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(54) Title: BIODEGRADABLE TEXTILES AND METHODS OF THEIR MANUFACTURE

(57) Abstract: The invention concerns biodegradable textile materials designed mainly for medical uses. They contain a plurality of fibres prepared from the melt of lactide-glycolide copolymer or from the melt of a homogeneous blend of the lactide-glycolide copolymer with atactic poly(hydroxybutyrate). The textile materials take the form of nonwoven, knitwear or braided band for surgery sutures. The invention encompasses also melt methods of preparing biodegradable textile materials.



Biodegradable textiles and methods of their manufacture

The invention relates to biodegradable textiles and methods of the manufacture of biodegradable textiles primarily for medical uses.

Biodegradable polymeric fibers made of polylactide by melt spinning are described, amongst other, in following publications : monograph "Biodegradable and sustainable fibres," edited by R.S.Blackburn, Woodhead Publishing Limited, 2005, „Biodegradable fibres made of poly-lactic acid" in Chemical Fibres International, vol.46, no.5, 1996r. and monograph "Poly(lactic acid):Synthesis, Structures, Properties and Application" editor .R.Auras L-T, et al, 2010..Thanks to easy processing by melt spinning , unique properties and renewable resources, polylactide fibers have found application in the production of a wide range of textiles like apparel, home textiles, nonwoven for agriculture and hygiene, and geotextiles.

The use of polylactide as at least one of the components of staple- or continuous fibers is known from the American- US 6506873 and European EP 0977912 patents. According to these patents, textiles are prepared from the melts of lactide- polymers and copolymer and their blends with other biodegradable and non-degradable polymers by melt spinning, spun bond and melt blown techniques. Nonwoven described in the patents can have utility in agriculture, and medical-, hygienic- and filtration materials.

Known from the American patents : US 5525706, US 5807973, US 6111060 and US 6355772 are nonwoven products made of compositions of lactide polymers containing additives which stabilize the polymer in the course of processing. The applied polymeric lactide compositions contain polylactide bonds as the greater part, unreacted lactide in the amount of less than 2% and water in an amount below 2000 ppm. The nonwoven is made by direct spinning from the melt (spun bond and melt blown techniques) or by forming from staple fibers. On account of various additives contained in the lactide polymer, the biodegradable textiles as described in above patents are not suited for uses in medical bioresorbable devices.

Known from the US 6905987 and EP1381720 patents are biodegradable melt-spun fibers containing copolymers of poly(hydroxalkanoates) and polymers or copolymers of lactic acid. The fibers may be formed either as mono-component made of a polymer blend or bi-component of the sheath/ core type where the sheath is made up of lactide polymers while the core contains poly(hydroxalkanoates) copolymers. Described are also nonwoven materials prepared with a content of at least 2% of such fibers where the nonwoven is made by direct spinning from the melt (spun bond) or by forming from staple fibers. The nonwoven can have utility in many products : hygienic like diapers, napkins, suspensory, and medical like dressing materials, surgical bandages and dental threads.

Biodegradable polymeric fibers made of aliphatic polyesters and co-polyesters such as polyglycolide and polylactide by melt-spinning and drawing are also known from the US 2006/0159918. The invention relates to continuous and staple fibers ,crimped or smooth, mono-and bi-component. Thanks to special spinning conditions and/or use of crystallization-retarding additives, the fibers maintain their tenacity when stored at ambient temperature of 20-30 °C and relative humidity of 70-100%.

Known is also the use of lactide/glycolide copolymers in the manufacture of medical products inclusive fibers. Multifilament surgery sutures are made of a polymer containing 90% of glycolic acid and 10 % of L-lactic acid . Surgery sutures obtained from a polymer containing a higher amount of lactide than glycolide to slow down the degradation process are known from the publication “Biodegradable polymers as biomaterials”, Lakshmi S. Nair, Cato T. Laurencin, Prog.Polym.Sci 32,2007,762-798.

A method for the manufacture of knitwear designed for dressings made of bioresorbable polymers on the base of glycolide, lactide and/or lactones is known from the Polish patent application P.389377 and from the publication “Assessment of a new generation of biodegradable copolymers for uses in the technology of medical knitwear”) in the periodical „Techniczne Wyroby Włókiennicze”, 2008, p.56-62. Notwithstanding the above described solutions for the preparation of fibers and textiles containing lactide or

copolymers of lactide with other polymers, effective methods are still sought for the manufacture of lactide products bearing properties adequate to medical application.

