for therapeutic purposes were anticipated [4]. It was reported that other metallic and metal oxides NPs also exhibited antimicrobial properties [34].

A suspension of an emulsion paint with the addition of a mixture of 0.1-20 wt.% of anhydrous copper silicate $CuSiO_3$ with vegetable oils were used to coat the inner surfaces of pots and containers used for growing plants and flowers [37]. In the sol-gel process were obtained mesoporous copper silicate xerogels with a high specific surface area (463 m^2/g) and a pore size of 2 nm, showing antibacterial properties which were dependent on the CuPs concentration [38].

T. Jesionowski *et al.* prepared polyester (PES) films containing 2 or 8 wt.% hybrid oxide composite CuO·SiO_2, which exhibited the excellent antibacterial properties against *Pseudomonas aeruginosa* bacteria [39]. Similar composites of polyolefins (LDPE or PP) containing 2-8 wt.% CuO·SiO_2 had increased a thermal resistance and thermal diffusivity as well as exhibited good biocidal properties [40]. Silica NCs containing Cu(0) MPs and Cu(I) compounds showed higher antibacterial effectiveness than Cu(II) compounds - against *Xanthomonas alfalfae* and *Escherichia coli* bacteria. Phytotoxicity studies in greenhouse conditions (with the participation of *Vinca sp.* and *Hamlin orange*) provided NCs, which were safe for plants and could be used as biocides in agriculture [41].

Within previous years many research works done in our Institute concerned on the incorporation of metal oxides into the structure of textile materials, providing good antimicrobial properties. It was found that micronized particles of the metal oxides (ZnO, TiO_2), introduced into the structure of the polyester non-woven fabric by dip-coating procedure, showed bioactivity against various bacterial colonies and selected fungi, as well as properties of absorption of UV light and the ability to photooxidize organic substances. Textile materials modified in this way could find many practical applications, especially for the production of protective clothing [42–44]. In addition, a polyester non-woven fabric and a cotton fabric modified by coating with dispersions containing ZnO or the ZnO·SiO_2 composite containing 30 wt. % of ZnO showed barrier properties against UV radiation, as expressed by ultraviolet protection factor (UPF) >45 and high absorption of UV radiation in the entire spectral range [45].

In the following years, a method of antimicrobial functionalization of polypropylene (PP) and polylactide (PLA) nonwovens, applying the *melt-blown* extrusion process, was developed, using

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copper silicate hydrate ($CuSiO_3 \cdot xH_2O$), with the addition of a wide range of various plasticizers (most often PEG600). The obtained PP and PLA nonwoven fabrics had excellent antibacterial properties against gram-negative bacteria *Escherichia coli* and against gram-positive bacteria *Staphylococcus aureus*, and also the very good antifungal properties against *Candida albicans* yeast fungus, already at the quite low $CuSiO_3$ hydrate content in these fibre composites of 0.5-1 wt.%. The growth reduction factor of these microorganisms (R) was greater than 98% [46,47]. Analogously, using the *melt-blown* technique, composite nonwoven fabrics were obtained from mixtures of polymers (PP and PLA, 1:1) with 0.5 wt.% of copper silicate hydrate ($CuSiO_3 \cdot xH_2O$, containing 18.5 % of H_2O), with the addition of 5 wt.% paraffin oil as the plasticizer. The PLA/PP/paraffin/$CuSiO_3$ composite nonwoven fabric had strong antibacterial properties as well - against *Escherichia coli* and *Staphylococcus aureus* bacteria. Thermal properties of all types of these composite nonwovens were tested using DSC method. Physicochemical parameters, specific surface area, surface morphology (by SEM method), elements content (by EDS method) and resistance to hydrolytic degradation (in alkaline and neutral environment) were also determined [48].

Due to the constant increase in the consumption of materials made of biodegradable polymers on a global scale, the research on the biofunctionalization of composite nonwovens with both conventional (PP and PES) and biodegradable polymers is of great importance, among which poly(lactic acid) (PLA) is the most important and widely used. The wide use of PLA results from its availability, good mechanical properties and relative ease of processing with various techniques (e.g., *melt-blown* technique) [49,50]. PLA has been used, among others, in medicine, in the production of various types of packaging that come into contact with food, and for obtaining a new generation of textile materials [50,51].

Biodegradable polymers are more expensive than traditional polymers and have slightly worse mechanical properties, as some of them in the pure state are, for example, quite stiff or brittle [49]. For this reason, in the processes of their processing, various plasticizers are used as additives. Poly(ethylene glycol) (PEG) is the most commonly used plasticizer for PLA [52] and polyhydroxyalkanoates (PHA) [50]. It was found that the addition of PEG200 to PLA in an amount of 1-7 wt.% causes a gradual decrease in the glass transition temperature (T_g) of PLA-PEG200 mixtures from 62.9 °C to 48.5 °C, and at the content of 10 wt.% PEG200 T_g reached 51.6 °C [52]. On the other hand, the flexibility and hydrophilicity of coatings made of poly(3-hydroxybutanoate) [P(3HB)] with PEG was greater than in the case of coatings made of P(3HB) alone, leading to the increased biocompatibility of such composite biomaterials [53].

Linen fabrics modified with 5-7 wt.% of copper silicate by dip-coating method showed excellent antimicrobial properties and barrier properties against UV radiation (with the high value of the UPF coefficient 64-131, and a UV light transmittance of 0.20-3.40) [54]. Also non-woven PLA composites with copper alginate exhibited good antibacterial properties (against *Escherichia coli* and *Staphylococcus aureus*), antifungal activity (to *Aspergillus niger* and *Chaetomium globosum*), and good barrier properties against UV radiation (UPF>40) [55].

The fabrics modified on the surface with CuO also had good antibacterial properties and were non-toxic to human skin. Thus, they could be used for the production of medical clothing [56]. Moreover, CuO nanoparticles showed the significant inhibitory effect on the development of *hepatitis C virus* (HCV) and effectively inactivated many other viruses, such as *rhinovirus 2*, *yellow fever virus*, *human influenza A*, *measles* and *parainfluenza type 3*, *Punta Toro*, *adenovirus type 1*, *cytomegalovirus*, *vaccinia*, and *herpes simplex type 1*. It proved the positive effect of the CuO NPs on the growth of the human body's immunity. Recently, the disappearance of the *SARS-CoV-2 virus* on copper surfaces after 4 hours was observed [57,58]. On the other hand, polyurethane coatings containing Cu_2O, applied to glass or stainless steel, very quickly inactivated *SARS-CoV-2* (99.9% within 1 hour) [59]. The copper particles (CuPs) also inactivated several infectious viruses: *bronchitis virus*, *polio virus*, *human immunodeficiency virus type 1* (*HIV-1*), other enveloped and non-enveloped viruses, single and double stranded DNA and RNA viruses. Thus, a strong contact killing ability of several viruses, including *SARS-CoV-2*, on the copper surfaces was confirmed. The increase of the copper

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content in plasma may enhance both innate and adaptive immunity in human. Due to its strong antiviral activity, CuPs may also have preventive and therapeutic effects against *COVID-19* [60].

The copper silicate is non-toxic and much cheaper than silver and its compounds and should find many different practical applications soon, especially for the development of a technology for the production of a new group of textile materials with strong antimicrobial (antibacterial and antifungal) properties, and even for deactivating various viruses, e.g. *SARS -CoV-2*.

2. Experimental part

2.1. Materials

polyester nonwovens:

- WIFP-270 of a surface mass of approx. 270 g/m^2 (Sieć Badawcza Łukasiewicz - Łódzki Instytut Technologiczny, Łódź, Poland),
- filter non-wovens: *FS G-4* of the surface mass of approx. 210 g/m^2 and *FS F-5* of the surface mass of approx. 240 g/m^2 (Filter Service Ltd., Zgierz, Poland),
- polyester non-woven (*aqua-jet*, *Hydronina*) having the surface mass of approx. 100 g/m^2 (Lentex, Lubliniec, Polska),

polylactide non-woven fabric (*PLA-350*) with the surface mass of approx. 350 g/m^2 (ZPHU Gramix, Brzeziny, Poland),
polyester fabric with a twill weave and the surface mass of approx. 140 g/m^2 (Andropol S.A., Andrychów, Poland),
textile fabrics:

- cotton-polyester fabric with 70 wt.% content of PES (*Figaro*), having a twill weave and the surface mass of approx. 170 g/m^2 (Andropol S.A., Andrychów, Poland),
- cotton fabric (*Medical*) with the plain weave and the surface mass of approx. 150 g/m^2 (Andropol S.A., Andrychów, Poland).

