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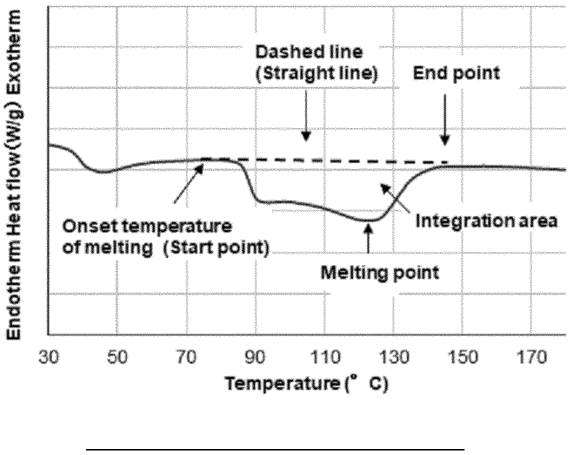
(54) BIODEGRADABLE THREE-DIMENSIONAL NETWORK STRUCTURE

(57) An object of the present invention is to provide a biodegradable three-dimensional network structure having excellent compression durability and high compression recovery after heat compression. The biodegradable three-dimensional network structure includes a linear fiber including a polybutylene adipate terephthalate resin having a weight average molecular weight of 35000 or more, wherein the biodegradable three-dimensional network structure has an apparent density of from 0.005 g/cm^3 to 0.30 g/cm^3 and a thickness of from 10 mm to 100 mm, and the linear fiber has a fiber diameter of from 0.2 mm to 2.0 mm and a crystalline melting enthalpy of 16 J/g or more.

[Fig. 1]



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Description

TECHNICAL FIELD

[0001] The present invention relates to a biodegradable three-dimensional network structure.

BACKGROUND ART

[0002] So far, various biodegradable three-dimensional network structures have been known. For example, Patent Document 1 discloses a biodegradable aquatic plant support for revetment greening. The biodegradable aquatic plant support consists of a spatial network structure in which a large number of curled continuous linear bodies including biodegradable thermoplastic resin are at least partially bonded to form three-dimensional random loops. Patent Document 2 discloses a biodegradable three-dimensional network-structured fiber assembly. The structure is formed through local bonding of fibers including at least a biodegradable resin and a resin to promote bonds at sites. Patent Document 3 discloses a biodegradable three-dimensional structure in which filaments consisting essentially of thermoplastic polylactic acid resin and having a fineness of from 300 to 100000 denier are repeatedly folded and bonded at most contact portions thereof.

CITATION LIST

PATENT DOCUMENTS

[0003]

Patent Document 1: JP-A-2001-32236
Patent Document 2: JP-A 2020-128608
Patent Document 3: JP-A 2000-328422

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0004] Patent Document 1 discloses a technique to improve plant supportability of the biodegradable network structure. Patent Document 2 discloses a technique to improve local bonding of fibers for a biodegradable network structure. Patent Document 3 discloses a stress-dispersing technique to compressive stress by appropriate responsive deformation of the stressed area due to coil or loop shaped portions formed in a biodegradable three-dimensional structure. Various attempts have been made to improve functions of biodegradable network structures, however, a biodegradable network structure having both of excellent compression durability and high compression recovery after heat compression has not yet been developed. The present invention was made in view of the above circumstances, and it is an object of the present invention to provide a biodegradable three-dimensional network structure having excellent compression durability and high compression recovery after heat compression.

SOLUTION TO THE PROBLEMS

[0005] The biodegradable three-dimensional network structure in accordance with an embodiment of the present invention is as follows.

[1] A biodegradable three-dimensional network structure including a linear fiber including a polybutylene adipate terephthalate resin having a weight average molecular weight of 35000 or more, wherein the biodegradable three-dimensional network structure has an apparent density of from 0.005 g/cm^3 to 0.30 g/cm^3 and a thickness of from 10 mm to 100 mm, and the linear fiber has a fiber diameter of from 0.2 mm to 2.0 mm and a crystalline melting enthalpy of 16 J/g or more.

Due to above features, the biodegradable three-dimensional network structure can have improved compression durability and compression recovery after heat compression. Preferred embodiments of the biodegradable three-dimensional network structure are as follows.

[2] The biodegradable three-dimensional network structure according to [1], wherein the linear fiber has a three-dimensional random looped shape.

[3] The biodegradable three-dimensional network structure according to [1] or [2], wherein the linear fiber has a

crystalline melting enthalpy of 30 J/g or less.

[4] The biodegradable three-dimensional network structure according to any one of [1] to [3], wherein the biodegradable three-dimensional network structure has an applicability to a cushion.

[5] The biodegradable three-dimensional network structure according to any one of [1] to [4], wherein the polybutylene adipate terephthalate resin has a weight average molecular weight of 150000 or less.

[6] The biodegradable three-dimensional network structure according to any one of [1] to [5], wherein the linear fiber has a melting point of 100°C or higher and 120°C or lower.

[7] The biodegradable three-dimensional network structure according to any one of [1] to [6], wherein the linear fiber has a hollow cross-sectional shape.

[8] The biodegradable three-dimensional network structure according to [7], wherein the linear fiber has a hollow rate of 1% or more and 30% or less.

[9] The biodegradable three-dimensional network structure according to [7], wherein the linear fiber has a hollow rate of 2% or more and 25% or less.

[10] The biodegradable three-dimensional network structure according to any one of [1] to [9], wherein the linear fiber has a crystalline melting enthalpy of 17 J/g or more.

[11] The biodegradable three-dimensional network structure according to any one of [1] to [10], wherein the linear fiber has a crystalline melting enthalpy of 28 J/g or less.

[12] The biodegradable three-dimensional network structure according to any one of [1] to [11], wherein the polybutylene adipate terephthalate resin has a weight average molecular weight of 37000 or more.

[13] The biodegradable three-dimensional network structure according to any one of [1] to [12], wherein the polybutylene adipate terephthalate resin has a weight average molecular weight of 120000 or less.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0006] According to the present invention, a biodegradable three-dimensional network structure having excellent compression durability and high compression recovery after heat compression can be provided due to above features.

BRIEF DESCRIPTION OF THE DRAWING

[0007] [Fig. 1] Fig. 1 is an exemplary endothermic/exothermic curve to measure a crystalline melting enthalpy of a linear fiber in a three-dimensional network structure.