The present invention relates to a technology for the production of textiles and its application in the manufacture of desirable biodegradable materials for mainly medical uses.

Biodegradable textiles of the present invention comprise a plurality of fibers prepared from a melt of the lactide / glycolide copolymer with average molecular mass in the range of 190000 – 300000, glass transition temperature of 53 - 60°C, melting temperature of 152 – 155°C, enthalpy of fusion of 41J/g, and with a content of unreacted monomers not exceeding 2 % wt.

The invention relates also to biodegradable textiles containing a plurality of fibers prepared from the melt of a homogeneous polymer blend with average weight polymer mass in the range of 100000 – 270000, glass transition temperature of 45 – 47°C, melting temperature of 149 – 152°C and enthalpy of fusion above 30J/g, composed in 82-98% wt. of lactide / glycolide copolymer, and in 2 - 18% wt of atactic poly(hydroxybutyrate) with a content of unreacted monomers not exceeding 2 % wt.

The lactide/glycolide copolymer is mass-synthesized with addition of a zircon initiator. The copolymer reveals a chain microstructure that contain both long lactidyl and glycolidyl segments and short alternately arranged elastic sequences of lactide and glycolide

The atactic poly(hydroxybutyrate) is prepared by anionic polymerization of the cyclic β -butyrolacton in the presence of t-butylamonium acetate

Products according to the invention can also take the form of nonwoven, knitwear and braided band.

The method to produce biodegradable textiles, according to the invention, consists in that either the dried up and unpurified lactide/glycolide copolymer or a dried up and

unpurified blend of the lactide/glycolide copolymer with atactic poly(hydroxybutyrate) possibly with a nanoadditive in the amount not exceeding 10%, and water content not exceeding 50 ppm is melted and then the molten polymer is extruded through a spinneret thus forming the textile materials in air atmosphere. The products are afterwards purified, and possibly dried up.

Bioglass, nanosilica or synthetic biocompatible phosphates like hydroxyapatite or calcium tri-calcium phosphate are used as bioadditives. Admixing of nanoadditives to the melt accelerates the mineralization of bones, an important behavior whenever the nonwoven finds application in bone implants.

The molten polymer is, according to the invention, extruded at the temperature of 200 – 230°C through a single-or multi-hole spinneret at a speed in the range of 80 – 800 m/min and throughput of 0,3 – 1,9 g/min per one hole. The formed fibers are then drawn at 50 – 60°C with a draw-ratio of 2-4, possibly stabilized at 100°C and up-taken on spools.

The thus formed continuous fibers can be cut to produce biodegradable staple fibers.

According to the invention, nonwoven can also be formed by pressing the molten polymer through consequential heating zones at the temperature of 90 – 220°C to a spinning head having the same temperature as the last heating zone. Hot air at 160 - 240°C is blown to the spinning head at the rate of 10 – 40 Nm³/h. The air splits the formed polymer streams to produce the nonwoven which is collected on a take-up device in the distance of 0,1 – 1m from the head.

According to the invention, nonwoven can also be formed by pressing the molten polymer through consequential heating zones at the temperature of 90 – 230°C to a spinning head having the same temperature as the last heating zone and collecting the fibres in nonwoven form on a flat electrode under voltage of 10-50 kV in a distance of 1– 10 cm from the head.

The nonwoven can be formed by pressing the molten polymer through consequential heating zones at the temperature of 90 – 230°C and next through a multi-hole spinneret having the same temperature as the last heating zone with throughput of 0.1 – 3.0 g/min/hole. The obtained fiber is drawn by means of air at speed of 800 – 4000 m/min, whereupon a fleece is formed which is integrated on a calendar at temperature of 20 – 50 °C and pressure of 0.1 – 1.0 MPa. The formed nonwoven is collected on a take-up device.

Admixing of nanoadditives to the melt accelerates the mineralization of bones, an important behavior whenever the nonwoven finds application in bone implants.

Thanks to absence of cytotoxicity, the nonwoven, knitwear and braids may find utility in medical devices like dressings, surgery sutures and bone implants.