2.2. Chemical Reagents

1. copper sulfate $Cu(SO_4)_2 \cdot 5H_2O$, pure (*Chempur,* Piekary Śląskie, Poland);
2. *Vitrosilicon 137S*, a water solution of sodium water glass, having a SiO_2:Na_2O molar ratio 3.3 (*CIECH Vitrosilicon,* 68-120 Iłowa, Poland);
3. *CELLOSIZE HEC QP-40* [(hydroxyethyl)cellulose + sodium acetate] (*Amerchol,* USA) – thickening agent;
4. poly(ethylene glycol) *Polikol 400* (PEG400) (*PCC Exol*, Poland) – a wetting agent;
5. poly(ethylene glycol) *Pluriol E600* (PEG600) (*BASF*, Germany) – the wetting agent;
6. water dispersion of styrene-acrylic resin *Revacryl 247®* (*Thorex,* Łódź, Poland) – a binder;
7. water dispersion of acrylic resin – *Talens Amsterdam Acrylic Binder 005* (*Talens,* Niderlands);
8. *Cinkarna CCA 100 BS*, water dispersion of acrylic resin, containing 20-22 % wt.% of nano-TiO_2 (~10 nm), (Cinkarna Celje, d.d., Slovenia);
9. water dispersion of acrylic resin *Dekoral Silver* (PPG DECO Sp. z o.o., Wrocław, Poland) – the binder,
10. acrylic photocatalytic water dispersion *Titanium IN* (*Pigment*, Szczecin, Poland) – the binder,
11. silicate photocatalytic water dispersion *Titanium FA* (*Pigment*, Szczecin, Poland) – the binder,
12. *Synexil DN-50*, water dispersion of poly(vinyl acetate, PVAc (*Synthos S.A.*, Oświęcim, Poland) – the binder,
13. poly(vinyl alcohol) *Mowiol 4-98* (*Fluka, Germany*) with a weight average molecular weight (M_w) ~27 000 g/mol) – thickening and pro-adhesion agent,
14. soluble starch (*Chempur*, Piekary Śląskie, Poland) – thickening and pro-adhesion agent,
15. glycerine, pure (*POCh*, Gliwice, Poland) – a plasticizer,
16. bis(2-etylohexyl adipate) (*Adoflex*) (*Zakłady Azotowe Kędzierzyn S.A.*, Kędzierzyn-Koźle, Poland) – the plasticizer,

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17. nanosilica *Aerosil 380* (*Evonik*, Germany) – a stabilizer of dispersions,
18. methyl silicone oil containing OH terminal groups, with a viscosity of 500 cP - *Polastosil M-200* (*Zakład Chemiczny „Silikony Polskie"*, Nowa Sarzyna, Poland) – an antifoaming agent,
19. enzyme *Texazym PES* (*INOTEX*, Dvůr Králové n.L, Czechia);
20. syntetic acrylic thickening agent *Lutexal Thickener HC* (BASF, Niemcy) - for our purpose it was diluted with demineralized water (1:3, w/w),
21. copper silicate hydrate $CuSiO_3 \cdot 18.5H_2O$ (Poznań University of Technology, Poznań, Poland) composed of: 35.23 wt.% CuO, 62.16 wt.% SiO_2, 18.52 wt.% H_2O, 0.02 wt.% Na_2O, and 0.01 wt.% K_2O), with a particle diameter in a range 1-100 μm [39];
22. titanium dioxide TiO_2 (*TK44*) (Poznań University of Technology, Poznań, Poland) with the average particle diameter of 615 nm and their polydispersity of 0.102; it was obtained from the anatase allotrope of TiO_2, having a commercial name *Tytanpol* (Police S.A., Szczecin, Poland), with the average particle diameter of 712-825 nm and the polydispersity of 0.218 – it was modified with 1 wt.% of N-2-aminoethyl-3-aminopropyl(trimethoxy)silane;
23. zinc oxide, ZnO (*Z11*) (obtained from Poznań University of Technology, Poznań, Poland) with the average particle diameter of 396 nm and their polydispersity of 0.161;
24. zinc lactate, p.a. (Xenon - Chemists' Cooperative, Rąbień, Poland);
25. hybrid oxide $ZnO \cdot SiO_2$, prepared as it was described in [45a].

2.3. Modification of the surface of nonwovens and polyester fabrics before the dip-coating process

An appropriate surface modification of textile materials, in particular hydrophobic polyester fiber, has a very significant impact on the effectiveness of the process of biocide modifiers' incorporation. In order to improve the wettability of the tested polymer nonwovens and increase the adhesion of the dispersion components to the surface of the nonwovens, the nonwovens were alkalized at room temperature by immersing them in a solution containing 2 wt.% NaOH and 4 wt.% Na_2CO_3 for 4 days. Then, the samples of nonwoven fabrics were drained from the excess of alkali solution in a horizontal two-shaft pad machine, immersed three times in demineralized water for 15 minutes an hour and again drained of excess liquid in a horizontal double-shaft pad machine, then dried at 120 °C for 4 minutes and heated in at 140 °C for 2 min. in the KTF-350S apparatus (Mathis, Switzerland).

However, in order to increase wettability and improve adhesive properties, two methods of initial surface modification of the polyester fabric were used:

(1) enzymatic treatment
and (2) alkali treatment.

(1) The enzyme treatment was carried out at 35 °C for 30 minutes in a bath containing 1-2 wt.% of an enzyme from the group of esterases Texazym PES, at pH 4.2 (adjusted by the addition of acetic acid). The bath ratio against polyester nonwovens was 10:1.
(2) Alkaline treatment was carried out at 98 °C for 60 min. in the bath containing sodium hydroxide with a concentration of 1.8 g/l, sodium carbonate (3.6 g/l) and a sequestering and wetting agent. The bath ratio was 10:1.

2.3.1. Synthesis of copper silicate hydrate in situ

Copper silicate hydrate $CuSiO_3 \cdot xH_2O$ was prepared by the *in situ* method, immediately before the dip-coating process of nonwoven fabrics, from diluted, 5 wt.% solutions of copper (II) sulphate pentahydrate $Cu(SO_4)_2 \cdot 5H_2O$ and sodium water glass Na_2SiO_3 (*Vitrosilicon S-137S* with a silicate module: $SiO_2 : Na_2O = 3.32$). However, for the preparation of aqueous dispersions, containing more than 3 wt.% of $CuSiO_3 \cdot xH_2O$, the powdered copper silicate hydrate $CuSiO_3 \cdot 18.5H_2O$ was also used in these studies – it was synthesized from copper nitrate and sodium water glass, as described in the literature [39].

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2.3.2. Description of the dip-coating method of nonwovens and polymer fabrics

Polymer nonwovens and fabrics were dip-coated with water dispersions containing copper silicate hydrate and other additives. Directly before the surfacing process, various auxiliary substances were added to the water dispersion of copper silicate: wetting agents [(poly(ethylene glycol): *Polikol 400* or *Pluriol E600*] and thickening agents (e.g. hydroxyethyl cellulose, HEC), other modifiers, dispersion stabilizer (nanosilica) and anti-foaming agent (methyl silicone oil) - in quantities adjusted to the assumed individual recipes of the surfacing process.

Most often, all aqueous dispersions (in demineralized water) contained 1,0 wt.% thickener based on (hydroxyethyl)cellulose (HEC) and generally 5-10 wt.% poly(ethylene glycol) *Polikol 400* (PEG) or *Pluriol E600*. In order to improve the stability of water dispersions and their binding properties with respect to textile materials, the addition of various acrylic resin dispersions (e.g. *Revacryl 247*, *Talens Amsterdam Acrylic Binder 005*) and a 2 wt.% aqueous solutions of starch or poly(vinyl alcohol) (PVA) were also used, and also a small addition of *Aerosil 380* nanosilica was used - for most of the dispersions. Moreover, 0.1 or 0.2 wt.% of antifoaming methyl silicone oil was added. When using 2-4 wt.% water dispersion of polyvinyl acetate (PVAc) the addition of 1-2 wt.% bis(2-ethylhexyl) adipate (Adoflex), and, if a diluted starch solution was used - 0.4-1.0 wt.% of glycerine were added - as plasticizers.

Water dispersions containing copper silicate and auxiliary substances were used for the antimicrobial modification of polymer nonwovens. Some of the dispersions also contained TiO_2, and one of the dispersions contained 5 wt.% $CuSiO_3$ and zinc lactate. The chemical composition of the water dispersions was slightly modified during the tests, e.g. in the case of the higher content of $CuSiO_3 \cdot xH_2O$ (5-7% by weight), higher amounts of PEG400 or PEG600 (7.5-10% by weight) were used, and various binders (acrylic or other).

The aqueous dispersions were prepared by mixing the weighed ingredients in the amounts given in the Table 1, using a four-blade *IKA RW 20* digital mechanical stirrer at a rotational speed of 2000 rpm for 2 minutes, and then they were homogenized with the rotational speed of 20,000 rpm, for 60 sec, using a digital homogenizer *IKA T25 Ultra Turrax®*, equipped with a dispersing element type *S25 N18G*.

The chemical compositions of most water dispersions used in the deep-coating process are given in the Table 1, and most often they were as follows:

$CuSiO_3 \cdot xH_2O$	–	1-7 wt.%,
Cellosize HEC QP-40	–	0.9-1.0 wt.%,
Polikol 400 (PEG400)	–	5-10 wt.%,
dispersion of chosen acrylic resin (or PVAc)	–	3-10 wt.%,
2 wt.% water solution of the soluble starch (or PVA)	–	25 wt.%,
nanosilica (*Aerosil 380*)	–	0.1-0.2 wt.%,
silicone oil (*Polastosil M200*)	–	0,1 wt.%,
other additives	–	changing amounts.