DESCRIPTION OF EMBODIMENTS

[0008] A biodegradable three-dimensional network structure according to one or more embodiments of the present invention includes a linear fiber including a polybutylene adipate terephthalate resin having a weight average molecular weight of 35000 or more, wherein the biodegradable three-dimensional network structure has an apparent density of from 0.005 g/cm^3 to 0.30 g/cm^3 and a thickness of from 10 mm to 100 mm, and the linear fiber has a fiber diameter of from 0.2 mm to 2.0 mm and a crystalline melting enthalpy of 16 J/g or more. Such features of the biodegradable three-dimensional network structure enable improvement in compression durability and compression recovery after heat compression. Description of each feature will be given below.

[0009] The three-dimensional network structure has an apparent density of from 0.005 g/cm^3 to 0.30 g/cm^3. The apparent density of 0.005 g/cm^3 or more leads to an increase in hardness of the three-dimensional network structure, resulting in a reduction in bottom touching feeling of the three-dimensional network structure when applied to a cushion. Therefore, the three-dimensional network structure has an apparent density of preferably 0.01 g/cm^3 or more, more preferably 0.02 g/cm^3 or more, further preferably 0.03 g/cm^3 or more, and further more preferably 0.05 g/cm^3 or more. In addition, the apparent density of 0.30 g/cm^3 or less leads to improvement in flexibility, thereby allowing the three-dimensional network structure to be suitably applied as cushioning material. Therefore, the apparent density is preferably 0.20 g/cm^3 or less, and more preferably 0.15 g/cm^3 or less. The apparent density of the three-dimensional network structure can be measured by a method described in Examples.

[0010] The three-dimensional network structure has a thickness of from 10 mm to 100 mm. The thickness of 10 mm or more make it easier for the three-dimensional network structure to be applied as cushioning material. The thickness is preferably 15 mm or more, more preferably 20 mm or more, and further preferably 22 mm or more. Considering the size of the manufacturing equipment, the thickness is 100 mm or less, preferably 90 mm or less, more preferably 80 mm or less, and further more preferably 50 mm or less. The thickness of the three-dimensional network structure can be measured by a method described in Examples.

[0011] The three-dimensional network structure includes a linear fiber. The linear fiber preferably has a three-dimensional random looped shape. In addition, the linear fiber is preferably a continuous linear body. The continuous linear body is a linear filament having continuous portion of at least 5 mm or more. The intersection portions of continuous linear bodies are bonded with each other, thereby enabling the formation of the three-dimensional network structure easier. Therefore, the three-dimensional network structure preferably has bonding portions where the intersection portions of the continuous linear bodies are bonded with each other.

[0012] The linear fiber may include a complex linear body of a sheath-core type, a side-by-side type, or an eccentric sheath-core type. The complex linear body may be a complex linear body including polybutylene adipate terephthalate resin in combination with another thermoplastic resin. Although the linear fiber may have either a hollow or a solid cross-section, a hollow cross-section is preferable from the viewpoint of weight reduction. In addition, the linear fiber with a hollow cross-section enables improvement in compression recovery after heat compression. The linear fiber may preferably have a modified cross-section. Such a shape of cross-section makes it easier for the three-dimensional network structure to have an appropriate hardness and cushioning property. The linear fiber has a hollow rate of preferably 1% or more, more preferably 2% or more, further preferably 5% or more, and preferably 30% or less, more preferably 25% or less, and further preferably 20% or less. The hollow rate of the linear fiber can be measured by a method described in Examples.

[0013] The linear fiber has a fiber diameter of from 0.2 mm to 2.0 mm. The fiber diameter of 0.2 mm or more enables the three-dimensional network structure to have improved hardness. Therefore, the fiber diameter is preferably 0.3 mm or more, and more preferably 0.4 mm or more. In addition, the fiber diameter of 2.0 mm or less improves fineness of the network structure and thus enhances cushioning property, and also make it easier for the network structure to have soften feel. Therefore, the fiber diameter is preferably 1.7 mm or less, more preferably 1.5 mm or less, and further more preferably 1.2 mm or less. The fiber diameter of the linear fiber can be measured by a method described in Examples. The linear fiber may have a contour of a cross-section of a circle, an oval, a polygonal, or a rounded polygonal shape. A fiber with a contour shape other than circular has a fiber diameter defined by the longest distance between any two points on the contour.

[0014] The linear fiber has a melt flow rate (MFR) of preferably from 3 gl10min to 60 g/10min. MFR of the linear fiber of 3 gl10min or more leads to an increase in melt viscosity and thus an increase in a fiber diameter of the linear fiber. The linear fiber has MFR of more preferably 4 g/10min or more, further preferably 6 g/10min or more, further more preferably 8 gl10min or more, and particularly preferably 10 gl10min or more. In addition, MFR of 60 gl10min or less enables improvement in compression recovery after heat compression. The linear fiber has MFR of more preferably 50 gl10min or less, further preferably 40 gl10min or less, further more preferably 30 gl10min or less, and particularly preferably 25 gl10min or less. MFR of the linear fiber can be measured by a method described in Examples.

[0015] In case where a commercially available resin is used as a polybutylene adipate terephthalate resin for the linear fiber, water may be added when the resin has a low melt flow rate (MFR). The water-added resin is hydrolyzed during melt extrusion, and the resin will have increased MFR. This will lead to an increase in MFR of the linear fibers. In case where a resin has a high MFR, MFR of the resin can be reduced by drying the resin before melt extrusion. This will lead to a decrease in MFR of the linear fiber.

[0016] The linear fiber has a crystalline melting enthalpy of 16 J/g or more. The crystalline melting enthalpy of 16 J/g or more enables improvement in compression durability and compression recovery after heat compression of the three-dimensional network structure. The crystalline melting enthalpy is preferably 17 J/g or more, more preferably 18 J/g or more, further preferably 19 J/g or more, further more preferably 20 J/g or more, and particularly preferably 21 J/g or more. The crystalline melting enthalpy is preferably 30 J/g or less, and such a crystalline melting enthalpy can improve flexibility of the three-dimensional network structure and thus can reduce noise during compression and recovery from compression. The crystalline melting enthalpy is more preferably 28 J/g or less, and further preferably 26 J/g or less.

[0017] The crystalline melting enthalpy (J/g) of the linear fiber can be determined from the integration value calculated from the endothermic peak (melting peak) of an endothermic/exothermic curve obtained by measuring a sample weighed to mass of 2.0 mg ± 0.1 mg at a temperature rise rate of 20°C/min under a nitrogen atmosphere with a differential scanning calorimeter. The integration value can be obtained by determining a start point at which the endothermic/exothermic curve with the endothermic peak (melting peak) began to leave from a baseline of a low temperature side and an end point at which the curve began to contact with a baseline of a high temperature side, drawing a straight line connecting the start and end points, and integrating the area enclosed by the line and the curve. Fig. 1 shows an exemplary endothermic/exothermic curve. In Fig. 1, the dashed line is drawn by connecting the start and end points of the endothermic peak (melting peak), and the area enclosed by the dashed line and the curve will be integrated.