Cytotoxicity of the fibers and products thereof was assessed according to standard PN-EN ISO 10993-5:2001 by the method of direct contact on cell line L929 – line of fibroblast cells obtained from subcutaneous fat tissue of mice C3H (ATCC CCL 1) and by the method of indirect contact with the use of polar and non-polar extracts. The culture fluid Eagle without calf serum with addition of 100 j/ml penicillin, 100 µg/ml streptomycin and 2 mM/ml L-glutamine was used as polar extract, while, as non-polar extract, served the culture fluid Eagle with addition of 2% of calf serum, 100 j/ml penicillin, 100 µg/ml streptomycin and 2 mM/ml L-glutamine.

The invention is illustrated with following examples not limiting the scope of the invention.

Example 1

Fiber-grade lactide/glycolide copolymer (PLAGA) was synthesized by polymerization in the mass. The process was accelerated with zircon (IV) acetylacacetate and proceeded for 12 hours at temperature of 140 – 170°C and next for 24 hours at 100 – 120°C. The copolymer was characterized by molecular mass of $M_n = 130\,000$, glass transition temperature of $T_g = 54\,^{\circ}\text{C}$, melting temperature $T_m = 155\,^{\circ}\text{C}$ and enthalpy of fusion

$dH = 45$ J/g. It contained 84% of lactidyl mole units and 15% of glycolidyl mole units, unreacted L-lactide below 1 % and water below 50 ppm. The copolymer revealed a chain microstructure that comprises both long lactidyl and glycolidyl segments and short, alternately arranged, elastic lactile and glycolile sequences. The polymer was extruded through a single-hole spinneret at temperature of 210°C , and rate of 0,3 g/min., air-cooled, up-wound with 82m/min of speed, and next drawn by the ratio of 3,99 in a water bath at temperature of 56°C .

A monofilament was obtained with a chain microstructure and composition equal to that of the used copolymer PLAGA. The monofilament had a linear density of 9,3 dtex, tenacity of 33,8 cN/tex and elongation of 75 %

Example 2

A polymeric mixture [Blenda PLAGA + PHB (10% wt.)], was first prepared in a blending extruder at temperature of $145 - 160^{\circ}\text{C}$. It was characterized by $M_n = 100\ 000$, $T_g = 45^{\circ}\text{C}$, $T_m = 152^{\circ}\text{C}$, $dH = 35$ J/g, and contained 90% of the PLAGA copolymer prepared as in Example 1 with 84% of the lactidyl portion ($M_n = 120\ 000$) and 10% of the atactic poly(hydroxybutyrate) (PHB) ($M_n = 60\ 000$). The latter was prepared by anionic polymerization of the cyclic β -butyrylrolactone in the presence of *t*-butyloamonium acetate. The polymeric mixture with water content below 50 ppm was extruded through a single-hole spinneret at 215°C , with throughput of 0,3 g/min, The monofilament was air-cooled, collected on a spool with 82 m/min of speed and then drawn by 4,7 fold in a water bath at 51°C . A monofilament was obtained with structure and composition like of the [Blenda PLAGA + PHB (10% wt.)], with linear density of 7,9 dtex, tenacity of 25,7 cN/tex and elongation of 68 %.

Example 3

From the PLAGA copolymer containing 15% glycolide and below 2 % of the unreacted lactide with $M_n = 130\ 000$, weight average molecular mass of $M_w = 200\ 000$, $T_g = 54^{\circ}\text{C}$, $T_m = 157^{\circ}\text{C}$, $dH = 49$ J/g, prepared as in Example 1 with water content below 30 ppm, a fiber was melt-spun, and drawn. Spinning was carried out on an extruder spinning bank at 230°C with speed of 800 m/min and output of 18,6 g/min. The fiber

was next 3-fold drawn on a drawtwister on a hot godet at 58°C and collected on a spool with 230 m/min of speed.

A continuous fiber was obtained with a chain microstructure and composition like in the starting PLAGA copolymer with linear density of 80,4dtex, tenacity of 16,0cN/tex, elongation of 27,7% and shrinkage of 8,1% in water at 37 °C.

Example 4

From the continuous fibers prepared as in Example 3, a weft-knitted fabric was prepared using left-right stitch comprising a course of smooth stitches in the repeat and a tuck miss course made on every second needle of an opentop machine with cylinder dia of Ø 4" and needle gauge of 34. To form the rim of the band, a knitted fabric was prepared of fibers with the same parameters. Polyamide textured yarn was used at the start of the knitting and joining of two layers. The knitted fabric was manufactured at knitting speed of 350 rpm with tension of the feeding amounting to 1,5cN.