Weighed samples of the nonwovens or fabrics were deep-coated in a horizontal two-shaft padding machine, with the roller pressure of 30 kG/cm², in order to obtain the appropriate degree of application. Next, the textile materials were dried in a *KTF-350S* coater-heating device (Mathis, Switzerland) at the temperature 100 °C for 3 minutes, followed by heating at 140 °C for the next 1 minute.

2.3.3. Description of the coating method of polymer fabrics and nonwovens

For the fabric coating process, aqueous pastes containing the following ingredients in appropriate amounts were prepared, most often:

3-10 wt.%– reagents with antimicrobial properties (e.g. Cu silicate or/and metal oxide),
5-10 wt.% – wetting agent,
3-10 wt.% – binders and thickeners.

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Coating pastes were applied to the surface of selected fabrics or non-woven fabrics using a knife supported over a roller, using a laboratory kit for applying nanostructured coatings KTF-350S (Mathis, Switzerland). Coatings with a thickness of 0.1 mm were applied. The samples were dried and reheated under the same conditions as after the coating process. The degree of application of the so-called dry weight of hybrid modifiers and their surface weight of modified textile materials depended on the chemical composition of the dispersions used and on the type of fabric or non-woven fabric. The degree of dry substance application (SNS) was calculated from the formula:

$$SNS = \frac{m_p - m_s}{m_s} \cdot 100 \ [\%]$$

where: m_s - weight of the textile sample before coating [g]

m_P - weight of the textile material sample after coating, drying and heating [g].

In addition, the surface mass of each modified nonwoven or fabric sample [g/m^2] was determined.

2.3.4. Description of dip-coating and coating experiments (chosen examples)

The method of antimicrobial modification of nonwovens and fabrics illustrate the following examples, described in details.

Example 1

The polyester nonwoven fabric (*aqua-jet Hydronina*®) with a surface mass of 100 g/m^2 and dimensions 34 cm x 55 cm x 0.07 cm, was dip-coated in a roller pad machine (roller pressure of 30 kG/cm^2) with a water dispersion containing 6.0 wt.% copper silicate hydrate, 1.0 wt.% HEC and 10.0 wt.% PEG 400. After dip-coating, a weighed sample of the non-woven fabric was dried at 100 °C for 3 minutes and heated at 140 °C for 1 min. in the Mathis KTF-350S device. The modified samples of the nonwoven fabric, cooled down to room temperature for 1 hour, were weighed again, the degree of modifier deposition (26.0% by weight) was calculated and its antimicrobial properties were analyzed. The tested sample showed an antibacterial activity coefficient of A = 6.2, a bacteriostatic coefficient of S = 6.7, a bactericidal coefficient of L = 2.0, and a reduction in colony growth of gram-negative bacteria *Escherichia coli* (ATCC 25922) R = 96.8%, and the coefficient of antibacterial activity A = 5.2, bacteriostatic coefficient S = 5.4, bactericidal coefficient L = 2.0 and reduction of colony growth of gram-positive bacteria *Staphylococcus aureus* (ATCC 6538) R = 89.6%.

Table 1. Chemical compositions (in % by weight) of the selected water dispersions used in the process of dip-coating polymer non-wovens.

Components of dispersions	Water dispersion number																			
	1	**2**	**5**	**6**	**7**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**
$CuSiO_3 \cdot xH_2O$ [a]	3.0	5.0	3.0	2.0	1.0	1.0	3.0	5.0	5.0	7.0	.9	7,0	5.0	5.0	7.0	5.0	5.0	7.0	5.0	5.0
Cellosize HEC QP-40	1.5	1.0	1.0	0.9	0.9	0.9	0.8	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Polikol 400 (PEG400)	7.5	5.0	-	-	-	-	6.0	7.5	-	-	10.0	10.0	7.5	7.5	-	7.5	7.5	10.0	10.0	10.0
Pluriol E600 (PEG600)	-	-	7.5	5.0	5.0	5.0	-	-	7.5	10.0	-	-	-	-	10.0	-	-	-	-	-
Copolymer dispersion *Revacryl 247*	-	5.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cinkarna 100 BS	-	-	-	-	-	-	-	-	-	-	1.0 [b]	2.1 [b]	4.2 [b]	-	-	5.0 [b]	5.0 [b]	-	-	-
Talens Amsterdam Acrylic Binder 005 [c]	4.5	-	3.0	5.0	3.0	5.0	3.0	1.0	1.0	1.0	-	-	-	-	1.0	-	-	-	-	-
Acrylic dispersion *Dekoral Silver* [c]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.0	2.0	-	-	-
Photocatalytic acrylic dispersion *Titanium IN* [c]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	25.0	-
Photocatalytic silicate dispersion *Titanium FA* [c]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	25.0
Zinc lactate cz.	-	-	-	-	-	-	-	-	-	-	-	-	-	5.0	-	-	-	-	-	-
Glycerine	-	-	0.5	0.4	0.4	0.4	0.5	1.0	1.0	1.0	0.5	0.5	0.5	0.5	1.0	0,5	0.5	0.5	0.5	0.5
Synexil DN-50	-	-	-	-	-	-	1.0	4.0	4.0	4.0	2.50	2.0	2.0	2.0	4.0	2.0	-	-	-	-
Bis(2-ethylhexyl adipate) (*Adoflex*)	-	-	-	-	-	-	0.5	2.0	2.0	2,0	1.25	1.0	1.0	1.0	1.0	1.0	-	-	-	-
2 wt.% water solution of soluble starch	-	-	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0

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5 wt.% water solution of PVA	-	10.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Nanosilica (*Aerosil 380*)	-	-	-	-	-	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Silicone oil (*Polastosil M200*)	-	-	-	-	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Demineralized water	83.5	74.0	60.0	61.5	64.5	62.5	60.0	53.2	53.2	48.7	48.5	43.2	37.7	51.7	49.7	33.9	34.9	31.2	33.2	33.2

[a] – copper silicate hydrate $CuSiO_3 \cdot xH_2O$ with a water content of 18.5% by weight was used; [b] – the numbers indicate the content of TiO_2 in the water dispersion used in the dip-coating process; [c] – in commercial aqueous dispersions (*Talens Amsterdam Acrylic Binder 005*, *Dekoral Silver*, *Titanium IN* and *Titanium FA*) the content of TiO_2 was not determined

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Example 2

The polyester nonwoven fabric (*aqua-jet Hydronina*) with the surface mass of 100 g/m^2 and dimensions of 34 cm x 55 cm x 0.07 cm was dip-coated in a roller pad machine (roller pressure of 30 kG/cm^2) with the water dispersion containing 6.0 wt.% of composite oxide hydrate $ZnO{\cdot}SiO_2{\cdot}xH_2O$ [45]), 1.0 wt.% HEC, 10.0 wt.% PEG 400 and 10 wt.% *Revacryl 247®* styrene acrylic resin. After padding, the weighed sample of this nonwoven fabric was dried at 100 °C for 3 minutes and annealed at 140 °C for 3 minutes 1 min. in the Mathis KTF-350S device. The modified samples of the nonwoven fabric, cooled down to room temperature (RT) for 1 hour, were weighed again, the degree of the modifier deposition was calculated (28.4% by weight) and its antimicrobial properties were analyzed. The tested sample showed the antibacterial activity coefficient of A = 6.0, the bacteriostatic coefficient of S = 6.6, the bactericidal coefficient of L = 2.1 and the reduction in colony growth of gram-negative bacteria *Escherichia coli* (ATCC 25922) R = 97.0% and the antibacterial activity coefficient of A = 4.8, bacteriostatic coefficient S = 4.9, bactericidal coefficient L = 0.6 and reduction of colony growth of Gram-positive *Staphylococcus aureus* (ATCC 6538) R = 70.8%.

Example 3

A polyester twill fabric with a surface mass of 140 g/m^2 and a wetting angle of 112.6° was subjected to enzymatic treatment at 35 °C for 30 minutes in a bath containing 1, 1.5 or 2 wt.% *Texazym PES®* esterase enzyme at pH 4.2 (adjusted by the addition of acetic acid). The bath ratio was 10:1. The enzymatically modified samples of PES fabrics were dried at 100 °C for 2 minutes. After the enzymatic modification, the wetting angle between the PES fabric surface and water decreased to 82.9°, 66.9° and 35.9°, for the enzyme content in the bath: 1, 1.5 or 2 wt.%, respectively. The PES fabric sample with dimensions of 34 cm x 55 cm x 0.04 cm, modified with 2 wt.% *Texazym PES®* enzyme, coated with a paste containing 10.21 wt.% copper silicate hydrate $CuSiO_3{\cdot}xH_2O$, 5.11 wt.% PEG 600, 10.21 wt.% *Revacryl 247®* and 1.72 wt.% synthetic acrylic thickener *Lutexal Thickener HC®*. The coating paste was applied to the surface of the fabric using the supported knife technique (knife over a roller), using a laboratory device for applying nano-structured coatings KTF-350S by Mathis. The thickness of the coating was adjusted by adjusting the feeding gap with a feeler gauge. The width of the gap between the knife and the roller used was 0.1 mm. Immediately after the coating process, a sample of the PES nonwoven fabric was dried and heated at 160 °C for 2 minutes in the KTF-350S apparatus by Mathis. The tested sample showed the antibacterial activity coefficient of A = 5.5, the bacteriostatic coefficient of S = 5.4, the bactericidal coefficient of L = 2.2, and the reduction in the growth of *Candida albicans* fungus (ATCC 10231) R = 99.5%.