[0018] In case where a commercially available resin having a crystalline melting enthalpy lower than the desired range is used as a polybutylene adipate terephthalate resin for forming the linear fiber, annealing may be conducted as described later to control it to be in a desired range.

[0019] The polybutylene adipate terephthalate resin is biodegradable and is a copolymer of adipic acid, terephthalic acid, and butanediol. The biodegradability of the polybutylene adipate terephthalate resin is expected to provide one solution to solve problems in waste disposal and microplastics. Adipic acid, terephthalic acid, and butanediol need not be copolymerized at the same time and may be copolymerized in multiple steps. The polybutylene adipate terephthalate resin is preferably a thermoplastic resin.

[0020] To synthesize the polybutylene adipate terephthalate resin, small amount of any component other than adipic acid, terephthalic acid, and butanediol can be used as "other copolymerization component". Examples of the other copolymerization component include a modifier for chain extension or end capping, and any dicarboxylic acid other than adipic acid and terephthalic acid. These may be used alone or in combination.

[0021] Examples of above mentioned other dicarboxylic acid include oxalic acid, malonic acid, succinic acid, glutaric acid, pimelic acid, and suberic acid. These dicarboxylic acid may be used alone or in combination.

[0022] The modifier may be, for example, a polyisocyanate compound or a glycol compound. The polyisocyanate compound may be, for example, a diisocyanate compound. Examples of the diisocyanate compound include hexamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, xylylene diisocyanate, 1,5-naphthylene diisocyanate, p-phenylene diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, tetra-methyl xylene diisocyanate, carbodiimide modified MDI, and polymethylene phenyl polyisocyanate. These compounds may be used alone or in combination. The glycol compound may be a diol other than butanediol or a polyalkylene glycole. Examples of the diol include methanediol, ethanediol, propanediol, pentanediol, hexanediol. Example of the polyalkylene glycole include polymethylene glycol, polyethylene glycol, polypropylene glycol, and polybutylene glycol (polytetramethylene glycol). These diols and polyalkylene glycols may be used alone or in combination.

[0023] The polybutylene adipate terephthalate resin may be a biodegradable synthetic polymer compound in a positive list of so-called 'green plastic' (biodegradable plastic) with a classification number A-1 published by Japan BioPlastics Association. Specifically, ecoflex (registered trademark) (manufactured by BASF Japan Ltd.), Eastar Bio (available from GSI Creos Corporation, manufactured by NOVAMONT S.P.A.), A400 (ECOPOND KD 1024, manufactured by GP, Eastar Bio, Ultra, KINGFA), and TUNHE PBAT TH-801T (manufactured by XINJIANG BLUE RIDGE TUNHE CHEMICAL INDUSTRY JOINT STOCK). These may be used alone or in combination.

[0024] The polybutylene adipate terephthalate resin has a weight average molecular weight (g/mol) of 35000 or more, thereby enabling improvement in compression recovery after heat compression. The weight average molecular weight is preferably 37000 or more, and more preferably 40000 or more. The weight average molecular weight of 150000 or less leads to enhanced elasticity. The weight average molecular weight is preferably 150000 or less. The weight average molecular weight of 120000 or less can decrease melt viscosity of the polymer. The weight average molecular weight is more preferably 120000 or less. The resin included in the linear fiber preferably has a weight average molecular weight (g/mol) within the above range. The weight average molecular weight can be determined by a method such as gel permeation chromatography (GPC).

[0025] The linear fiber may include another biodegradable resin other than polybutylene adipate terephthalate resin. Examples of the biodegradable resin other than polybutylene adipate terephthalate resin preferably include polylactic acid, polylactic acid/polycaprolactone copolymer, polylactic acid/polyether copolymer, polyethylene terephthalate succinate, polybutylene succinate, polybutylene succinate adipate, polyglycolic acid, polycaprolactone, polyvinyl alcohol, cellulose acetate. These resins may be used alone or in combination. Details of the resins are shown in the positive list of green plastic (biodegradable resin) with a classification number A-1 published by Japan BioPlastics Association. The linear fiber may include a resin other than biodegradable resin. Examples of the resin include thermoplastic resins such as polyurethane and polyester.

[0026] The linear fiber may include a resin synthesized from petroleum-derived monomers, however, biomass-derived monomers are preferable from the viewpoint of lowering environmental load. As to the biomass-derived monomers, monomers, for example, shown in a positive list with a classification number A (biomass-derived plastic) published by Japan BioPlastics Association may be given as examples.

[0027] The total content of the adipic acid component, terephthalic acid component, and butanediol component in 100 mol% of whole components constituting the polybutylene adipate terephthalate resin is preferably 70 mol% or more, more preferably 80 mol% or more, further preferably 90 mol% or more, further more preferably 95 mol% or more, and particularly preferably 99 mol% or more.

[0028] The linear fiber may contain additives such as a deodorant agent, an antibacterial agent, an antifungal agent, an anti-mite agent, an anti-odor agent, an antimycotic agent, an aromatic agent, a flame retardant, a moisture absorbing/releasing agent, an antioxidant, and a lubricant. These may be used alone or in combination.

[0029] The linear fiber includes the polybutylene adipate terephthalate resin in an amount of preferably 50% by mass or more, more preferably 60% by mass or more, further preferably 80% by mass or more, further more preferably 90% by mass or more, particularly preferably 95% by mass or more, and most preferably 98% by mass or more in 100% by mass of the linear fiber. The linear fiber may consist of polybutylene adipate terephthalate resin.

[0030] The linear fiber has a melting point of preferably 100°C or higher and 120°C or lower, thereby enabling the three-dimensional network structure to have improved compression recovery after heat compression. The melting point is more preferably 115°C or lower. Annealing treatment conducted as described later can lower the melting point of the polybutylene adipate terephthalate resin, thereby making it easier for the linear fiber to have a melting point of 120°C or lower.

[0031] The three-dimensional network structure may include a multilayered structure. The multilayered structure may be (i) a structure having top and back surface layers, each surface layer including a linear fiber having different finesse, (ii) a structure having top and back surface layers, each surface layer having different apparent density, or (iii) a structure including laminated long and/or short fiber nonwoven fabric. Examples of the method for forming the multilayered structure include a method for fusing and fixing the layers by heating, a method for bonding the layers with an adhesive, and a method for binding the layers by sewing or using a band.

