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(54) A METHOD FOR BIOFUNCTIONALIZATION OF TEXTILE MATERIALS

VERFAHREN ZUR BIOFUNKTIONALISIERUNG VON TEXTILMATERIALIEN

PROCÉDÉ POUR BIOFONCTIONNALISATION DE MATÉRIAUX TEXTILES

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Description

[0001] The present invention relates to a method for biofunctionalization of textile materials which leads to obtaining antibacterial and antifungal properties.

[0002] Giving the textile materials antibacterial and antifungal properties proves very important in case of their special uses, particularly in the manufacturing of sanitary materials and protective clothing components.

[0003] It has been known for quite some time that copper oxide possesses antibacterial, antiviral and antifungal properties [e.g. G. Borkow, J. Gabbay, FASEB J., vol. 18, 1728-1737 (2004); Antimicrobial Agents and Chemotherapy, vol. 51, 2605-2607 (2007); International Journal of Antimicrobial Agents, vol. 33, 587-590 (2009); Formatex, 197-209 (2011); The Open Biology Journal, vol. 6, 1-7 (2013); International Journal of Pharmaceutical Research and Developments, vol. 6, 72-78 (2014)]. Although relative to most microorganisms, small concentrations of copper are sufficient, typically, higher doses are used to inhibit the growth of certain microorganisms and obtain bactericidal activity [New Journal of Chemistry, vol. 35, 1198 (2011)]. Permanent biocidal properties of textiles containing 3-10% of copper were described by Gabbay, Borkow et al. [Journal of Industrial Textiles, vol. 35 (2006) 323-335].

[0004] The publication by C.C. Trapalis et al. [Journal of Sol-Gel Science and Technology, vol. 26, 1213-1218 (2003)] describes a method for obtaining thin composite silicate coatings containing copper (Cu / SiO₂) on glass plates. By means of the sol-gel method, as a result of hydrolysis using stoichiometric amount of water, and subsequent condensation of tetraethoxysilane Si(OC₂H₅)₄ with acetylacetonate copper Cu(acac)₂ in acidic environment (pH = 3) a homogeneous solution of a green color was obtained, which was heated at 70 °C for 2 hours, then cooled to room temperature and applied by immersion onto microscopic glass plates. The thin layers of copper silicate were heated under oxidizing and reducing atmospheres at the temperature up to 500 °C in order to form Cu nanoparticles. The structure of the coatings was examined by X-ray diffraction (XRD) method and by UV-Vis spectroscopy and HIRBS. The obtained coatings showed high antibacterial activity against *Escherichia coli* strains which was increasing together with the increase of metal concentration, and decreasing with the increase of heat treatment temperature during the process of forming Cu nanoparticles. However, the most effective antimicrobial properties were exhibited by the coatings which were not thermally treated under an oxidizing or reducing atmosphere.

[0005] The Journal of Physical Chemistry B, vol. 110, 24923-24928 (2006) describes a deposition of copper on the surface of spherical silica nanoparticles in order to obtain a hybrid structure of Cu-SiO₂ nanocomposite.

[0006] SiO₂ nanoparticles served as a substrate for the continuous deposition of copper. The chemical structure and morphology of the nanocomposite was examined by the X-ray photoelectron spectroscopy (XPS) method, scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM-EDX) and transmission electron microscopy (TEM). The copper nanoparticles homogeneously formed on the surface of SiO₂ nanoparticles did not undergo aggregation and exhibited excellent antibacterial activity with respect to multiple microorganisms.

[0007] Mesoporous copper-doped silica xerogels of a large specific surface area (463 m²/g) and a pore size of 2 nm, exhibiting antibacterial properties depending on the concentration of copper were also obtained in the sol-gel process [Biomedical Materials, vol. 4, 045008 (2009)].

[0008] Ren et al. [International Journal of Antimicrobial Agents, vol. 33 (2009) 587-590] found that the minimum bactericidal concentration of nanoparticles CuO in relation to bacteria *Pseudomonas aeruginosa* is approx. 5000 µg/ml. At the same time, they suggested that releasing of copper ions into the local environment was necessary for preserving microbial activity.

[0009] However, by applying the atomic absorption spectroscopy method (AAS) it was revealed that there was no simple correlation between the amount of copper released from the polymer matrix, and inhibition of bacterial growth. Most likely, this effect was caused by other factors, such as, for example smoothness of the surface. Another reason could be the release of organic polymer compounds.

[0010] It was demonstrated that the highest activity against bacteria was exhibited by CuO nanoparticles with dimensions of 1-10 nm [Nanotechnology, vol. 16 (2005) 2346-2353, Dyes and Pigments, vol. 73 (2007) 298-304].