A knitted twin-layer band was obtained in closed form, $7,0 \pm 0,1$ cm wide with circuit of $30,0 \pm 0,1$ (after relaxation and finishing), characterized by : thickness of $0,75 \pm 0,04$ mm, average air permeability of 5532 ± 142 mm/s and - average elasticity degree of 24 %.

The band is designed for medical uses as bandage - supporting material and protection of local skin defects on mainly arms and legs .

Example 5

A plaited band designed for surgery sutures was prepared from fibers made as in Example 3 composed of 12 loosely twisted filaments having a chain microstructure. The yarn wound on spindle bobbins of the braiding machine, was fed to the interlacing zone with tension of 20 - 22 cN. A compensation of the yarns was secured in the course of braiding on the break-preventing level of 60 - 65cN. The yarn was prepared as a circular sliver from 4 single wefts with the interlacement of 1:1. The interlacement density was controlled by the take- up speed to the length of $1,1 \pm 0,1$ / mm. A band was obtained with linear density of $33,9 \pm 0,3$ tex and thickness of $0,22 \pm 0,02$ mm. The yarn wound on perforated bobbins was finished by a 5-minute wash in distilled water at 40°C followed by several immersions in a 95 % refined ethanol. The yarn still on bobbins

was dried at ambient temperature of 25°C. Sutures were obtained with tenacity of 18,3cN/tex and 19,0cN/ tex, conditioned and wet accordingly, and elasticity degree of 55,7.

The yarns made up to pieces of desired length, were wound under sterile conditions onto specially prepared elements of the dressing structure. The yarns designed for medical application were X-ray sterilized with the dose of 28 kGy.

Example 6

From the polymer blend [Blenda PLAGA + PHB (9 % wt.)], with $M_n = 100\,000$, $M_w = 230\,000$, $T_g = 46^\circ\text{C}$, $T_m = 150^\circ\text{C}$, $dH = 30\text{ J/g}$, containing 91% wt of the PLAGA copolymer, characterized by $M_n = 130\,000$, $M_w = 200\,000$, $T_g = 54^\circ\text{C}$, $T_m = 153^\circ\text{C}$, $dH = 49\text{ J/g}$, prepared as in Example 1, containing 15% of glycolide and 9% wt of α -PHB prepared as in Example 2, a granulate was obtained with water content of 30 ppm. Fibers were spun from such granulate in a process consisting of melt-spinning and drawing. Spinning was carried out on an extruder spinning bank at 207°C through a 12-hole spinneret with speed of 800 m/min and output of 18,6g/min. The fiber was next drawn on a drawtwister on a hot godet at 63°C and collected on a spool with 496 m/min of speed.. Continuous fiber was obtained with a composition and structure like that of [Blenda PLAGA + PHB (9 % wt)] with linear density of 63,3 dtex, tenacity of 24,2 cN/tex, elongation of 21,1%, shrinkage of 14,8 % in water at 37°C . The fiber was subjected to cytotoxicity testing according to standard PN-EN ISO 10993-5:2001. The result was 0 cytotoxicity

Example 7

From fibers made as in Example 6, a plaited band designed for surgery sutures was prepared composed of 12 loosely twisted filaments having a chain microstructure. The yarn, wound on spindle bobbins of the braiding machine, was fed to the interlacing zone with tension of 18 - 22cN. A compensation of the yarns was secured in the course of braiding on the break-preventing level of 60 - 65cN. The yarn was prepared as a circular sliver from 8 single wefts with the interlacement of 1:1. The interlacement density was controlled by the take-up speed to the length of $0,5 \pm 0,1 / \text{mm}$. A band was obtained with linear density of $46,7 \pm 0,3\text{ tex}$ and thickness of $0,39 \pm 0,02\text{ mm}$. The yarn wound on perforated bobbins was finished by a 5-minutes wash in distilled water

at 40°C followed by several immersions in a 95 % refined ethanol. The yarn still on bobbins was dried at ambient temperature of 25°C. Sutures were obtained with tenacity of 19,2 cN/tex and 16,8cN/tex , conditioned and wet accordingly, and elasticity degree of 64,1. The yarns made up to pieces of desired length, were wound under sterile conditions onto specially prepared elements of the dressing structure. The yarns designed for medical application were X-ray sterilized with the dose of 28 kGy. The sutures were subjected to cytotoxicity testing according to standard PN-EN ISO 10993-5:2001. The result was 0 cytotoxicity.