[0032] The shape of the three-dimensional network structure is not particularly limited, and may have, for example, a plate, triangular, quadrangular such as polygonal, cylindrical, spherical shape, or combinations thereof may also be allowed. The three-dimensional network structure may be obtained by molding with baffles when resin is melt extruded, or may be molded by a method such as cutting or hot pressing.

[0033] The three-dimensional network structure has a 70°C compressive residual strain of preferably 30% or less, thereby enabling improvement in compression recovery after heat compression. The 70°C compressive residual strain is more preferably 25% or less, and further preferably 23% or less. The 70°C compressive residual strain may be 1% or more, or 5% or more. The 70°C compressive residual strain can be measured by a method described in Examples.

[0034] The three-dimensional network structure has a 25%-compression hardness of preferably 5.0 N/φ50mm or more and 100 N/φ50mm or less. The 25%-compression hardness of 5.0 N/φ50mm or more can reduce the bottom touching feeling of the three-dimensional network structure when applied to a cushion. Therefore, the 25%-compression hardness is more preferably 5.4 N/cp50mm or more, further preferably 6.0 N/cp50mm or more, and further more preferably 7.0 N/φ50mm or more. The 25%-compression hardness of 100 N/φ50mm or less can enhance cushioning property. Therefore, the 25%-compression hardness is more preferably 80 N/cp50mm or less, further preferably 60 N/cp50mm or less, and further more preferably 30 N/φ50mm or less. The 25%-compression hardness can be measured by a method described in Examples.

[0035] The three-dimensional network structure is preferably free from a bonding promoter. The absence of a bonding promoter prevents excessive hardening generated by excessive bonding due to bonding promoter in the three-dimensional network structure. In addition, a decrease in fineness of the three-dimensional network structure caused by excessively increased bonding area per one bonding point may be prevented. Examples of the resin which can promote bonding include polycaprolactone, polybutylene succinate, polybutylene sebacate terephthalate, and polybutylene azelate terephthalate.

[0036] The three-dimensional network structure may be colored. A color agent such as a pigment or a dye can be used. The color agent may be contained in the resin before melt spinning, or the linear fibers may be coated with a color agent by immersion in or application of it after the formation of the three-dimensional network structure.

[0037] The three-dimensional network structure is preferably applied to a cushion. The cushion may be resilient enough to support objects or may be able to reduce impact. Examples of the cushion include cushions for office chairs, furniture, sofas, bedding such as beds, cushions for seats of vehicles such as trains, automobiles, two-wheeled vehicles, child safety seats, and baby buggies, shock-absorbing mats such as floor mats and members for preventing collision and nipping.

[0038] The three-dimensional network structure can be formed, for example, by the following method. The polybutylene adipate terephthalate resin is distributed from a multi-row nozzle having a plurality of orifices to another nozzle having orifices, and then discharged downward from the nozzle at a spinning temperature of the resin (at a temperature which is melting point +20°C or higher and lower than melting point +180°C). Then, a three-dimensional network structure is formed by bringing continuous linear bodies into contact with each other in a melt state and fusing contact portions thereof, then the structure is sandwiched at both faces with take-up conveyors each equipped with a net, and cooled with a cooling water in a cooling tank. The distance between the nozzle face and the surface of the cooling water is preferably 15 cm or more, and more preferably 20 cm or more, thereby enabling improvement in the hollow rate and the finesse of the network structure of the fibers. The distance is preferably 40 cm or less, and more preferably 35 cm or less, thereby enabling the production of spatial network structure having an appropriate apparent density and a fiber diameter. After cooling, the solidified spatial network structure is drawn, then drained or dried, and the spatial network structure having two or one smoothed side can be obtained. With regard to these spinning/cooling processes, descriptions in Japanese Patent Laying-Open No. H7-68061 can be referenced. In case where only one surface needs to be smoothed, continuous linear bodies are discharged on an inclined take-up net, and the linear bodies are contacted with each other and fuses at contact portions thereof in a melt state. While the spatial network structure is being formed, the shape only on the take-up net touching side of the structure may be loosened and the structure may be cooled. Thus obtained three-dimensional network structure may be subjected to an annealing treatment. The three-dimensional network structure may be subjected to a drying treatment instead of an annealing treatment.

[0039] Water is preferably added to the resin before the resin is discharged from a nozzle. Water is added preferably at 0.005% by mass or more with respect to 100% by mass of the solid content of the resin, thereby allowing promoted degradation of the resin in the production process of the three-dimensional network structure or improvement in flexibility of the resin. In addition, water is added preferably at 2.0% by mass or less, thereby enabling prevention of excessive degradation of the resin in the production process of the three-dimensional network structure and thus facilitating improvement in compression recovery after heat compression. The amount of added water is more preferably 1.0% by mass or less, further preferably 0.5% by mass or less, and further more preferably 0.2% by mass or less. Water may be added to the resin in any manner. For example, the resin may be absolutely dried in vacuum at 100°C for 12 hours or longer before discharged from a nozzle, and a predetermined amount of water may be added with respect to 100% by mass of absolutely dried resin.

[0040] Before melt extrusion, the polybutylene adipate terephthalate resin preferably has a melt flow rate (MFR) which is smaller than desired MFR of the three-dimensional network structure by from 0.5 to 20. Since thermal degradation and shear degradation of the resin is caused during melt extrusion, controlling of MFR before melt extrusion as described above enables production of three-dimensional network structure having desired MFR.

[0041] After melt-molding, the polybutylene adipate terephthalate resin is cooled preferably with cooling water. The polybutylene adipate terephthalate resin may shrink in molding by the time the resin is solidified by cooling. Because of the molding shrinkage phenomenon, the three-dimensional network structure should preferably be formed to have a width and a thickness in consideration of molding shrinkage, and the shrinkage in molding can be reduced by lowering the solidification temperature of melting resin (hereinafter merely 'solidification temperature'). Therefore, the temperature of the cooling water is preferably 20°C or lower, and more preferably 15°C or lower. The resin is preferably cooled with cooling water with the cooling time of preferably 30 seconds or more. The resin is preferably solidified by cooling in a water tank.

[0042] The annealing treatment may be conducted in a commercially available hot-air drying oven or may be in a warm water bath. The annealing temperature is 70°C or higher. The annealing treatment under such conditions can improve a crystalline melting enthalpy. The temperature is preferably 75°C or higher, and more preferably 80°C or higher. In addition, the annealing temperature is 105°C or lower. The annealing temperature lower than the temperatures can also improve a crystalline melting enthalpy.