[0011] Nanosilica which was modified on the surface with copper particles was used to remove the odor of mercaptans and sulfur compounds from petroleum. According to the publication in Langmuir, vol. 26, 15837-15844 (2010), silica modified by the addition of copper also exhibited antibacterial properties.

[0012] In the copper silicate CuO - SiO₂ antibacterial and antifungal properties of the copper oxide as well as virucidal activity are connected to biocompatibility, non-toxicity and a variety of silica surfaces.

[0013] Copper silicate is used in medicine and biology, for instance, in controlled release of drugs and thermal treatment of tumors. An additional advantage of copper silicate CuO - SiO₂ is the possibility to modify its surface and properties using hydrophobic substances, simple chemical processes and organofunctional compounds [Bioelectrochemistry, vol. 87, 50-57 (2012)]. The publication in the Nanoscale Research Letters journal, vol. 6, 594-602 (2011) reveals that cotton textiles impregnated with silica sol containing 0.5 - 2 % by weight of copper nanoparticles, having dried exhibited excellent antibacterial properties against both gram-negative and gram-positive bacteria. In order to block hydroxyl groups of silica, some samples were subjected to modification in reaction with hexadecyl(trimethoxy)silane. According to an article

in the Journal of Biomedical Nanotechnology, vol. 8, 558-566 (2012), SiO₂ core-shell structured nanoparticles containing approx. 0.1 of added μg Cu (in the form of insoluble copper hydroxide) possessed significantly better antibacterial properties against bacteria *Escherichia coli* and *Bacillus subtilis* than that observed for the Cu(OH)₂ alone.

[0014] In the case of core-shell structured CuSiO₃ the minimum concentration inhibiting the growth of these bacteria was 2.4 μg Cu/mL. However, from the publication in the Journal of Agricultural and Food Chemistry (2014; dx.doi.org/10.1021/jf502350w) it is known that silica nanocomposites with copper compounds of different valencies, especially enhanced by adding the compounds Cu (0) and Cu (I), exhibited a higher antibacterial efficacy than the compounds Cu (II) against *Xanthomonas alfalfae* and *Escherichia coli* bacteria.

[0015] Phytotoxicity studies performed (in *Vinca* sp. and Hamlin orange) under greenhouse conditions showed that these nanocomposites are safe for plants and can be used as biocides in agriculture.

The AMB Express magazine, vol. 3, 53 (2013) publishes an article describing very good antimicrobial properties of nanocomposites Cu-SiO₂, obtained in the form of thin layers using the CVD method, against multiple hospital pathogens (*Acinetobacter baumannii*, *Klebsiella pneumoniae*, *Stenotrophomonas maltophilia*, *Enterococcus faecium*, *Staphylococcus aureus* and *Pseudomonas aeruginosa*). The SEM method confirmed the nanostructure of Cu particles in the silica matrix. The tested shells of nanocomposites Cu-SiO₂ can also be used for microbial protection of metal and ceramic surfaces.

[0016] From an article in the Digest Journal of Nanomaterials and Biostructures, vol. 8, 869-876 (2013) it is known that copper alginates and zinc alginates and their silica composites exhibit stronger antimicrobial activity than regular Cu and Zn saline solutions against *Enterococcus faecalis* strains, despite the fact that they were used in a lower concentration. In addition, these hybrid materials showed to be biocompatible and did not cause cytotoxic effects against eukaryotic cells. They can therefore be useful in the gradual drug release and tissue engineering while preserving a high microbial activity over a long period of time. The information published in the journal Colloids and Surfaces B: Biointerfaces, vol. 108, 358-365 (2013), shows that copper nanoparticles deposited on the surface of sodium montmorillonite (MMT) or intercalated inside its layered structure exhibited high stability in air (more than 3 months) and an excellent microbiological activity against a multiple bacterial colonies: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Enterococcus faecalis*, causing loss of > 90 % of bacteria after 12 h.

[0017] Cytotoxicity tests revealed minimal adverse effect of this nanocomposite on human cells when the minimum concentration inhibiting the growth of micro-organisms (MBC) was too high. In spite of that, the prospects of employing nanocomposite MMT-Cu for therapeutic purposes is promising.