Example 4

The PES *FS F-5* polyester nonwoven fabric with a surface mass of approx. 240 g/m^2 was alkalized for 4 days at room temperature in an aqueous solution with a concentration of 2 wt.%. NaOH and 4 wt.% Na_2CO_3. Then it was pressed in a roller wringing machine, immersed in demineralized water and again pressed in a wringing machine. After drying in the KTF-350S apparatus (Mathis) (at the temperature of 120 °C for 4 minutes and at 140 °C for 2 minutes), a weighed sample of this PES non-woven fabric (with dimensions of 34 cm x 55 cm x 0.8 cm) was dip-coated in a padding machine (at the roller pressure of 30 kG/cm^2) with water dispersion No. 14 (according to the data in Table 1), previously mixed for 2 minutes with a mechanical paddle stirrer at the speed of 2000 rpm, and containing 7.0 wt.% copper silicate hydrate and other components of the mixture. After dip-coating, a weighed sample of the PES *FS F-5* nonwoven fabric was dried at 120 °C for 4 minutes and heated at 140 °C for 2 minutes in the Mathis KTF-350S device. The modified PES FS F-5 samples, cooled for 1 hour, were weighed again, their surface mass was determined (402.3 g/m^2), the degree of modifier deposition was calculated (25.6 wt.%) and their antimicrobial properties were tested. The tested sample showed the reduction in colony growth of Gram-negative *Escherichia coli* (ATCC 25922) R > 99.98%, the reduction in growth of Gram-positive bacteria *Staphylococcus aureus* (ATCC 6538) R = 99.5%, and the reduction in growth of *Candida albicans* fungus (ATCC 10231)) R = 49.5%.

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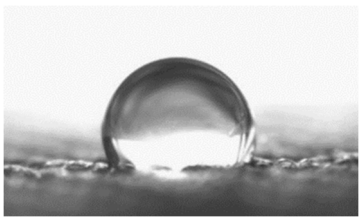
Example 5

The *WIFP-270* PES nonwoven fabric with the surface mass of approx. 270 g/m² was alkalized for 4 days at room temperature in the aqueous solution with a concentration of 2 wt.% NaOH and 4 wt.% Na_2CO_3, was pressed in the roller wringing machine, immersed in demineralized water and again pressed in the wringing machine. After drying in the Mathis KTF-350S apparatus (at 120 °C for 4 minutes and at 140 °C for 2 minutes), the weighed sample of this PES non-woven fabric with dimensions of 34 cm x 55 cm x 0.35 cm was dip-coated in a roller pad (with roller pressure of 30 kG/cm²) with water dispersion No. 16 (according to the data in the Table 1), containing 5 wt.% of copper silicate hydrate and 2.1 wt.% TiO_2, and other components of the mixture. After dip-coating, the weighed sample of the *WIFP-270* PES nonwoven fabric was dried at 120 °C for 4 minutes and heated at 140 °C for 2 minutes in the Mathis KTF-350S device. The modified samples of the PES *WIFP-270* nonwoven fabric, cooled for 1 hour to RT, were weighed again. Their surface mass was determined (394.2 g/m²), the degree of modifier deposition was calculated (31.2% by weight) and its antimicrobial properties were tested. The tested sample showed the reduction in the colony growth of Gram-negative bacteria *Escherichia coli* (ATCC 25922) R > 99.97%, the reduction in growth of Gram-positive bacteria *Staphylococcus aureus* (ATCC 6538) R = 99.7%, and the reduction in growth of *Candida albicans* (ATCC 10231)) R = 58.8%.

Example 6

The *WIFP-270 PES* nonwoven fabric with the surface mass of approx. 270 g/m² was alkalized for 4 days at room temperature in an aqueous solution with the concentration of 2 wt.% NaOH and 4 wt.% Na_2CO_3. Then, it was pressed in the roller wringing machine, immersed in demineralized water and again pressed in the wringing machine. After drying in the Mathis KTF-350S device (at the temperature of 120 °C for 4 minutes and at 140 °C for 2 minutes), the weighed sample of the PES non-woven fabric with dimensions of 34 cm x 55 cm x 0.35 cm was dip-coated in the roller padder (at the roller pressure of 30 kG/cm²) with water dispersion No. 17 (according to data in the Table 2), previously mixed for 2 minutes with the paddle mechanical stirrer at the speed of 2000 rpm, containing 5.0 wt.% of copper silicate hydrate and 4.2 wt.% TiO_2 and other components of the mixture. After padding, the weighed sample of the *WIFP-270* nonwoven fabric was dried at 120 °C for 4 minutes and heated at 140 °C for 2 minutes in the Mathis KTF-350S apparatus. The modified samples of the PES *WIFP-270* nonwoven fabric, cooled for 1 hour to RT, were weighed again, their surface mass was determined (464.7 g/m²), the degree of modifier deposition was calculated (41.0% by weight) and the antimicrobial properties were tested. The tested sample showed the reduction in colony growth of Gram-negative *Escherichia coli* (ATCC 25922) R > 99.97%, the reduction in colony growth of Gram-positive bacteria *Staphylococcus aureus* (ATCC 6538) R = 99.5%, and a reduction in growth of *Candida albicans* fungus (ATCC 10231)) R = 80.9%.

Table 2. Results of contact angle tests ($_W$, $_F$, and $_{DIM}$) for three standard liquids (water, formamide, and diiodomethane, respectively), a surface free energy (SFE) of polyester fabric samples and sample images of water drops on the surfaces of tested polyester fabrics.

Wetted surface	Image for a drop of water	Contact angle deg]			Surface free energy (SFE) [mJ/m²]		
		$_W$	$_F$	$_{DIM}$	$_S^{LW}$	$_S^{AB}$	$_S$
PES fabric (unmodified)		112.6	79.0	0.0	50.8	0.1	**50.9**

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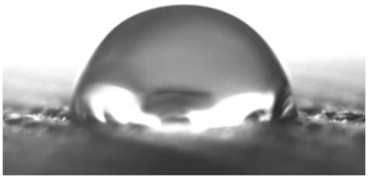
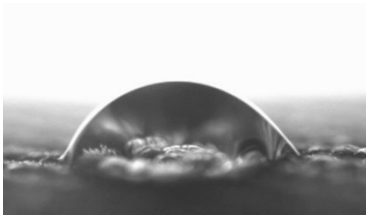
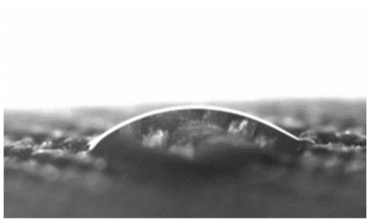
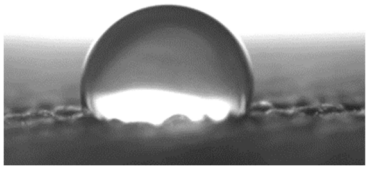
PES fabric + 1 % *Texazym*		82.9	46.8	0.0	50.8	1.1	**51.9**
PES fabric + 1,5 % *Texazym*		66.9	28.6	0.0	50.8	5.3	**56.1**
PES fabric + 2 % *Texazym*		35.9	11.2	0.0	50.8	8.7	**59.5**
PES fabric after alkalization		103.2	62.7	0.0	50.8	2.0	**52.8**

2.3.5. Evaluation of antimicrobial activity of polymeric nonwovens modified with aqueous dispersions containing copper silicate

The analysis of biological activity of selected samples of functionalized polymer nonwovens was carried out in the Biodegradation and Microbiological Research Laboratory of our Institute. The biological activity of the surface of biofunctionalized polymer nonwovens was analyzed in appropriate antibacterial tests against the following microorganisms: colonies of gram-negative bacteria *Escherichia coli* (ATCC 11229), gram-positive *Staphylococcus aureus* (ATCC 6538), and in antifungal tests against the fungus *Candida albicans* (ATCC 10321) - according to the PN-EN ISO 20743 standard.

2.3.6. Scanning Electron Microscopy (SEM)

A surface morphology of polymeric nonwovens, before and after biofunctionalization process was analyzed by Scanning Electron Microscopy (SEM). The microscopic analysis of fibers and fibrins, forming nonwovens physical structures, was performed using a scanning electron microscope, model Quanta 200 (FEI Company), equipped with a Q150R S vacuum sputtering machine. The SEM microscopic analysis was carried out in a high vacuum, using the energy of the probe beam 5 ekV. A magnification of obtained SEM pictures was from 100 to 1000 times.