[0043] The annealing time is preferably 1 minute or more, thereby enabling improvement in crystalline melting enthalpy. The annealing time is more preferably 5 minutes or more, further preferably 10 minutes or more, and further more preferably 15 minutes or more. In addition, the annealing time is preferably 60 minutes or less, thereby enabling reduction in yellowing, odor, and molecular weight loss of the polybutylene adipate terephthalate resin because of polymer degradation and deterioration in annealing. Further, productivity can be improved. The annealing time is more preferably 50 minutes or less.

[0044] After solidification by cooling, the spatial network structure is preferably kept under given temperature in the range of 20°C to 50°C for 1 minute or more before annealing. In annealing treatment, the thickness of the spatial network structure may change in some cases due to its own weight, however, the change in thickness can be reduced by keeping the structure in the range of 20°C to 50°C after cooling. For example, after solidification by cooling in a water tank, the structure may be dried with a continuous dryer which has an first area to keep the structure at relative low temperature and a subsequent area to anneal the structure at relative high temperature.

[0045] The three-dimensional network structure before annealing has a water content of preferably 15% or less, thereby enabling a reduction in degradation of the resin. The water content is more preferably 12% or less, and further preferably 10% or less. The water content is calculated from the following formula. The mass of the three-dimensional network structure after vacuum drying is measured after vacuum drying at 90°C for 2 hours.

[0046] Water content of three-dimensional network structure (%)={(mass of three-dimensional network structure before vacuum drying)-(mass of three-dimensional network structure after vacuum drying)}/(mass of three-dimensional network structure before vacuum drying)×100

[0047] Additives having a deodorant and antibacterial property, an antifungal property, an anti-mite property, an anti-odor property, an aromatic property, a flame-retardant property, and a moisture absorbing/releasing property may be added in any step from the production of the resin to molding steps of the resin for the spatial network structure. In the production process of the spatial network structure, additives for functionalization, such as an antioxidant and a lubricant, may be added to the polybutylene adipate terephthalate resin as a raw material. These may be used alone or in combination. The amount of additives for functionalization may be preferably adjusted depending on the color tone and quality of the resin after being melted while they are being kneaded into a resin in melt extrusion.

[0048] Examples of the antioxidant include known phenol-based antioxidant, phosphite-based antioxidant, thioether-based antioxidant, benzotriazole-based UV absorber, triazine-based UV absorber, benzophenone-based UV absorber, N-H type hindered amine-based light stabilizer, and N-CH_3 type hindered amine-based light stabilizer, and at least one selected from them are preferably contained in the resin.

[0049] Examples of the phenol-based antioxidant include 1,3,5-tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 4,4'-butylidenebis(6-tert-butyl-m-cresol), 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid stearyl, pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], Sumilizer AG 80, and 2,4,6-tris(3',5'-di-tert-butyl-4'-hydroxybenzyl)mesitylene.

[0050] Examples of the phosphite-based antioxidant include 3,9-bis(octadecyloxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecane, 3,9-bis(2,6-di-tert-butyl-4-methylphenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5]undecane, 2,4,8,10-tetrakis(1,1-dimethylethyl)-6-[(2-ethylhexyl)oxy]-12H-dibenzo[d,g][1,3,2]dioxaphosphocin, tris(2,4-di-tert-butylphenyl)phosphite, tris(4-nonylphenyl)phosphite, 4,4'-isopropylidenediphenol C12-15 alcohol phosphite, diphenyl(2-ethylhexyl)phosphite, diphenyl isodecyl phosphite, triisodecyl phosphite, and triphenyl phosphite.

[0051] Examples of the thioether-based antioxidant include bis[3-(dodecylthio)propionate]2,2-bis[[3-(dodecylthio)-1-oxopropyloxy]methyl]-1,3-propanediyl and 3,3'-ditridecyl thiobispropionate.

[0052] In order to prevent thermal degradation of the resin, a phenol-based antioxidant and a phosphite-based antioxidant may be preferably mixed and used. The content of these two types of antioxidants is preferably 0.05% by mass or more and 1.0% by mass or less with respect to 100% by mass of the resin composition.

[0053] Examples of the lubricant include hydrocarbon-based waxes, higher alcohol-based waxes, amide-based waxes, ester-based waxes, and metal soap. The lubricant is added, if needed, at 0.5% by mass or less with respect to 100% by mass of the resin composition on a mass basis.

[0054] The present application claims benefit of priority to Japanese Patent Application No. 2021-058475 filed on March 30, 2021. The entire contents of the specification of Japanese Patent Application No. 2021-058475 filed on March 30, 2021 are incorporated herein by reference.

EXAMPLES

[0055] Hereinafter, the present invention will be specifically described with Examples. However, the scope of the present invention is not limited by the following Examples. The present invention can be carried out with modifications within a range conforming to the gist described above and/or below, and all of which are included in the technical scope of the present invention.

[0056] Measurement and evaluation of the characteristic values of the three-dimensional network structure in Examples from 1 to 7 and Comparative Examples from 1 to 3 were conducted by the following methods. The sample size described below was the standard size for the measurement, however, samples in available size were alternatively used in case of insufficiency in sample numbers.

1. Fiber diameter

[0057] The three-dimensional network structure was cut into the planar size of 10 cm×10 cm, and a linear fiber was collected at the length of about 5 mm from each of ten points of the sample. The diameters of the collected linear fibers were measured with an optical microscope by focusing on the measurement site of the fibers, and the average of the fiber diameters from the ten points was determined (n=10).

2. Hollow rate

[0058] From the three-dimensional network structure, ten linear fibers were randomly collected. Each of the linear fibers was then cut into a round-slicing direction and placed on cover glass in a standing state along the fiber axis. The cross-section of the fiber was observed by an optical microscope. For the observation, only linear fibers each having a hollow cross-section were selected. The area within the perimeter line (a) and the area of hollow region (b) of each fiber were calculated, then the hollow rate was calculated based on the following formula, and the average of the hollow rate of the selected hollow linear fibers was determined.

$$\text{Hollow rate}(\%)=(b)/(a)\times 100$$

3. Thickness and apparent density

[0059] The three-dimensional network structure was cut into the size of 10 cm×10 cm in the longitudinal and transverse directions, and the obtained sample was left standing for 24 hours with no load. After that, the height of the sample was determined by measuring the sample at one center point with a thickness gauge (model: FD-80N, manufactured by Kobunshi Keiki Co., Ltd.), and the height was determined as a thickness of the three-dimensional network structure. Further, the sample was weighed with an electronic balance. The volume of the sample was calculated by multiplying the height and the area of the sample (multiplication of vertical and horizontal length, 100 cm^2), and the apparent density was then determined by dividing the weight of the sample by the volume. The operation was repeated three times, and the averages of the thickness and the apparent density of the three-dimensional network structure were obtained (n=3).