[0018] The Journal of Materials Science, vol. 41, 5208-5212 (2006) describes strong antibacterial properties of monodisperse copper nanoparticles of 2 - 5 nm deposited on magnesium silicate [Mg₈Si₁₂O₃₀(OH)₄·(H₂O)₄·8H₂O] (sepiolite) against *Staphylococcus aureus* and *Escherichia coli* bacteria. Their effectiveness proved to be comparable with biological activity of triclosan. From the information published in the Journal of Materials Chemistry B, vol. 2, 846-858 (2014) it is known that Cu²⁺ ions incorporated into the structure of layers of calcium silicate CaSiO₃, deposited by electrophoresis on the surface of titanium, are released gradually from such a coating and exhibit good antibacterial activity against strains of *Escherichia coli*, *Staphylococcus aureus*, while showing higher corrosion resistance against pure titanium. However, CaSiO₃ does not have antibacterial properties on its own. According to the article published in the journal Biochimica et Biophysica Acta, vol. 1840, 3264-3276 (2014) strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* is exhibited by both spherical copper nanocomposites and silver with mullite (3Al₂O₃·2SiO₂). However, the microbial activity of copper nanocomposite with mullite was higher than that of silver nanocomposite with mullite, which was likely due to smaller particle size of the latter. Both nanocomposites exhibited good cytocompatibility at a concentration of 1 mg/ml (MBC) and showed therapeutic properties in the treatment of wounds in mice.

[0019] The invention relates to a method for biofunctionalization of textile materials using copper silicate in the hydrate form, which is premixed with the polymer component, a plasticizer and an antioxidant, then the whole is heated until the polymer melts, and then the molten composition is subjected to pneumothermal extrusion and blowing the molten polymer in a stream of hot air. Copper silicate hydrate is used in an amount of 0.1 - 4 % by weight.

According to the invention, polymers selected from the group consisting of polypropylene (PP) and its copolymers, polylactide (PLA), polyhydroxyalkanoate (PHA), polyethylene (PE) and / or mixtures thereof are used as polymer components. Alternatively, a concentrate is used which comprises 1 - 25 % by weight of copper silicate hydrate with a selected polymer and mixed with the same or another polymer and the remaining ingredients in such weight proportions that the content of copper silicate hydrate in the manufactured fabric is 0.1 - 4 % by weight.

[0020] Plasticizers used are compounds having a liquid consistency selected from the group comprising: oligomers of ethylene glycol or propylene glycol, copolymers of ethylene glycol and propylene glycol, monoalkyl ethers of ethylene glycol oligomers, glycerin esters, citric acid esters or tartaric acid esters, pentaerythritol esters, dialkyl diesters of phthalic acid, paraffin oil, epoxy resin, hydroxyalkyl or hydroxy ether derivatives of polysiloxanes, oligoesters of silicic acid, oligo(dimethylsiloxanediol), polycarbonate diol, polycaprolactone, or polycaprolactone diol. Plasticizers are used in an amount of 1.5 - 15 % by weight in relation to the mass of polymer or the mass of polymer mixture, preferably 2.5 - 5 % by weight. In order to improve processing conditions (increase of thermal resistance of the polymer mass) an addition

of an antioxidant: 2,2'-Methylenebis(6-tert-butyl-4-methylphenol) (MBMTBP) or 2,2'-Methylenebis(6-tert-butyl-4-ethylphenol) (MBETBP) to the component system was applied. The antioxidants are used in the amount of 0.05 - 0.5 % by weight with respect to the mass of the polymer or the mass of polymer mixture, preferably 0.15 - 0.30 % by weight.

[0021] The invention is illustrated by the following examples without limitation thereto.

Example 1 (sample 5 in Table 1).

[0022] 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polypropylene granulate HL 512 FB (PP), followed by 2 % by weight of powdered anhydrous copper silicate.

[0023] The equipment for manufacturing bioactive textile material comprises: screw extruder, a melt-blowing head, compressed air heater and the receiving device in the form of a moving drum. PP processing parameters were as follows:

- Temperature of the extruder in zone 1: 240 °C,
- Temperature of the extruder in zone 2: 280 °C,
- Temperature of the extruder in zone 3: 285 °C,
- Head temperature: 240 °C,
- Air heater temperature: 260 - 280 °C,
- Screw rotation speed: 50 rpm,
- Polymer yield: 3.4 g/min,
- Air flow rate: 8.8 m³/h

[0024] After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polypropylene non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 2 (sample 2 in Table 1).

[0025] 25.0 g of polypropylene granulate grafted with maleic anhydride (PP-g-MA) and 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 75.0 g of polypropylene granulate HL 512 FB (PP) followed by 1 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0026] PP processing parameters were as follows:

- Temperature of the extruder in zone 1: 240 °C,
- Temperature of the extruder in zone 2: 280 °C,
- Temperature of the extruder in zone 3: 285 °C,
- Head temperature: 240 °C,
- Air heater temperature: 260 - 280 °C,
- Screw rotation speed: 50 rpm,
- Polymer yield: 3.4 g/min,
- Air flow rate: 8.8 m³/h

[0027] After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polypropylene non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 3 (sample 3 in Table 1).