Example 8

From PLAGA copolymer with the content of 15% glycolide and about 1% of unreacted monomers ($M_n = 150\,000$, $M_w = 360\,000$, $T_g = 54^\circ\text{C}$, $T_m = 152^\circ\text{C}$, $dH = 40\text{ J/g}$) and 20ppm of water fibers were spun and drawn. The spinning was carried out on an extruder spinning bank through a 12-hole spinneret at 225°C , with speed of 800 m/min and throughput of 16,0 g/min. The fiber was next drawn on a draw-winder on a hot godet (55°C) and hot plate (100°C) with speed of 267 m/min and draw ratio of 2,58. A fibre was prepared featured by linear density of 84dtex, tenacity of 19,9cN/tex, elongation of 27,3%, and shrinkage of 8,8 % (at 37°C) .

Example 9

From a polymer blend with 10 ppm of moisture containing 90% of the copolymer as in Example 8 and 10% of α -PHB having $M_n = 110\,000$, $M_w = 280\,000$, $T_g = 44^\circ\text{C}$, $T_m = 150^\circ\text{C}$, $dH = 29\text{ J/g}$, a fiber was formed in a two-step process consisting of spinning and drawing. The spinning was carried out on an extruder spinning bank through a 12-hole spinneret at 215°C , with speed of 800m/min and throughput of 22g/min. The fiber was next drawn on a draw-winder on a hot godet (50°C) with speed of 267 m/min and draw ratio of 2,31.

A fiber was obtained having linear density of 126dtex, tenacity of 20,3cN/tex, elongation of 31,4 % , and shrinkage of 33 % (at 37°C).

The spun fiber was also drawn on a draw-winder on a hot godet (50°C) and hot plate at 100°C . with the draw ratio of 2,43.

A fiber was obtained having linear density of 118 dtex, tenacity of 18,9 cN/tex, elongation of 31,5 %, and shrinkage of 18 % (at 37 °C).

Example 10

From the polymer as in Example 3, a fiber was formed in a two-step process consisting of spinning and drawing. The spinning was carried out on an extruder spinning bank through a 12-hole spinneret at 225°C, with speed of 800 m/min and throughput of 15,7 g/min. Next, the fiber was drawn on a draw-winder on a hot godet (55°C) with speed of 267 m/min and draw ratio of 2,98. The drawn fiber was then rewound to skeins and cut into staples 60 mm in length. Staple fiber was obtained with linear density of 6,02 dtex, tenacity of 24,1 cN/tex, elongation of 41%, shrinkage of 5% (w 37°C). A fleece was prepared from the fiber by carding on a drum card. The carding was made twice. After a seven-fold combining of the elemental fleeces with a cross orientation of the fibers, a fleece was obtained with the surface density of 60g/m². The fleece was first needled on a Befama needling machine with following parameters of the needling: 15x18x49x3 ½ RB, punch density 60cm⁻² needling depth 8mm. This was followed by the main 2-fold needling process with changed side of the needling at following parameters: 15x18x49x3 ½ RB, punch density 60cm⁻² needling depth 12 mm .

A fleece was obtained with surface density of 58,6 g/m², 0,8 mm thick , with air permeability of 624 l/m²s, sorption capacity of 2,4 g/g and sorption rate of 1,35 µl/cm²/s.

Cytotoxicity of the nonwoven was tested according to standard PN-EN ISO 10993-5:2001, The test result was 0 toxicity.