3. Research results and discussion

The aim of this research was to develop stable water dispersions of various chemical compositions, intended for the biofunctionalization of textile materials. In our studies, dispersants from the group of synthetic acrylic and vinyl polymers, and a natural poly-saccharide polymer

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(soluble starch) were used. These compositions formed homogeneous and stable water dispersions containing microorganism growth inhibitors, out of a group of different hybrid modifiers:

- copper silicate $CuSiO_3 \cdot xH_2O$ (which is a synthetic version of minerals: *chrysicolla* and *dioptase*),
- titanium dioxide, zinc oxide, zinc silicate $ZnO \cdot SiO_2$ and zinc lactate
- or their mixtures.

Such compositions were used for antimicrobial biofunctionalization of textile materials, i.e. polyester (PES) and polylactide (PLA) nonwovens, as well as cotton, polyester and cotton-polyester fabrics.

In our research we used stable aqueous dispersions that contained 1-11 wt.% of copper silicate hydrate, most preferably in an amount of at least 5-7 wt.% titanium dioxide in the form of micronized powder (*TK44*) or in the form of the commercial acrylic-aquous dispersion containing 20-22 wt.% TiO_2 nanoparticles (*Cinkarna 100BS*) and emulsion paints containing the addition of titanium dioxide (*Talens Amsterdam* and *Dekoral Silver*) and acrylic (*Titanium IN*) or silicate (*Titanium FA*) water dispersions with photocatalytic properties.

As dispersants and pro-adhesion agents, above mentioned stable dispersions contained diluted aqueous solutions of poly(vinyl alcohol) (PVA) or soluble starch in the amount of 2.0-5.0% by weight. As a thickening agent in these stable dispersions, (hydroxy-ethyl)cellulose (with the addition of sodium acetate) was used in the amount of 0.5-2.0% by weight, most often 0.8-1.5 wt.%. As wetting agents, they contained liquid poly(ethylene glycol) (either *Polikol 400* or *Polikol 600*, or *Pluriol E600*) in the amount of 5-10% by weight, and as plasticizers - they contained bis(2-ethylhexyl) adipate (*Adoflex*) in the amount of 25-50% by weight or/and glycerin in the amount of 0.4-1.0 wt.% (most often 0.5 wt.%) - with respect to the amount of water dispersion of poly(vinyl acetate) (*Synexil DN-50*) used.

A hydroxyl terminated methyl silicone oil (*Polastosil M200*) was used as an anti-foaming agent in the dispersions, in the amount of 0.1-0.25% by weight, most often 0.1 wt.%.

3.1. An improvement of a surface wettability and hydrophilicity of textile materials

In order to improve the wettability of the surface, an enzymatic treatment of nonwovens and fabrics was carried out at the temperature of 30-35 °C, in an aquous solution containing 1-2 wt.% enzyme *Texazym PES* (from the group of esterases), at pH 4-4.5. A bath volume to textile weight (so called the *bath ratio*) was 10:1. Alkaline treatment of the tested PES nonwovens was carried out at room temperature by immersing them in the solution of 2-6 wt.% NaOH and Na_2CO_3 for 3-4 days, then the non-woven fabric was squeezed from the excess alkali solution, rinsed in water, squeezed again, dried and heated at 120-140 °C.

Whereas the alkaline treatment of fabrics was carried out at the temperature of 95-98 °C, for 60 minutes, in the bath containing sodium hydroxide at the concentration of 1.8 g/l, sodium carbonate at the concentration of 3.6 g/l and a sequestering and wetting agent. The ratio of bath volume to the textile weight used was also 10:1.

The effectiveness of the pretreatment of polyester textile carriers was evaluated by determining the contact angle and a surface free energy (SFE), using the goniometric method. As the result of the modification of the polyester fabric (PES) surface with the use of an enzyme from the group of esterases, *Texazym PES* (1-2 wt.%), the hydrophilicity of PES fibers was improved, resulting in a decrease in the contact angle (against water) from 112.6 for the initial PES fabric to 82.9 , 66.9 and 35.9 for the PES fabric after modification with the *Texazym PES* enzyme, used at concentrations of: 1.0, 1.5 and 2.0 wt.%, respectively. It was accompanied with an increase in the SFE from 50.9 mJ/m^2 for the original PES fabric to values of 51.9, 56.9 and 59.5 mJ/m^2, respectively. The results of these tests are given in the Table 2.

However, as the result of the alkaline treatment of the polyester fabric, the contact angle, measured with a water drop, decreased from 112.6 for the initial PES fabric to 103.2 , and the SFE increased from 50.9 mJ/m^2 for the initial PES fabric to 52.8 mJ/m^2 after alkalization.

The stable water dispersions described above were used for the biofunctionalization of polyester or biodegradable PLA nonwovens (with the surface mass of 100-350 g/m^2), using the dip-coating

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method for biofunctionalization of cotton, polyester and cotton-polyester fabrics with the surface mass of 100-170 g/m^2, which were initially subjected to the enzymatic or alkaline treatment. The initial surface modification improved the wettability and adhesive properties of hydrophobic polymer fabrics and nonwovens (PES and PLA).

3.2. Evaluation of the results of antimicrobial modification of the properties of nonwovens and fabrics, modified with aqueous dispersions containing copper silicate

The biological activity of the surface of biofunctionalized polymer nonwovens was analyzed in appropriate antibacterial tests against the following microorganisms: against colonies of gram-negative *Escherichia coli* (ATCC 11229) and gram-positive *Staphylococcus aureus* (ATCC 6538), and in antifungal tests against *Candida albicans* (ATCC 10321) - according to the PN-EN ISO 20743 standard. The results of the analysis of biological activity of selected samples of the functionalized polymer nonwovens are summarized in the Table 3.

Table 3. The antibacterial and antifungal properties of the selected PES and PLA nonwovens modified by dip-coating method with the dispersions containing copper silicate hydrate $CuSiO_3 \cdot xH_2O$ *, titanium dioxide and other components (% by weight) - according to the compositions given in the Table 1.

No.	Type of nonwoven fabric sample	*Escherichia coli* (ATCC 25922)	*Staphylococcus aureus* (ATCC 6538)	*Candida albicans* (ATCC 10231)
1.	PES WIFP-270 + 1.0% $CuSiO_3$	89.7	43.0	0.0
2.	PES FS G-4 + 1.0% $CuSiO_3$	97.4	16.8	0.0
3.	PES FS F-5 + 1.0% $CuSiO_3$	99.1	20.6	1.4
4.	PLA-350 + 1.0% CuSiO	> 99.4	28.0	0.0
5.	PES WIFP-270 + 2.0% $CuSiO_3$	99.6	59.1	26.8
6.	PES WIFP-270 + 3.0% $CuSiO_3$	99.8	66.9	27.8
7.	PES WIFP-270 + 5.0% $CuSiO_3$	> 99.8	87.6	30.6
8.	PES FS F-5 + 5.0% $CuSiO_3$	99.4	98.7	35.4
9.	PLA-350 + 5.0% $CuSiO_3$	> 99.8	97.0	30.8
10.	PES WIFP-270 + 7.0% $CuSiO_3$	> 99.98	94.4	37.6
11.	PES FS F-5 + 7.0% $CuSiO_3$	> 99.98	99.5	49.5
12.	PLA-350 + 7.0% $CuSiO_3$	> 99.98	> 99.9	38.6
13.	PES WIFP-270 + 6.9% $CuSiO_3$ + 1.0% TiO_2	> 99.97	92.2	48.5
14.	PES WIFP-270 + 7.0% $CuSiO_3$ + 2.1% TiO_2	> 99.97	99.7	58.8

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15.	PES WIFP-270 + 5.0% $CuSiO_3$ + 4.2% TiO_2	> 99.97	99.5	80.9
16.	PES WIFP-270 + 5.0% $CuSiO_3$ + 5.0% TiO_2	> 99.99	99.4	87.5
17.	PES FS F-5 + 5.0% $CuSiO_3$ + 5.0% TiO_2	99.06	98.1	93.9
18.	PES FS F-5 + 5.0% $CuSiO_3$ + 5.0% TiO_2 + 2% *Dekoral Silver*	95.63	94.6	92.7
19.	PES WIFP-270 + 5.0% $CuSiO_3$ + 5.0% TiO_2 + 2% *Dekoral Silver*	97.08	92.6	98.0
20.	PES WIFP-270 + 5.0% $CuSiO_3$ + 25% *Ti-IN*	> 99.87	97.7	89.2
21.	PES FS F-5 + 5.0% $CuSiO_3$ + 25% *Ti-IN*	> 99.97	94.8	95.0

* - copper silicate hydrate $CuSiO_3 \cdot xH_2O$ with 18.5 wt.% content of H_2O was used.

The polymeric PES and PLA nonwovens, modified on the surface with compositions containing the copper silicate hydrate, showed very good antibacterial properties against gram-negative bacteria *Escherichia coli*, already at the content of 1 wt.% $CuSiO_3 \cdot xH_2O$ in the aqueous dispersions, and against gram-positive bacteria *Staphylococcus aureus* - from the content of at least 5 wt.% of $CuSiO_3 \cdot xH_2O$ in the aqueous dispersions. The bacterial growth reduction factor (R) was greater than 99% for most of the samples tested.