[0028] 10.0 g of polypropylene concentrate containing 10 % by weight of powdered copper silicate hydrate (k-PP) and 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 90.0 g of polypropylene granulate HL 512 FB (PP).

[0029] PP processing parameters were as follows:

- Temperature of the extruder in zone 1: 240 °C,
- Temperature of the extruder in zone 2: 280 °C,
- Temperature of the extruder in zone 3: 285 °C,
- Head temperature: 240 °C,
- Air heater temperature: 260 - 280 °C,
- Screw rotation speed: 50 rpm,
- Polymer yield: 3.4 g/min,
- Air flow rate: 8.8 m³/h

[0030] After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polypropylene non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 4 (sample 10 in Table 1).

[0031] 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 1 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0032] PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 50 rpm,
- Polymer yield: 5.4 g/min,
- Air flow rate: 6.7 m³/h

[0033] After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polylactide non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 5 (sample 13 in Table 1).

[0034] 5.0 g of polycaprolactone diol PCL Capa[™] 2054 (Perstorp) with an average molecular weight of 550 g/mol (PCL-diol) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 1 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0035] PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 40 rpm,
- Polymer yield: 5.0 g/min,
- Air flow rate: 6.8 m³/h

[0036] After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polylactide non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity

tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 6 (sample 25 in Table 2).

[0037] 2.5 g of polycarbonate diol Desmophen C XP 2716 with an average molecular weight of 650 g/mol were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 0.5 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0038] PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 72 rpm,
- Polymer yield: 6.8 g/min,
- Air flow rate: 4.7 m³/h

[0039] After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polylactide non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 7 (sample 24 in Table 1).

[0040] 2.5 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 0.5 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0041] PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 72 rpm,
- Polymer yield: 6.8 g/min,
- Air flow rate: 5.0 m³/h

[0042] After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polylactide non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 8 (sample 26 in Table 1).

[0043] 1.5 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 0.5 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0044] PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,

- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 60 rpm,
- Polymer yield: 5.9 g/min,
- Air flow rate: 6.1 m³/h

[0045] After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polylactide non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 9 (sample 20 in Table 1).

[0046] 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 0.1 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0047] PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 72 rpm,
- Polymer yield: 6.8 g/min,
- Air flow rate: 4.0 m³/h

[0048] After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polylactide non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 10 (sample 7 in Table 1)

[0049] 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polypropylene granulate HL512 FB, followed by 4 % by weight of powdered copper silicate hydrate having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O.

[0050] PP processing parameters were as follows:

- Temperature of the extruder in zone 1: 240 °C,
- Temperature of the extruder in zone 2: 280 °C,
- Temperature of the extruder in zone 3: 285 °C,
- Head temperature: 240 °C,
- Air heater temperature: 260 - 280 °C,
- Screw rotation speed: 59.2 rpm,
- Polymer yield: 3.6 g/min,
- Air flow rate: 8.5 m³/h

[0051] After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, the process of extrusion of the composite polypropylene non-woven fabric was initiated using the melt-blown method. The resulting non-woven fabric was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus*

aureus), and the *Candida albicans* fungus.

Example 11 (sample 40 in Table 3).

5 **[0052]** 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polypropylene granulate HL512 FB (PP), followed by 1 % by weight of powdered copper silicate hydrate (having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O) as well as 0.15% by weight 2,2'-methylenebis (6-tert-butyl-4-methylphenol) (MBMTBP).

10 **[0053]** PP processing parameters were as follows:

- Temperature of the extruder in zone 1: 240 °C,
- Temperature of the extruder in zone 2: 280 °C,
- Temperature of the extruder in zone 3: 285 °C,
- 15 - Head temperature: 240 °C,
- Air heater temperature: 260 - 280 °C,
- Screw rotation speed: 50.0 rpm,
- Polymer yield: 3.4 g/min,
- Air flow rate: 8.8 m³/h

20 **[0054]** After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, in the process of extrusion using the melt-blown method a composite polypropylene non-woven fabric was obtained and it was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

25 Example 12 (sample 41 in Table 3).

30 **[0055]** 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 1 % by weight of powdered copper silicate hydrate (having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O) as well as 0.20 % by weight 2,2'-methylenebis (6-tert-butyl-4-methylphenol) (MBMTBP).

[0056] PLA processing parameters were as follows:

- 35 - Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- 40 - Screw rotation speed: 72.0 rpm,
- Polymer yield: 6.8 g/min,
- Air flow rate: 4.0 m³/h

45 **[0057]** After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, in the process of extrusion using the melt-blown method a composite polylactide non-woven fabric was obtained and it was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*staphylococcus aureus*), and the *Candida albicans* fungus.