Example 11

Prior to the forming of fibers, a regranulate was prepared by mixing of the copolymer of glycolide and L-lactide (PLAGA) (M_n = 200 000) containing 84% of l-lactide and 16% of glycolide and about 1% of unreacted l-lactide with poly(ethylene glycol) PGE 400 (mole mass of 400, delivered by Sigma Aldrich) in amount of 4 %wt. (calculated on the polymer mass), adding 1,5 % wt.(on polymer mass) of nanohydroxyapatite. The

blending was done in the twin-screw extruder Minilab at 170°C and 50 rpm of the screw. The blend was pressed through a forming head having a 2 mm outlet, the streaming monofilament was rapidly quenched and cut to 2mm pieces. Such prepared regranulate was extruded through a concurrent twin-screw extruder. Temperature in the singular heating sectors of the extruder was in the range from 110°C to 170°C, the screw was rotating at 70 rpm. The polymer melt was pressed with a metering pump at 10 rpm to a spinning head at 180°C. The spun fiber was drawn with the ratio of 1:2 on godets with temperature of 60 - 70°C, and next quenched on a cooling godet at 10°C. The such formed fiber was collected on a cruciform packing.. It was next purified by removing the unreacted lactide and other post-reaction residues. A fiber was obtained with a chain microstructure and composition of that of the used copolymer PLAGA with linear density of 8,2 dtex, tenacity of 17,07 cN/tex, elongation at break of 3,26% and shrinkage of 0% at 60°C (dry condition).

Example 12

Prior to the forming of fibers, a regranulate was prepared by blending of a mixture of the copolymer of glycolide and L-lactide (PLAGA) with the atactic poly(hydroxybutyrate) [Blenda PLAGA + PHB (10% wt.)] having the same properties as in Example 6 with poly(ethylene glycol) PGE 400 (mole mass 400 g/mole) in the amount of 1,5 % calculated on the mass of the polymer. The blending was done in the twin-screw extruder Minilab at 170°C and at 100 rpm of the screw. The extruded monofilament was cut into 2 mm pieces. Such prepared regranulate was extruded through a concurrent twin-screw extruder. Temperature in the singular heating zones of the extruder was in the range from 110°C to 170°C; the screw was rotating at 100 rpm. The polymer melt was pressed with a metering pump at 10 rpm to a spinning head at 180°C. Hot air at 190°C was also blown to the spinning head with the throughput of 20 m³/h, splitting the formed polymer streams, and producing a web. The nonwoven was collected on a take-up device in a distance of 20cm. The material was next purified by removing the unreacted lactide and other post-reaction residues.

A nonwoven 1,5 mm thick was obtained with the surface density of 140 g/m² and free water sorption after 8 hours amounting to 3,5 g fluid/g sample (according to standard EN13726-1:2005).

Example 13

Prior to the spinning a regranulate was prepared as in Example 12 from the mixture of the copolymer glycolide/lactide (PLAGA) with polyethylene glycol PGE 400 in the amount of 2,5 % on the polymer mass and with the nano-additive of calcium phosphate in the amount of 1,5 % wt on polymer mass. The regranulate was next passing through a concurrent twin-screw extruder at temperature in the sequential heating zones from 110°C do 170°C, and 80 rpm of the screw. The melt was pressed through a metering pump at 10 rpm to the spinning head at 180°C. Air at 200°C and throughput of 20 m³/h was also blown to the spinning head. The air splits the streaming polymer forming the web. The nonwoven was collected in a distance of 20 cm. Unreacted lactide and other post-reaction residues were washed out of the nonwoven. A 1,6 mm thick nonwoven was obtained with surface density of 150 g/m² and a free sorption of water after 8 hours amounting to 4,6 g_{fluid}/g_{sample} (according to standard EN13726-1:2005)

Example 14

From fibers having properties as in Example 11 a fleece was prepared by carding on a laboratory Befama drum card. The carding was made twice with the feeding of 30 g/field of the feeder. Mass of the elemental fleece was 9,8 g. The elemental fleeces were many times laid on each other to attain the surface density of the combined fleece of about 300g/m². The compounded fleece consisted of 9 layers with a criss-cross orientation of the fibers. It was then reinforced by needling with lacing needles on Befama needling machine. First a rough needling was made with following parameters: needling number 15x18x40x3 ½ RB, punch density 60 cm⁻² needling depth 8mm. The main needling was made on the Artos needling machine (Heuer Co) at following parameters : needling number 15x17x42x3 ½ RB, punch density 130 cm⁻² needling depth 12 mm, nine-fold needling with changed side. Next, the fleece was compressed for 15 seconds at 120°C and pressure of 7 bar to condense the porosity structure and limit the pores' dimensions. A fleece was obtained with surface density of 333 g/m², 2,6 mm thick, air permeability of 33 l/m²s, sorption capacity of 8,8 g/g and sorption rate of V_{max}= 2,31 µl/cm²/s.