Very good antifungal properties against the fungus *Candida albicans* were found for the PES and PLA nonwoven fabrics modified with the dispersions containing 5-7 wt.% $CuSiO_3 \cdot xH_2O$ and 4.2-5.0 wt.% TiO_2. The addition of TiO_2 caused a significant and improvement in the anti-fungal properties of PES and PLA nonwovens modified in this way. For the samples of PES *WIFP-270* and *FS F-5* nonwovens modified with the water dispersions containing 5.0 wt.% $CuSiO_3 \cdot xH_2O$ and 4.2-5.0 wt.% TiO_2 (and alternatively having also the addition of other commercial dispersions containing TiO_2) the growth reduction factor of the fungus *Candida albicans* (R) reached values in the range of 80.9-98.0% (see the Table 3).

3.2.1. The scanning electron microscopy (SEM) of non-woven samples

The scanning electron microscopy (SEM) provides imaging of surfaces or cross sections of various types of materials, enabling their testing and analysis. In Figures 1-8 are presented the SEM pictures of the starting polymeric non-woven fabrics, used in our studies, and obtained biofunctionalized non-woven samples - after dip-coating and drying processes. On these pictures it can be seen that microparticles of coating compositions very well adhere to surfaces of the fibers, which form the network of PES nonwovens.

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(a) (b)

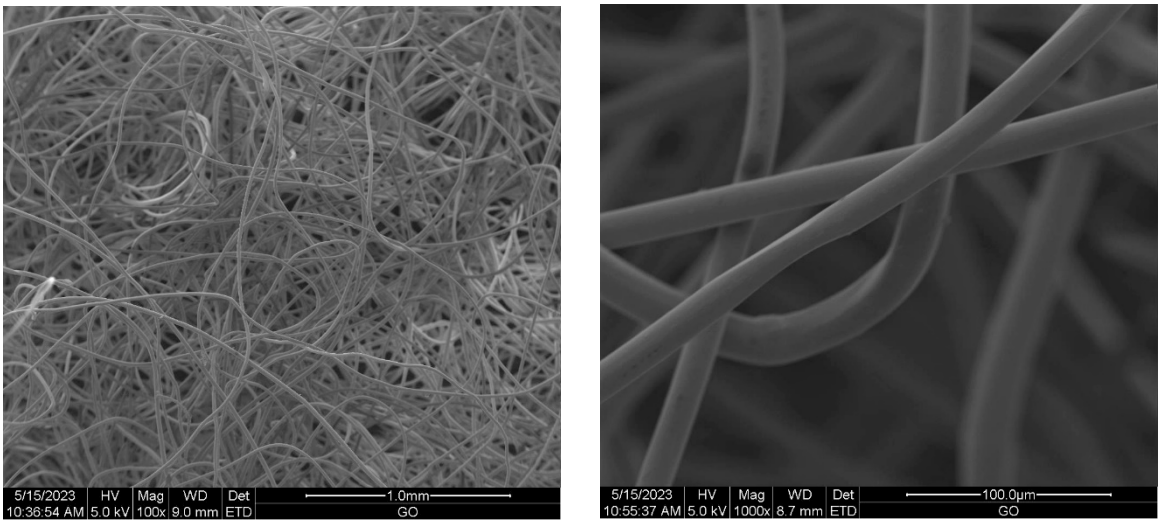

Figure 1. The SEM images of unmodified PES non-woven *WIFP-270*; magnification: x100 (a) and x1000 (b).

(a) (b)

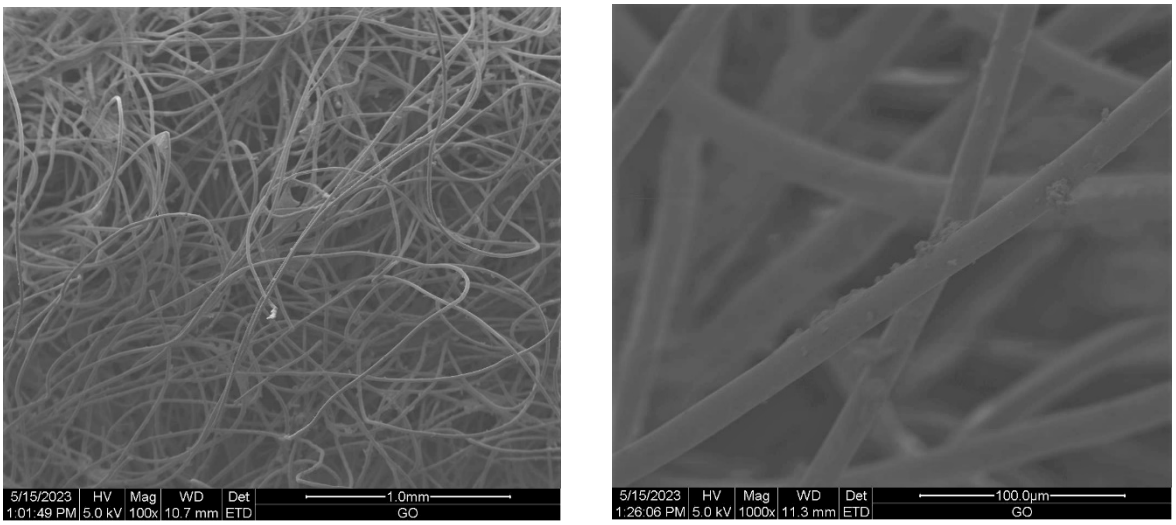

Figure 2. The SEM images of PES non-woven *WIFP-270* (from exp. No. 20 in Tab.1 and No. 16. in Tab. 2), modified with 5.0 wt.% $CuSiO_3$ and 5.0 wt.% TiO_2; magnification: x100 (a) and x1000 (b).

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(a) (b)

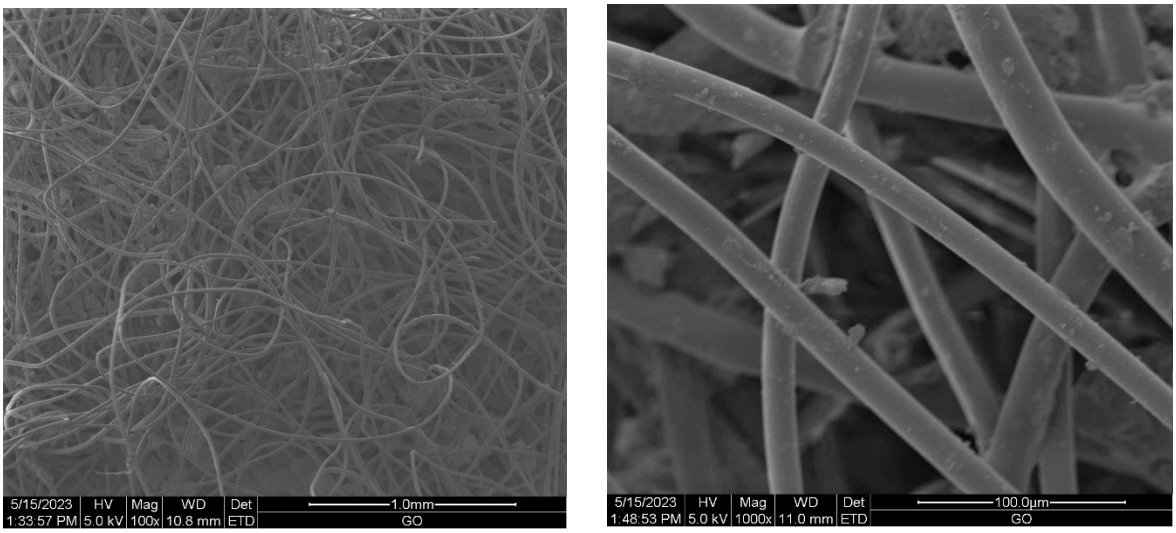

Figure 3. The SEM images of PES non-woven *WIFP-270* (from exp. No. 21 in Tab.1 and No. 19. in Tab.2), modified with 5.0 wt.% $CuSiO_3$ + 5.0 wt.% TiO_2 + 2 wt.% *Dekoral Silver*; magnification: x100 (a) and x400 (b).