Example 13 (sample 42 in Table 3).

50 **[0058]** 5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polypropylene granulate HL512 FB, followed by 1 % by weight of powdered copper silicate hydrate (having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O) as well as 0.25 % by weight 2,2'-methylenebis (6-tert-butyl-4-ethylphenol) (MBETBP).

55 **[0059]** PP processing parameters were as follows:

- Temperature of the extruder in zone 1: 240 °C,

- Temperature of the extruder in zone 2: 280 °C,
- Temperature of the extruder in zone 3: 285 °C,
- Head temperature: 240 °C,
- Air heater temperature: 260 - 280 °C,
- Screw rotation speed: 50.0 rpm,
- Polymer yield: 3.4 g/min,
- Air flow rate: 8.8 m³/h

After setting the above parameters specified for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, in the process of extrusion using the melt-blown method a composite polypropylene non-woven fabric was obtained and it was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

Example 14 (sample 43 in Table 3).

5.0 g of ethylene glycol oligomer with an average molecular weight of 600 g/mol (Polikol 600 - PEG) were added to 100.0 g of polylactide granulate (PLA) Ingeo 32510, followed by 1 % by weight of powdered copper silicate hydrate (having the following chemical composition: 35.23 % by weight CuO, 62.16 % by weight SiO₂, 18.52 % by weight H₂O, 0.02 % by weight Na₂O and 0.01 % by weight K₂O) as well as 0.30 % by weight 2,2'-methylenebis (6-tert-butyl-4-ethylphenol) (MBETBP).

PLA processing parameters were as follows:

- Temperature of the extruder in zone 1: 195 °C,
- Temperature of the extruder in zone 2: 245 °C,
- Temperature of the extruder in zone 3: 260 °C,
- Head temperature: 260 °C,
- Air heater temperature: 270 - 290 °C,
- Screw rotation speed: 72.0 rpm,
- Polymer yield: 6.8 g/min,
- Air flow rate: 4.0 m³/h

After setting the above parameters specified for PLA processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then, in the process of extrusion using the melt-blown method a composite polylactide non-woven fabric was obtained and it was subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherichia coli*), Gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus.

The test results presented in Table 1 and Table 3 point to bactericidal and fungicidal properties of composite non-woven fabrics modified with copper silicate hydrate.

Table 1.

Chemical compositions of composite non-woven fabrics (with PP or PLA) containing Polikol 600-PEG (or PCL-diol or other plasticizers), and hydrous copper silicate CuSiO ₃ ·xH ₂ O and the results of their microbiological tests						
Sample No.	Polymer	PEG (PCL-diol *)	CuSiO ₃ ·xH ₂ O	R [%] (L) <i>Escherichia coli</i> (ATCC 25922)	R [%] (L) <i>Staphylococcus aureus</i> (ATCC 6538)	R [%] (L) <i>Candida albicans</i> (ATCC 10321)
		[phr]	[phr]			
1	PP/PLA ^a	5	2	98.90 (1.9)	97.39 (1.6)	99.68 (2.3)
2	PP/PP-g-MA ^b	5	1	74.12 (0.5)	82.53 (0.8)	98.06 (1.7)
3	PP/k-PP ^c	5	1	74.93 (0.5)	82.38 (0.8)	97.92 (1.7)
4	PP	5	1	73.76 (0.5)	82.24 (0.8)	97.80 (1.7)
5	PP	5	2 ^{**}	98.70 (1.9)	97.16 (1.6)	99.54 (2.3)

(continued)

Chemical compositions of composite non-woven fabrics (with PP or PLA) containing Polikol 600-PEG (or PCL-diol or other plasticizers), and hydrous copper silicate $\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$ and the results of their microbiological tests