Example 15

From the PLAGA copolymer containing 16% of glycolide, 84 % of L-lactide and about 1% of unreacted L-lactide with $M_w = 200\,000$, $T_g = 54^\circ\text{C}$ and $T_m = 157^\circ\text{C}$, a nonwoven was formed on Minilab apparatus with a single-point head for melt blowing. High voltage isolated by means of an isolating shield, the copolymer was pressed through the spinneret at 195°C and 75 rpm of the screw. Temperature of the head was kept at 220°C . Process air at 220°C at rate of $11\text{ Nm}^3/\text{h}$ was blown to the head along with the polymer. The air flow was next cut off and the screw rpm reduced to 10, and fiber was formed using a flat electrode under the voltage of 30 kV as take-up device. The distance between the head and the electrode was 10 cm.

A nonwoven was produced composed of fibers $19\mu\text{m}$ thick. Surface density of the fleece was of $30\text{g}/\text{m}^2$, thickness 0,18 mm, tenacity 1,67 N/5cm and elongation 8 %.

Example 16

From the PLAGA copolymer containing 16% of glycolide, 84 % and below 1% of unreacted L-lactide with $M_n = 102\,000$, $M_w = 224\,000$, $T_g = 52^\circ\text{C}$ and $T_m = 150^\circ\text{C}$ $\Delta H = 0,8\text{J/g}$ with water content below 10 ppm, obtained as in Example 1, a nonwoven was formed from the melt. The polymer was extruded through a single-screw extruder at temperature of the consecutive heating zones in the range of $160 - 225^\circ\text{C}$. The molten polymer was pressed through a spinneret with 467 holes with a metering pump at rate of 0,1 g/min/hole. The fiber was from the spinneret directed to 9 mm wide guide chute where the fiber was drawn at speed of 1900 m/min by means of air supplied from a pneumatic unit at 15°C and pressure by 1000 Pa higher than atmospheric. The drawn fiber was then guided to a fleece-forming chute. The fleece was collected on a travelling transporter band below which vacuum was maintained by 300 Pa lower than atmospheric. The fleece was first compounded with a pressing roller at 45°C and next by calendering with rollers at 40°C and pressure of 0,5 MPa. Take-up speed of the nonwoven was 2m/min.

A nonwoven was produced with surface density of $51,8\text{g}/\text{m}^2$, thickness 0,275mm, air permeability of $658\text{ l}/\text{m}^2/\text{s}$ sorption capacity of 6,33g/g, sorption rate of $5,57\mu\text{m}/\text{cm}^2/\text{s}$, tenacity of 22N/cm and elongation of 10 %.

Claims

1. Biodegradable textile materials characterized in that they contain a plurality of fibers prepared from a melt of the copolymer of lactide with glycolide with average molecular mass in the range of 190 000 – 300 000, glass transition temperature of 53 - 60°C, melting temperature of 152- 155°C and enthalpy of fusion -above 41J/g, with a content of unreacted monomers in the amount not exceeding 2% wt.
2. Biodegradable textile materials according to Claim 1 characterized in that they contain a plurality of fibers prepared from a melt of a homogeneous polymer mixture with average molecular mass in the range of 100 000 – 270 000, glass transition temperature of 45 - 47°C, melting temperature of 149- 152°C and enthalpy of fusion above 30J/g, consisting in 82-98% wt. of the copolymer of lactide and glycolide, in 2-18% wt. of atactic poly(hydroxybutyrate) and of unreacted monomers in the amount not exceeding 2 % wt.
3. Biodegradable textile materials according to Claim 1 or 2 characterized in that they are provided as product in nonwoven form.
4. Biodegradable textile materials according to Claim 1 or 2 characterized in that they are provided as product in knitwear form.
5. Biodegradable textile materials according to Claim 1 or 2 characterized in that they are provided as product in the form of braided band.
6. Biodegradable textile materials according to Claim 1 characterized in that the copolymer of lactide and glycolide has a chain microstructure containing long lactidyle and glycolidyle segments and alternate elastic lactyl and glycolyl sequences, and was obtained by synthesis in the mass in the presence of a zirconium initiator.