(a) (b)

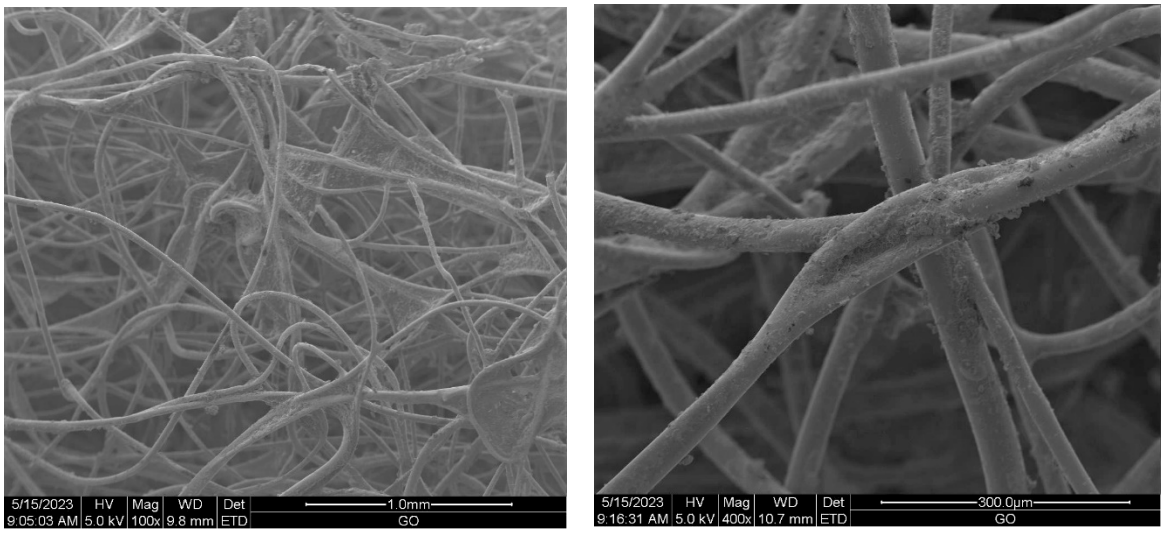

Figure 4. The SEM images of PES non-woven *WIFP-270* (from exp. No. 23 in Tab.1 and No. 20 in Tab. 2), modified with 5.0 wt.% $CuSiO_3$ and 25.0 wt.% *Titanium IN;* magnification: x100 (a) and x400 (b).

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(a) (b)

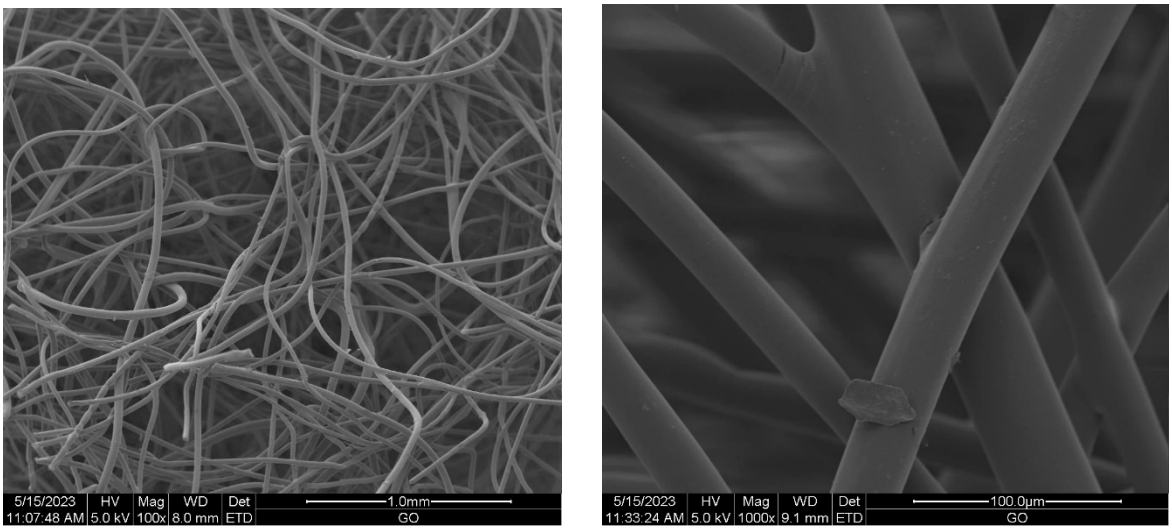

Figure 5. SEM images of unmodified PES non-woven *FS F-5*; magnification: x100 (a) and x1000 (b).

(a) (b)

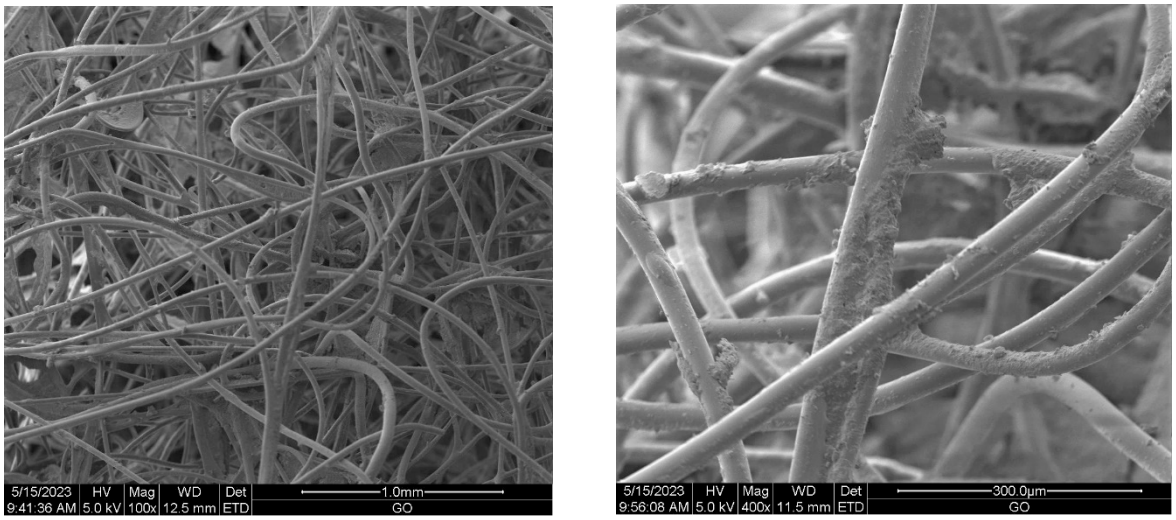

Figure 6. The SEM images of PES non-woven *FS F-5* (from exp. No. 20 in Tab.1 and No. 17. in Tab. 2), modified with 5.0 wt.% $CuSiO_3$ and 5.0 wt.% TiO_2; magnification: x100 (a) and x400 (b).

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(a) (b)

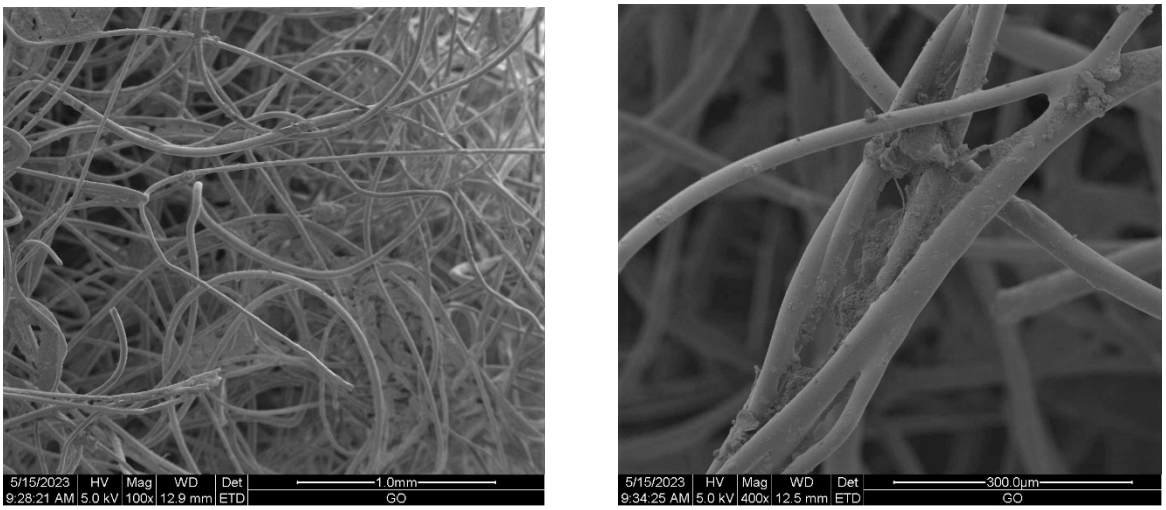

Figure 7. The SEM images of PES non-woven *FS F-5* (from exp. No. 21 in Tab.1 and No. 18 in Tab. 2), modified with 5.0 wt.% $CuSiO_3$ + 5.0 wt.% TiO_2 + 2 wt.% *Dekoral Silver;* magnification: x100 (a) and x400 (b).