Sample No.	Polymer	PEG (PCL-diol *)	$\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$	R [%] (L) <i>Escherichia coli</i> (ATCC 25922)	R [%] (L) <i>Staphylococcus aureus</i> (ATCC 6538)	R [%] (L) <i>Candida albicans</i> (ATCC 10321)
6 and 15	PP PP	5 5	3 3	>99.94 (>3.2) >99.70 (>3.4)	98.20 (1.7)	80.40 (0.7)
7	PP	5	4	>99.94 (>3.2)	99.98 (3.7)	99.82 (2.7)
8	PP/PE ^d	15 ^e	1	>99.92 (>3.2)	99.94 (3.6)	99.80 (2.6)
9	PHA ^f	5	1	>99.97 (>3.7)	99.8 (2.6)	>99.79 (1.2)
10	PLA	5	1	>99.94 (>3.2)	99.97 (3.6)	>99.74 (1.1)
11	PLA	5	2	>99.94 (>3.2)	99.98 (3.9)	>99.74 (1.1)
13	PLA	(5)*	1	>99.96 (>3.4)	99.6 (2.4)	84.7 (0.8)
16	PLA	5	0.50	>99.96 (>3.4)	93.0 (1.2)	51.0 (0.3)
17	PLA	(5)*	0.50	>99.98 (>3.7)	99.8 (2.6)	84.4 (0.8)
18	PLA	5	0.25	>99.98 (>3.7)	99.2 (2.6)	47 (0.3)
20	PLA	5	0.10	>99.98 (>3.6)	52.84 (0.3)	62.3 (0.4)
23	PLA	5 ^g	1	>99.98 (>3.7)	99.52 (2.3)	80 (0.7)
24	PLA	2.5	0.50	>99.98 (>3.7)	99.91 (3.0)	23.3 (0.1)
26	PLA	1.5	0.50	>99.98 (>3.7)	35.71 (0.2)	31.4 (0.2)

Description:

[0065]

phr - parts by weight per 100 parts of polymer wt.,

R - growth reduction factor for bacteria R,

L - growth reduction factor for bacteria L,

* - polycaprolactone diol PCL Capa™ 2054 (Perstorp) was used,

** - anhydrous copper silicate was used,

a - a mixture of PP (HL 512 FB) and PLA (Ingeo 32510) in a weight ratio of 1:1 was used,

b - a mixture of PP (HL 512 FB) and polypropylene grafted with maleic anhydride (PP-g-MA) in a weight ratio of 3:1, was used,

c - a mixture of PP (HL 512 FB) and concentrated polypropylene containing 10% by weight $\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$ (k-PP), in a weight ratio of 9:1 was used,

d - a mixture of PP and polyethylene (with an average molecular weight of 35,000 g/mol) in a weight ratio of 9:1 was used,

e - paraffin oil was used,

f - [(R)-3-hydroxybutanoate] Biomer (r) P209F was used as PHA,

g - PEG Polikol-400 was used.

Table 2.

Chemical compositions of the remaining bioactive composite non-woven fabrics with PLA (or PP), containing Polikol 600-PEG (or other plasticizers), hydrous copper silicate $\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$ and antioxidants (Samples: 40-43)

Sample No.	PEG (or other plasticizer) [phr]	$\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$ [phr]
25	2.5 ^a	0.5
27	10	1
28	5 ^b	1
29	5 ^c	1
30	5 ^d	1
32	5 ^e	1
33	5 ^f	1
34	2.5 ^g	0.5
35	15	1.5
36	5 ^h	1
37	5 ⁱ	1
38	5 ^j	1
39	5 ^k	1

Description:

[0066]

phr - parts by weight per 100 parts of polymer wt.,

a - polycarbonate diol Desmophen C XP 2716 was used,

b - PEG Polikol 300 was used,

c - copolymer of ethylene oxide and propylene oxide (Rokopol 30P10) was used,

d - dioctyl phthalate (DOP) was used,

e - PEG Polikol 200 was used,

f - copolymer of ethylene oxide and propylene oxide (ROKAmer 2950) was used,

g - ethyl silicate 40 was used,

h - oligo(dimethylsiloxanediol) Polastosil® M-200 was used,

i-hydroxy ether polysiloxane graft copolymer - poly[dimethylsiloxane-co-[3-[2-[(2-hydroxyethoxy)propyl]methylsiloxane was used,

j - epoxy resin Epidian 601 was used,

k - paraffin oil was used,

1-polypropylene HL 512 FB was used.

Table 3.

Chemical compositions of the composite non-woven fabrics (with PP or PLA), containing Polikol 600-PEG and hydrous copper silicate $\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$ and the results of their microbiological tests.

Sample No.	Polymer	PEG 600	$\text{CuSiO}_3 \cdot x\text{H}_2\text{O}$	R[%] (L) <i>Escherichia coli</i> (ATCC 25922)	R [%] (L) <i>Staphylococcus aureus</i> (ATCC 6538)	R[%] (L) <i>Candida albicans</i> (ATCC 10321)
		[phr]	[phr]			
40	PP ¹	5	1	73,94 (0,5)	82,53 (0,8)	97,18 (1,7)
41	PLA ²	5	1	>99,94 (>3,2)	99,97 (3,6)	>99,74 (1,1)
42	PP ³	5	1	73,65 (0,5)	82,36 (0,8)	97,31 (1,7)
43	PLA ⁴	5	1	>99,96 (>3,6)	99,27 (2,3)	90,8 (0,9)

Description:

[0067]

phr - parts by weight per 100 parts of polymer wt.,

R - growth reduction factor for bacteria,

L - growth reduction factor for bacteria L,

¹-an addition of 0.15 phr of 2,2'-Methylenebis(6-tert-butyl-4-methylphenol)(MBMTBP) was used,

²-an addition of 0.20 phr of 2,2'-Methylenebis(6-tert-butyl-4-ethylphenol) (MBETBP) was used.