4. Melting point (Tm)

[0060] Samples were collected from the three-dimensional network structure, and weighed to the mass of 2.0 mg±0.1 mg. The measurement was conducted with a differential scanning calorimeter (model: Discovery DSC25, manufactured by TA Instruments) under conditions of a temperature rise rate of 20°C/min and a nitrogen atmosphere. The endothermic peak (melting peak) temperature was determined from the obtained endothermic/exothermic curve. The operation was repeated three times, and the average of the melting point was determined (n=3).

5. Crystalline melting enthalpy

[0061] Samples were collected from the three-dimensional network structure, and weighed to the mass of 2.0 mg±0.1 mg. The measurement was conducted with a differential scanning calorimeter (model: Discovery DSC25, manufactured by TA Instruments) under conditions of a temperature rise rate of 20°C/min and a nitrogen atmosphere. The crystalline melting enthalpy (J/g) was determined from the integration value of the endothermic peak (melting peak) of the obtained endothermic/exothermic curve. The integration value of the endothermic peak (melting peak) was obtained by determining a start point at which the endothermic/exothermic curve with the endothermic peak (melting peak) began to leave from a baseline of a low temperature side and an end point at which the curve began to contact with a baseline of a high temperature side, drawing a straight line connecting the start and end points, and integrating the area enclosed by the line and the curve. The operation was repeated three times, and the average of the crystalline melting enthalpy was determined (n=3). The temperature at the start point was defined as an onset temperature of melting (°C).

6. Melt flow rate (MFR)

[0062] The three-dimensional network structure was cut into small pieces and vacuum dried at 80°C for 2 hours or more. After that, the melt flow rate (MFR) was quickly measured so as to avoid the absorption of water contained in the air by the sample. The measurement was conducted with a melt indexer (model: F-F01, manufactured by Toyoseiki Co., Japan) in accordance with ISO 1133. The measurement temperature was 190°C and the test load was 2.16 kg. The operation was repeated three times, and the average of the melt flow rate was determined (n=3).

7. Weight average molecular weight

[0063] A sample was collected from the three-dimensional network structure in an amount of 40 mg, which is 10 times as much as a sample for usual measurement, cut into small pieces to reduce sample variability, and dissolved into a solvent. The sample solution was diluted with chloroform to adjust the sample concentration to 0.05%. The solution was filtrated through a membrane filter of 0.2 pm, and thus obtained sample solution was analyzed by GPC under the following conditions. The molecular weight was calculated through conversion based on the standard polystyrene.

Apparatus: TOSOH HLC-8320GPC
Column: TSKgel SuperHM-H×2+TSKgel SuperH2000 (TOSOH)
Solvent: chloroform
Flow velocity: 0.6 ml/min
Concentration: 0.05%
Injection volume: 20 pL
Temperature: 40°C
Detector: RI, UV 254 nm
8. 70°C compressive residual strain

[0064] The three-dimensional network structure was cut into the planar size of 10 cm×10 cm, and the thickness (c) of the sample before treatment was measured by the method described in above 2. Then, the sample after the measurement was sandwiched in a tool capable of holding the sample in a 50%-compression state, placed in a dryer set at 70°C, and left standing for 22 hours. After that, the sample was taken out from the dryer and cooled, compression strain of the sample was removed, and the thickness (d) of the sample after 30 minutes of left standing was measured. These values of thickness were applied to the formula of {(c)-(d)}/(c)×100 to determine the 70°C compressive residual strain. The operation was repeated three times, and the average of the 70°C compressive residual strain was determined (n=3).

9. 25%-compression hardness

[0065] The three-dimensional network structure was cut into the planar size of 10 cm×10 cm, and the obtained sample was left standing for 24 hours with no load in an environment of 23°C±2°C. Subsequently, 25%-compression hardness was measured in an environment of 23°C ± 2°C with Autograph (model: AG-X plus, manufactured by Shimadzu Corporation) in accordance with the method E of ISO 2439: 2008. Specifically, a compression board having a diameter (φ) of 50 mm was placed at the center position of the sample, and a thickness at a load of 0.5 N was measured and defined as an initial thickness. The position of the compression board at this time was defined as a zero position. The sample was preliminary compressed to 75% of the initial thickness at a speed of 100 mm/min once, then the compression board was returned to the zero position at the same speed, and the sample was left standing for 4 minutes in that state. After that, the sample was immediately compressed to 25% of the initial thickness at a speed of 100 mm/min, and the load at this time was measured. The measured load was determined as 25%-compression hardness (N/φ50mm). The operation was repeated three times, and the average of the 25%-compression hardness was determined (n=3).

[0066] The polybutylene adipate terephthalate resin of type TH-801 (manufactured by XINJIANG BLUE RIDGE TUNHE CHEMICAL INDUSTRY JOINT STOCK) was used. The resin had a weight average molecular weight of 12.3×10^4 g/mol and a melt flow rate (MFR) of 4 g/10min.

Example 1

[0067] To a nozzle for discharging molten resin, a water tank containing cooling water was disposed in such a manner that the surface of the water was positioned 17 cm below the nozzle face. The temperature of the cooling water was set to 12°C. A pair of take-up conveyors was disposed in the water tank, partially positioned above the surface of the water. Each of the take-up conveyors was equipped with an endless net made of stainless and having a width of 20 cm, and disposed parallel to the width direction of the nozzle face. The width of opening portion between the endless nets (the distance between the endless nets) was 30 mm. Then, aluminum plates were disposed perpendicular to the net direction to form side portions, and water was flown at a rate of 1.0 L/min to mold side portions.

[0068] A nozzle which had an effective surface with lengths in the width direction of 96 mm and in the thickness direction of 31 mm, and round hole shape orifices each with an outer diameter of 0.5 mm and in a staggered arrangement at 6 mm of inter-hole spacing was used as the nozzle for discharging molten resin. The resin raw material was absolutely dried and water was added to it at 0.01% by mass with respect to 100% by mass of the solid content of the resin. After that, the resin was discharged downward from the nozzle at a spinning temperature of 260°C and at a discharge rate from a single hole of 1.0 g/min.