(a) (b)

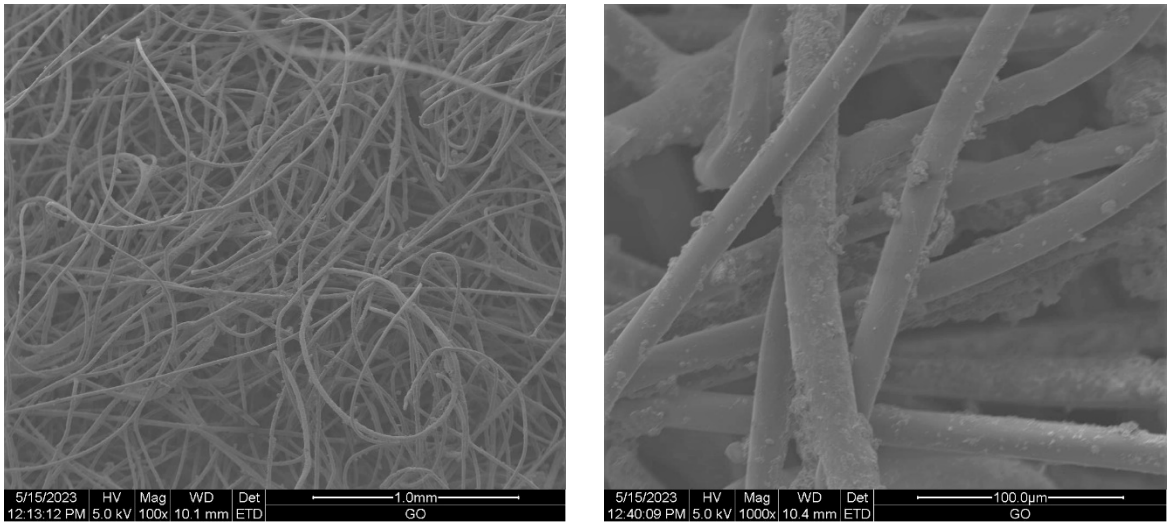

Figure 8. The SEM images of PES non-woven *FS F-5* (from exp. No. 23 in Tab.1 and No. 21 in Tab.2),. modified with 5.0 wt.% $CuSiO_3$ and 5.0 wt.% *Titanium IN;* magnification: x100 (a) and x1000 (b).

3.3. Evaluation of the results of the antimicrobial modification of the properties of fabrics (and nonwovens) with copper silicate and composite hybrid oxide $ZnO{\cdot}SiO_2$ by the dip-coating and coating methods

The results of the conducted research on the antimicrobial modification of fabrics and one PES nonwoven fabric are presented only in the form of a following summary. The surfaces of these textile materials were first by treatment with 2.0 wt.% of *Texazym PES*, before biofunctionalization process – as it has been described in a subchapter 3.1.

This part of our studies has shown that:

1. the cotton fabric *Medical*, polyester fabric, the cotton-polyester fabric *Figaro*, and also polyester non-woven fabric *Hydronina*, biofunctionalized by the dip-coating method with the dispersions containing 6.0 wt.% $CuSiO_3 \cdot xH_2O$ (or the composite hybrid oxide $ZnO \cdot SiO_2$) exhibited:

(a) against the gram-negative bacteria *Escherichia coli*

- strong antibacterial properties (an antibacterial activity coefficient A reached the values in a range: 3.1-6.2 for the samples modified with $CuSiO_3 \cdot xH_2O$ and 3.7-6.0 - for the samples modified with $ZnO \cdot SiO_2$),
- strong and significant bacteriostatic properties (a bacteriostatic coefficient S reached the values in the range: 3.0-6.7 - for the samples modified with $CuSiO_3 \cdot xH_2O$ and 2.1-6.6 - for the samples modified with $ZnO \cdot SiO_2$),
- good bactericidal properties (a bacterial growth reduction factor R was: 77.5-96.8% - for the samples modified with $CuSiO_3 \cdot xH_2O$, and 72.3-97.0% - for the samples modified with $ZnO \cdot SiO_2$);

(b) against gram-positive bacteria *Staphylococcus aureus*

- strong or significant antibacterial properties (the antibacterial activity coefficient A reached the values in the range: 2.5-6.2 for the samples modified with CuSiO3·xH2O and 2.8-4.8 - for the samples modified with ZnO·SiO2),
- strong and significant bacteriostatic properties (the bacteriostatic coefficient S reached the values in the range: 2.6-6.5 for samples modified with CuSiO3·xH2O, and 3.0-5.2 - for the samples modified with ZnO·SiO2)
- and good and significant bactericidal properties (the bacterial growth reduction factor R was: 89.6-99.0% - for the samples modified with CuSiO3·xH2O, and 70.8% - for the sample modified with ZnO·SiO2).

2. For all samples of the PES fabric and PES nonwoven Hydronina, modified by coating method with the paste containing approx. 10 wt.% CuSiO3·xH2O, the growth reduction factor of Candida albicans R reached the values in the range: 97.9-99.6%, the antibacterial activity coefficient A was in the range: 4.8-5.6, the bacteriostatic coefficient S had the same value 4.8-5.6, and the bactericidal coefficient L was in the range: 1.6-2.4.
3. The obtained composite-polymer textile materials also showed a good inhibitory effect on the development of the mold fungus Chaetomium globosum. The samples of the textile materials coated with CuSiO3 hydrate, and especially the polyester fabric subjected to biomodification with 7.0 wt.% CuSiO3·xH2O, showed a clear effect of antifungal activity against the fungus Chaetomium globosum, which grew on the surface of the samples only in the range of 0-25%.
4. The new biofunctionalized textile materials obtained by coating method (mainly cotton, cotton-polyester and polyester fabrics) with pastes containing: (a) CuSiO3 or (b) CuSiO3 + ZnO, or (c) CuSiO3 + TiO2 particles introduced onto the surface and incortporated into their structures also showed good barrier properties against UV radiation (UPF > 50), and the lowest transmittance (T average was 2.5-3.5), which was characteristic for the textile products subjected to the initial alkaline or biochemical (enzymatic) modifications, followed by the biofunctionalization with mixtures containing a total of 10 wt.% of CuSiO3·xH2O and TiO2 (or ZnO) in a weight ratio of 7:3 or 1:1.

The results of the microbiological tests of the PES fabrics and PES nonwoven *Hydronina*, modified by the coating method with pastes containing approx. 10 wt.% $CuSiO_3 \cdot xH_2O$ are listed in the Table 4.

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Table 4. The results of microbiological activity tests of PES fabric and nonwoven samples modified by the coating method with a paste containing about 10 wt.% $CuSiO_3 \cdot xH_2O$ containing PEG 600 and the thickener agent *Lutexal HC*.

Sample No.	Sample type	$CuSiO_3 \cdot xH_2O$	PEG 600	*Revacryl 247*	*Lutexal HC*	Microbiological activity against the fungus *Candida albicans* (ATCC 10321)			
		[wt.%]				**A**	**S**	**L**	**R** [%]
1	PES nonwoven fabric (*Hydronina*)	10.36	5.18	10.36	1.67	**5.6**	**5.6**	**2.4**	**99.6**
2	PES fabric (untreated)	10.36	5.18	10.36	1.67	**5.1**	**5.0**	**1.8**	**98.7**
3	PES fabric alkalized	10.36	5.18	10.36	1.67	**4.8**	**4.8**	**1.6**	**97.9**
4	PES fabric + *Texazym* (1.5 wt.%)	10.21	5.11	10.21	1.72	**5.5**	**5.4**	**2.2**	**99.5**

Signs: **A** – an antibacterial activity coefficient, **S** – a bacteriostatic coefficient, **L** – a bactericidal coefficient.

Evaluation criteria according to EN ISO 20743 (2013)

Evaluation of antimicrobial activity	Reduction of microbial growth, **A** value
Lack	**A** < 0,5
Weak	0,5 ≤ **A** < 2
Significant	2 ≤ **A** < 3
Strong	**A** ≥ 3

4. Conclusions

The PES and PLA polymer nonwovens, modified on the surface with stable water compositions containing copper silicate hydrate, showed very good antibacterial properties against the gram-negative bacteria *Escherichia coli*, already at the content of 1 wt.% $CuSiO_3 \cdot xH_2O$ in the aqueous dispersions, and against the gram-positive bacteria *Staphylococcus aureus* - at the content of at least 5 wt.% $CuSiO_3 \cdot xH_2O$ in the aqueous dispersions. The bacterial growth reduction factor (R) was greater than 99% for most of the samples tested.

Moreover, good antifungal properties against the fungus *Candida albicans* were found for the PES and PLA nonwoven fabrics, modified with dispersions containing 5-7 wt.% $CuSiO_3 \cdot xH_2O$ and 4.2-5.0 wt.% TiO_2. The addition of TiO_2 caused the significant improvement in the anti-fungal properties of the PES and PLA nonwovens modified in this way. For the samples of PES *WIFP-270* and *FS F-5* nonwovens modified with the water dispersions containing 5.0 wt.% $CuSiO_3 \cdot xH_2O$ and 4.2-5.0 wt.% TiO_2 (and possibly with the addition of other dispersions containing TiO_2) the growth reduction factor of the fungus *Candida albicans* (R) reached the values in the range of 80.9-98.0% (see the Table 3).

The polymer nonwovens biofunctionalized with the water dispersions containing $CuSiO_3$ hydrate and TiO_2 can be used in the production of the filters for hospital air conditioning systems and for the automotive industry, as well as in air purification devices. On the other hand, fabrics modified antimicrobially in a similar way by the dip-coating or coating methods (or with dispersions containing ZnO or zinc silicate $ZnO \cdot SiO_2$) can be applied, for example, for the manufacture of garden furniture.

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