³-an addition of 0.25 phr of (MBMTBP) was used.

⁴-an addition of 0.20 phr of (MBETBP) was used.

Claims

- The method for biofunctionalization of textile materials by extrusion, wherein a polymer component is premixed with copper silicate, a plasticizer and an antioxidant, then heated to melt, after which the molten composition is subjected to pneumothermal extrusion of liquid-polymer composite in hot air stream, **characterized in that** the copper silicate is used in the form of a hydrate.
- The method according to claim 1, **characterized in that** the copper silicate hydrate comprises 18.52 % by weight H_2O .
- The method according to claim 1, **characterized in that** the copper silicate hydrate is used in the amount of 0.1 - 4 % by weight.
- The method according to claim 1, **characterized in that** the copper silicate is used in the form of a concentrate containing copper silicate hydrate with polymer in the amount of 1 - 25 % by weight.
- The method according to claim 1, **characterized in that** the polymer components used include polymers selected from the group consisting of polypropylene and its copolymers, polylactide, polyhydroxyalkanoates, polyethylene and/or mixtures thereof.
- The method according to claim 1, **characterized in that** the plasticizers have a liquid consistency.
- The method according to claim 1, **characterized in that** the plasticizers used include compounds selected from the group consisting of oligomers of ethylene glycol or propylene glycol, copolymers of ethylene glycol and propylene glycol, monoalkyl ethers of ethylene glycol oligomers glycerin esters, citric acid esters or tartaric acid esters, pentaerythritol esters, dialkyl diesters of phthalic acid, paraffin oil, epoxy resin, oligoesters of silicic acid, oligo(dimethylsiloxanediol), hydroxyalkyl or hydroxy ether derivatives of polysiloxanes, polycaprolactone, polycaprolactone diol or polycarbonate diol.

8. The method according to claim 1 or 7, **characterized in that** the plasticizer used is an ethylene glycol oligomer.
9. The method according to claim 1, **characterized in that** the plasticizers are used in the amount of 1.5 - 15 % by weight with respect to the mass of the polymer or the mass of polymer mixture, preferably 2.5 - 5 % by weight.
10. The method according to claim 1, **characterized in that** the antioxidants used include derivatives of tert-butylphenol, preferably 2,2'-methylenebis (4-methyl-6-tert-butylphenol) or 2,2'-methylenebis (4-ethyl-6-tert-butylphenol).
11. The method according to claim 1 or 10, **characterized in that** the antioxidants are used in the amount of 0.05 - 0.5 % by weight with respect to the mass of the polymer or the mass of polymer mixture, preferably 0.15 - 0.30 % by weight.

Patentansprüche

1. Verfahren der Biofunktionalisierung von Textilmaterialien durch Extrusion, wobei Polymerkomponente zunächst mit Kupfersilikat, Weichmacher und Antioxidationsmittel vermischt wird, das Ganze wird geheizt, bis Polymer geschmolzen ist, und anschließend wird die geschmolzene Masse dem Prozess einer pneumothermalen Extrusion der flüssigen Polymerlegierung im Heißluftstrom unterzogen, **dadurch gekennzeichnet, dass** Kupfersilikat in Form von Hydrat verwendet wird.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Kupfersilikat-Hydrat 18,52 Gew.-% Wasser enthält.
3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Kupfersilikat-Hydrat in der Menge von 0,1 - 4 Gew.-% verwendet wird.
4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Kupfersilikat als Konzentrat mit Gehalt von 1-25 Gew.-% Kupfersilikat-Hydrat mit Polymer verwendet wird.
5. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** als Polymerkomponenten ausgewählte Polymere aus der Polypropylen und seine Copolymere, Polylactid, Polyhydroxyalkane, Polyäthylen und/oder deren Mischung umfassenden Gruppe verwendet werden.
6. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Weichmacher flüssige Konsistenz haben.
7. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** als Weichmacher Verbindungen aus folgender Gruppe verwendet werden: Ethylenglykol- oder Propylenglykol-Oligomere, Ethylenglykol- und Propylenglycolcopolymere, Monoalkyl-Ethylenglykol-Oligomeren-Äther, Glycerinester, Zitronensäure oder Vinylsäureester, Pentaerythrit-Ester, Phthalsäure-Alkyldiester, Paraffinöl, Epoxidharz, Kieselsäure-Oligoester, Oligo-Dimethylsiloxandiol, Hydroxyalkyl- oder Hydroxyether-Polysiloxan-Derivate, Polycaprolacton, Polycaprolacton-diol, oder Polycarbon-diol.
8. Verfahren nach Anspruch 1 oder 7, **dadurch gekennzeichnet, dass** als Weichmacher Ethylenglykol-Oligomer verwendet wird.
9. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Weichmacher in der Menge von 1,5-15 Gew.-% im Verhältnis zur Polymermasse oder Masse der Polymermischung verwendet werden, vorteilhaft 2,5 - 5 Gew.-%.
10. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** als Antioxidationsmittel *tert*-Butylphenol-Derivate verwendet werden, vorteilhaft 2,2'-Methylenbis(4-methyl-6-tert-butylphenol) oder 2,2'-Methylenbis(4-ethyl-6-tert-butylphenol).
11. Verfahren nach Anspruch 1 oder 10, **dadurch gekennzeichnet, dass** Antioxidationsmittel in der Menge von 0,05-0,5 Gew.-% im Verhältnis zur Polymermasse oder Masse der Polymermischung verwendet werden, vorteilhaft 0,15-0,30 Gew.-%.