[0069] The molten resin was discharged as filaments in the opening portion between the nets of the conveyers, which is also defined by the nets of the conveyers and the aluminum plates of the side portions. The discharged filaments were in the form of continuous linear bodies and then curled on the surface of the net to a looped shape. The looped shape fibers fused at contact portions thereof and formed spatial network structure. The spatial network structure in a molten state was sandwiched at both faces by the take-up conveyors, drawn into the cooling water at a take-up speed of 0.86 m/min, and solidified to have flattened faces in both the thickness and side directions. After that, the three-dimensional network structure was cut into a predetermined size and left standing for 1 hour in a space set to a temperature of 25°C. Thus obtained spatial network structure had a water content of 9%, and was annealed by drying with hot air at 80°C for 20 minutes to form the three-dimensional network structure having a width of 100 mm. The linear fiber of the three-dimensional network structure had a circular cross-section.

Example 2

[0070] The three-dimensional network structure was obtained in the same manner as Example 1 except that the amount of added water was 0.30% by mass with respect to 100% by mass of the solid content of the resin, a nozzle had triple bridge orifices each of which had an outer diameter of 5.0 mm and an inner diameter of 4.4 mm, was designated to form a hollow cross-section, and was positioned in a staggered arrangement at 8 mm of inter-hole spacing, a spinning temperature was 231°C, a discharge rate from a single hole was 1.5 g/min, a take-up speed was 0.92 m/min, and a drying temperature was 105°C. The linear fiber of the three-dimensional network structure had a hollow cross-sectional shape.

Example 3

[0071] The three-dimensional network structure was obtained in the same manner as Example 2 except that the amount of added water was 0.40% by mass with respect to 100% by mass of the solid content of the resin, a spinning temperature was 230°C, and a drying temperature was 90°C.

Example 4

[0072] The three-dimensional network structure was obtained in the same manner as Example 3 except that the amount of added water was 0.01% by mass with respect to 100% by mass of the solid content of the resin, a spinning temperature was 240°C, and the distance between the nozzle face and the cooling water was 25 cm.

Example 5

[0073] The three-dimensional network structure was obtained in the same manner as Example 1 except that water was not added to the raw material resin after drying, a discharge rate from a single hole was 0.5 g/min, and a take-up speed was 0.64 m/min.

Example 6

[0074] The three-dimensional network structure was obtained in the same manner as Example 3 except that the amount of added water was 0.20% by mass with respect to 100% by mass of the solid content of the resin, a spinning temperature was 190°C, and the distance between the nozzle face and the cooling water was 30 cm.

Example 7

[0075] The three-dimensional network structure was obtained in the same manner as Example 5 except that a spinning temperature was 210°C, a discharge rate from a single hole was 1.0 g/min, and a take-up speed was 1.28 m/min.

Comparative Example 1

[0076] The three-dimensional network structure was obtained in the same manner as Example 1 except that the amount of added water was 2.5% by mass with respect to 100% by mass of the solid content of the resin, a discharge rate from a single hole was 0.9 g/min, the distance between the nozzle face and the cooling water was 18 cm, and a take-up speed was 0.52 m/min.

Comparative Example 2

[0077] The three-dimensional network structure was obtained in the same manner as Example 4 except that the amount of added water was 0.02% by mass with respect to 100% by mass of the solid content of the resin, the resin was dried at a temperature from 20 to 25°C for 2 days, and annealing was not conducted.

Comparative Example 3

[0078] The three-dimensional network structure was obtained in the same manner as Example 2 except that a spinning temperature was 230°C, a take-up speed was 1.54 m/min, and a drying temperature was 107°C.

[0079] Table 1 shows production conditions and the characteristics of the obtained three-dimensional network structure in Examples from 1 to 7 and Comparative Examples from 1 to 3. In Table 1, the characteristics are the average of the values by operations of multiple times.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1	Comparative Example 2	Comparative Example 3
Production step	Amount of added water (% by mass)	0.01	0.30	0.40	0.01	0.00	0.20	0.00	2.50	0.02	0.30
	Spinning temperature (°C)	260	231	230	240	260	190	210	260	240	230
	Discharge rate from a single hole (g/min)	1.0	1.5	1.5	1.5	0.5	1.5	1.0	0.9	1.5	1.5
	Distance between nozzle face and cooling water (cm)	17	17	17	25	17	30	17	18	25	17
	Take-up speed (m/min)	0.86	0.92	0.92	0.92	0.64	0.92	1.28	0.52	0.92	1.54
	Water content in the three-dimensional network structure before annealing (% by mass)	9	10	9	11	12	8	12	16	12	10
	Annealing temperature (°C)	80	105	90	90	80	90	80	80	-	107
	Annealing time (min)	20	20	20	20	20	20	20	20	-	20

(continued)

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1	Comparative Example 2	Comparative Example 3
Three-dimensional network structure	Fiber diameter (mm)	0.63	0.72	0.71	0.90	0.56	0.72	0.75	0.28	0.90	0.75
	Hollow rate (%)	0	2.8	2.7	14.0	0	17.4	0	0	13.8	3.4
	Apparent density (g/cm^3)	0.069	0.060	0.055	0.055	0.053	0.051	0.056	0.044	0.056	0.039
	Thickness (mm)	25.3	23.4	23.9	27.0	25.9	26.3	24.6	28.9	26.8	21.4
	Melt flow rate (MFR) (g/ 10min)	7	22	23	8	6	22	5	71	7	22
	Weight average molecular weight (g/mol)	105000	75000	71000	103000	113000	76000	123000	30000	111000	51000
	Melting point (°C)	119.5	114.0	101.4	110.0	124.5	101.9	124.2	124.5	124.0	112.7
	Onset temperature of melting (°C)	84.8	106.6	93.1	93.4	84.6	94.6	85.3	85.0	87.1	107.0
	Crystalline melting enthalpy (J/g)	20.4	16.0	18.4	21.7	23.5	21.3	22.0	19.6	15.1	14.4
	70° C compressive residual strain (%)	20.1	28.2	19.1	21.1	20.2	16.7	23.5	31.2	38.5	32.1
	25%-compression hardness (N/ φ50mm)	12.7	5.4	8.7	5.5	7.5	8.1	7.6	5.3	4.8	1.8

[0080] The three-dimensional network structure obtained in Examples from 1 to 7 had high compression durability and high compression recovery after heat compression. Further, in Examples from 1 to 6, the polymers had reduced melt viscosity in discharge, thereby allowing the formation of finely looped shape. The obtained three-dimensional network structure had excellent surface and appearance quality.

[0081] The three-dimensional network structure obtained in Comparative Example 1 had a low weight average molecular weight and was inferior in compression recovery after heat compression. In addition, the three-dimensional network structure obtained in Comparative Example 1 was slightly yellowed. This yellowing may be caused due to the effect of high water content in the three-dimensional network structure before annealing.