7. Biodegradable textile materials according to Claim 2 characterized in that the atactic poly(hydroxybutyrate) is prepared by an anionic polymerization of the cyclic β -butyryllacton in the presence of t-butylammonium acetate.
8. A method for preparing biodegradable textile materials from a melt characterized in that the dried up and unpurified lactide - glycolide copolymer or dried up and unpurified mixture of the lactide - glycolide copolymer with atactic poly(hydroxybutyrate) possibly with an bioactive nano-additive in the amount not exceeding 10 %, and with water content not exceeding 50 ppm is subjected to melting, and the molten polymer is next extruded through a spinneret and formed into textile materials in air atmosphere whereupon the materials are purified and possibly dried.
9. A method according to Claim 9 characterized in that bioglass, nanosilcate or synthetic, biocompatible derivatives of phosphates like hydroxyapatite or tri-calcium phosphate are used as bioactive nanoadditives.
10. A method according to Claim 8 characterized in that the continuous fibers are formed by pressing of the molten polymer at temperature of 200 – 230°C through a spinneret at fiber speed of 80 – 800 m/min with throughput per one hole of 0,3 – 1,9 g/min , and, next, the fibers are drawn at temperature of 50 – 60°C and draw ratio of 2 to 4, possibly stabilized at temperature of about 100 °C and wound up on spools.
11. A method according to Claim 10 characterized in that the continuous fibers are subjected to crimping and cutting.
12. A method according to Claim 6 characterized in that a nonwoven is formed by pressing the molten polymer through consecutive heating zones at temperature of 90 - 220°C to a spinning head at temperature equal to that of the last heating zone and, at the same time, blowing of air at temperature of 160 - 240°C to the

spinning head with throughput of 10 – 40 Nm³/h of dry air which splits the formed polymer streams, and the obtained fiber is collected on a take-up device in a distance of 0.1 to 1m from the spinning head.

13. A method according to Claim 8 characterized in that the molten polymer is pressed through the consecutive heating zones at temperature of 90 – 200°C to a forming head at temperature of the last heating zone, and is formed into a nonwoven on a flat electrode under the voltage of 10- 50 kV in a distance of 1 – 10 cm from the head.
14. A method according to Claim 8 characterized in that the molten polymer is formed to a nonwoven by pressing it through the consecutive heating zones at temperature of 90 – 230°C and next through a multi-hole spinneret at temperature of the last heating zone with throughput of 0,1 – 3,0 g/min/hole, and the obtained fiber is drawn by means of air at speed of 800 – 4000 m/min, and a fleece is formed which is condensed on a calender at temperature of 20 – 50°C and pressure of 0,1 – 1,0 MPa, and the produced nonwoven is collected on a take-up unit.

INTERNATIONAL SEARCH REPORT

International application No
PCT/PL2012/000069

A. CLASSIFICATION OF SUBJECT MATTER
INV. D04H1/435 D04H1/55 D04B1/14 A61L17/12 C08G63/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D04H D04B A61L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 038 540 A2 (AESCULAP AG & CO KG [DE]) 27 September 2000 (2000-09-27) paragraphs [0036], [0024] - [0029], [0032], [0011], [0013], [0062]; claims 1,21,22	1,3-5
A	----- US 6 277 927 B1 (ROBY MARK S [US] ET AL) 21 August 2001 (2001-08-21) column 5, lines 3-5; claim 8; example 1	1-14
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A	----- US 3 839 297 A (WASSERMAN D ET AL) 1 October 1974 (1974-10-01) column 6, lines 1-10 ----- -/-	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 April 2013

Date of mailing of the international search report

13/05/2013

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/PL2012/000069

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/152349 A1 (3M INNOVATIVE PROPERTIES CO [US]; MOORE ERIC M [US]; SCHOLZ MATTHEW T) 17 December 2009 (2009-12-17) claims 1,2 -----	1-14
A	EP 1 375 706 A1 (ETHICON INC [US]) 2 January 2004 (2004-01-02) claim 1 -----	8-14
A	US 5 320 624 A (KAPLAN DONALD S [US] ET AL) 14 June 1994 (1994-06-14) example 1 -----	8-14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/PL2012/000069

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1(completely); 3-6(partially)

biodegradable textile material characterized by one set of parameters

2. claims: 2, 7(completely); 3-6(partially)

biodegradable textile material characterized by another set of parameters

3. claims: 8-14

method for preparing biodegradable textile materials

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/PL2012/000069

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