Revendications

1. Le procédé de biofonctionnalisation de matériaux textiles par extrusion, où le composant polymère est pré-mélangé

avec du silicate de cuivre et avec un plastifiant et un antioxydant, le tout est chauffé pour faire fondre le polymère, puis la composition fondue est soumise au processus de l'extrusion pneumothermique de l'alliage liquide de polymère dans un courant d'air chaud, **caractérisé en ce que** le silicate de cuivre est utilisé sous la forme d'un hydrate.

- 5 **2.** Le procédé selon la revendication 1, caractérisé en ce que le silicate de cuivre contient 18,52 % en poids d'eau.
- 3.** Le procédé selon la revendication 1, caractérisé en ce que l'hydrate de silicate de cuivre est utilisé en une quantité de 0,1 à 4 % en poids.
- 10 **4.** Le procédé selon la revendication 1, caractérisé en ce que le silicate de cuivre est utilisé sous la forme d'un concentré contenant de 1-25 % en poids d'hydrate de silicate de cuivre avec le polymère.
- 5.** Le procédé selon la revendication 1, **caractérisé en ce qu'**en tant que les composants du polymère sont utilisés des polymères choisis du groupe contenant du polypropylène et ses copolymères, du polylactide, des polyhydroxyalcanoates, du polyéthylène et/ou leurs mélanges.
- 15 **6.** Le procédé selon la revendication 1, caractérisé en ce que les plastifiants ont consistance liquide.
- 7.** Le procédé selon la revendication 1, **caractérisé en ce qu'**en tant que plastifiant sont utilisés les composés choisis du groupe contenant : les oligomères de l'éthylène ou de polypropylène glycol, les copolymères de l'éthylène glycol et du propylène glycol, les éthers monoalkyliques d'oligomères de l'éthylène glycol ; les esters de glycérine, les esters de l'acide citrique ou de l'acide tartrique, les esters de pentaérythritol, les esters dialkyls de l'acide phtalique, l'huile de paraffine, la résine époxy, les oligoesters de l'acide silicique, les dérivés hydroxy éther de polysiloxanes, le polycaprolactone, le polycaprolactonediol, ou le diol de polycarbonate
- 20 **8.** Le procédé selon la revendication 1 ou 7, **caractérisé en ce qu'**en tant que plastifiant est utilisé un oligomère d'éthylène glycol.
- 9.** Le procédé selon la revendication 1, caractérisé en ce que les plastifiants sont utilisés en une quantité de 1,5-15 % en poids par rapport au poids du polymère ou au poids du mélange de polymères, de préférence de 2,5 à 5% en poids.
- 30 **10.** Le procédé selon la revendication 1, **caractérisé en ce qu'**en tant qu'antioxydant sont utilisés des dérivés de tert-butylphénol, de préférence 2,2' Méthylène-2,2'-bis(méthyl-4-tert-butyl-6-phénol ou 2,2'Méthylène-2,2'-bis(éthyl-4-tert-butyl-6-phénol).
- 35 **11.** Le procédé selon la revendication 1 ou 10, caractérisé en ce que les antioxydants sont utilisés en une quantité de 0,05-0,5 % en poids par rapport au poids de polymère ou au poids du mélange de polymères, de préférence de 0,15 à 0,30 % en poids.

REFERENCES CITED IN THE DESCRIPTION

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