[0082] The three-dimensional network structure obtained in Comparative Examples 2 and 3 had low crystalline melting enthalpy and were inferior in compression durability and compression recovery after heat compression.

Claims

1. A biodegradable three-dimensional network structure comprising a linear fiber comprising a polybutylene adipate terephthalate resin having a weight average molecular weight of 35000 or more,

   wherein the biodegradable three-dimensional network structure has an apparent density of from 0.005 g/cm^3 to 0.30 g/cm^3 and a thickness of from 10 mm to 100 mm, and
   the linear fiber has a fiber diameter of from 0.2 mm to 2.0 mm and a crystalline melting enthalpy of 16 J/g or more.

2. The biodegradable three-dimensional network structure according to claim 1, wherein the linear fiber has a three-dimensional random looped shape.

3. The biodegradable three-dimensional network structure according to claim 1 or 2, wherein the linear fiber has a crystalline melting enthalpy of 30 J/g or less.

4. The biodegradable three-dimensional network structure according to any one of claims 1 to 3, wherein the biodegradable three-dimensional network structure has an applicability to a cushion.

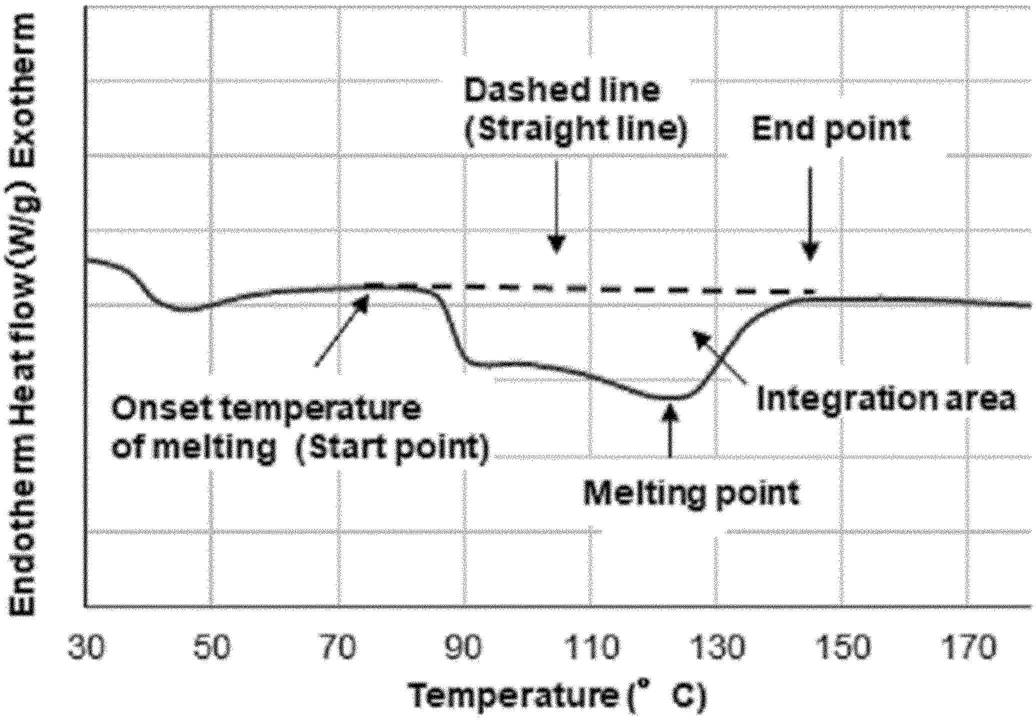
5. The biodegradable three-dimensional network structure according to any one of claims 1 to 4, wherein the polybutylene adipate terephthalate resin has a weight average molecular weight of 150000 or less.

6. The biodegradable three-dimensional network structure according to any one of claims 1 to 5, wherein the linear fiber has a melting point of 100°C or higher and 120°C or lower.

7. The biodegradable three-dimensional network structure according to any one of claims 1 to 6, wherein the linear fiber has a hollow cross-sectional shape.

8. The biodegradable three-dimensional network structure according to claim 7, wherein the linear fiber has a hollow rate of 1% or more and 30% or less.

[Fig. 1]


Endotherm Heat flow(W/g) Exotherm
Dashed line
(Straight line)
End point
Onset temperature
of melting (Start point)
Integration area
Melting point
30
50
70
90
110
130
150
170
Temperature (° C)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/012385

A. CLASSIFICATION OF SUBJECT MATTER

D04H 3/011(2012.01)i; ***A47C 27/22***(2006.01)i; ***D01F 6/62***(2006.01)i; ***D04H 3/16***(2006.01)i
FI: D04H3/011; D01F6/62 305Z; D01F6/62 306C; D01F6/62 306P; A47C27/22 A; D04H3/16 ZBP

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)

D04H1/00-18/04; D01F1/00-6/96; A47C27/00-27/22

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2004-149959 A (TOYO BOSEKI) 27 May 2004 (2004-05-27) claim 1, paragraphs [0001], [0008]-[0015]	1-8
A	JP 2020-128608 A (PANEFURI KOGYO KK) 27 August 2020 (2020-08-27) claims 1-2, 4-5, 10, paragraphs [0022]-[0023], [0033], fig. 1, 2	1-8
A	JP 11-247060 A (DAIWABO CO LTD) 14 September 1999 (1999-09-14) claim 1	1-8
A	US 2014/0065914 A1 (KIMBERLY-CLARK WORLDWIDE, INC.) 06 March 2014 (2014-03-06) claims, paragraphs [0026]-[0080]	1-8
A	US 2013/0309932 A1 (KIMBERLY-CLARK WORLDWIDE, INC.) 21 November 2013 (2013-11-21) claims, paragraphs [0018]-[0079]	1-8
A	JP 2017-132076 A (MASUTANI, Kazunari) 03 August 2017 (2017-08-03) claims 1, 5, paragraphs [0025]-[0032]	1-8

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
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“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 **23 May 2022**	Date of mailing of the international search report **31 May 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/012385

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/196474 A1 (KUREHA CORPORATION) 11 December 2014 (2014-12-11) entire text	1-8

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/012385

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 2004-149959 A	27 May 2004	(Family: none)	
JP 2020-128608 A	27 August 2020	(Family: none)	
JP 11-247060 A	14 September 1999	(Family: none)	
US 2014/0065914 A1	06 March 2014	WO 2008/008068 A1 KR 10-2009-0031799 A	
US 2013/0309932 A1	21 November 2013	US 2011/0059669 A1	
JP 2017-132076 A	03 August 2017	(Family: none)	
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- JP H768061 A **[0038]**
- JP 2021058475 A **[0054]**