



(51) International Patent Classification:

G06T 7/60 (2017.01) G06T 7/277 (2017.01)

G06T 7/73 (2017.01) G06V 10/74 (2022.01)

G06T 7/246 (2017.01) G06V 10/75 (2022.01)

(21) International Application Number:

PCT/US2024/041737

(22) International Filing Date:

09 August 2024 (09.08.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/532,012 10 August 2023 (10.08.2023) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: METHODS OF MAKING AND USING BIOCOMPOSITE COMPOSITIONS

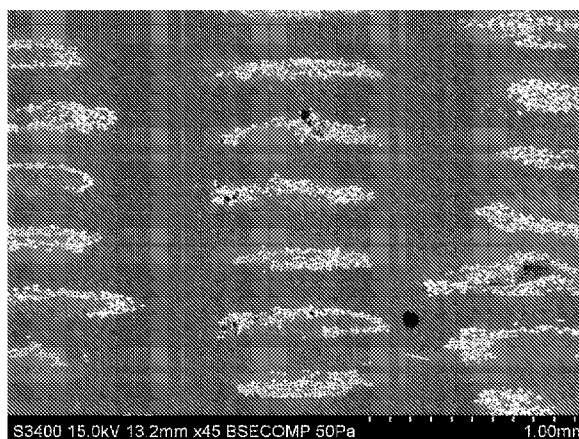


FIG. 1

(57) Abstract: Disclosed herein are methods of making and using biocomposite compositions comprising at least a polymeric component and a fiber component.



METHODS OF MAKING AND USING BIOCOMPOSITE COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims the benefit of U.S. Provisional Application No. 63/532,012, filed on August 10, 2023, which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The present disclosure relates to methods and compositions comprising biocompatible resorbable polymeric biocomposite compositions which may comprise glass, ceramic or mineral-based materials that may be fabricated into medical devices.

BACKGROUND

[0003] Resorbable polymers are known for making biocompatible resorbable articles, many of which are medical devices, including devices that are implanted in a subject. As used in the art and herein, the term resorbable may be used interchangeably with the terms absorbable, bioabsorbable, or biodegradable. Resorbable polymers may be combined with other materials to form a biocomposite composition. An example of a biocomposite composition may comprise resorbable polymers and fillers, such as fibers and/or particulates. For example, fibers of biodegradable glass can be combined with a resorbable polymer composition to form a biocomposite composition.

[0004] Biocomposite compositions and articles made therefrom may have characteristics that are different from those of compositions or articles made only of resorbable polymers. For example, polymeric biocomposites may have mechanical properties, e.g., modulus, strength and stiffness, that are different from those of a composition comprising only resorbable polymers. Biocomposite compositions and articles made from such compositions may differ in a variety of characteristics, which may depend on the type and amount of filler material in the biocomposite composition and/or article.

[0005] What is needed are biocomposite compositions and methods of making and using such biocomposite compositions, such as methods of making and using medical devices comprising

biocomposite compositions, that have characteristics that are effective for one or more applications of medical devices comprising such biocomposite compositions.

SUMMARY

[0006] The present disclosure comprises methods of making and using compositions comprising at least an absorbable polymeric component and a degradable fiber component. Disclosed herein are compositions and articles comprising a biocompatible biodegradable biocomposite, comprising, a continuous thermoplastic matrix, the matrix comprising an absorbable segmented block copolymer comprising at least a majority repeat unit derived from cyclic monomers selected from glycolide, lactide, caprolactone or dioxanone; and a plurality of microfibrinous degradable mineral-containing fibers, wherein the mineral-containing fibers exhibit tensile elongation of less than 5%. A biocomposite may further comprise one or more discrete bioceramic additives, such as β TCP, biphasic calcium phosphate, hydroxyapatite, allograft bone particulate, xenograft bone particulate, calcium phosphate, calcium sulfate, whitlockite, and bioactive glass, or combinations thereof. A discrete bioceramic additive may have a d90 of less than 100 μ m diameter, a d90 of less than 50 μ m diameter, a d90 of less than 20 μ m diameter, or a d90 of less than 10 μ m diameter, or other known d90 diameter bioceramic materials. A continuous thermoplastic matrix copolymer may have an inherent viscosity of greater than 0.9 dL/g; greater than 1.2 dL/g; greater than 1.5 dL/g, or other inherent viscosities that can be functional in disclosed biocomposites. A continuous thermoplastic matrix copolymer may have a melting temperature as measured by DSC of between 50°C and 225°C.

[0007] A biocomposite disclosed herein may have a continuous thermoplastic matrix copolymer with a density of between 0.8 g/cm³ and 1.6 g/cm³. A biocomposite disclosed herein may have microfibrinous degradable mineral-containing fibers that increase the tensile strength of the biocomposite by more than 50% in at least one test orientation. A biocomposite disclosed herein may have microfibrinous degradable mineral-containing fibers that increase the tensile modulus of the biocomposite by more than 50% in at least one test orientation. A biocomposite disclosed herein may have microfibrinous degradable mineral-containing fibers that increase the bending modulus of the biocomposite by more than 50% in at least one test orientation.

[0008] In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space. In an aspect, mineral-containing fibers may be organized into at least two primary directions. In an

aspect, mineral-containing fibers may be organized into 2-dimensional planes, wherein each plane comprises mineral-containing fibers organized in at least one primary direction. In an aspect, mineral-containing fibers may be organized into 2-dimensional planes, which may comprise more than two stacked planes, wherein each plane comprises mineral-containing fibers organized in at least one primary direction.

[0009] In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space and the mineral-containing fibers comprise bundles of mineral-containing fibers. In an aspect, bundles of mineral-containing fiber comprise between 5 and 5,000 fibers. In an aspect, mineral-containing fiber bundles are in the form of a woven, knit, or braided structure. Fiber bundles may be organized to follow a geometric path, and the geometric path may or may not vary in 3 dimensions. In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space wherein continuous mineral-containing fibers are continuously spanning the geometric boundaries of the biocomposite along the geometric path, for example spanning from one edge of the biocomposite to another edge of the biocomposite.

[0010] In an aspect, a biocomposite disclosed herein may comprise variations in density in adjacent meso-scale volumes of greater than 25%, or greater than 50%. In an aspect, a biocomposite disclosed herein may have meso-scale volumes exhibiting density of between 0 g/cm³ and 0.5 g/cm³, density of between 0.5 g/cm³ and 1.5 g/cm³, or density of between 1.5 g/cm³ and 3 g/cm³.

[0011] In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space wherein a primary direction exhibits tensile strength at least more than 100% of a tensile strength in a non-primary direction. In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space wherein a primary direction exhibits tensile modulus of at least more than 100% of a tensile modulus in a non-primary direction. In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space wherein a primary direction exhibits bending modulus of at least more than 100% of a tensile modulus in a non-primary direction.

[0012] In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space and the biocomposite has less than 10% creep in a primary direction at 37°C with 15% breaking stress applied for 24 hours, or less than 10% creep in a primary direction at 37°C with 15% breaking stress applied for 1 week. In an aspect, a biocomposite disclosed herein may have, within the continuous thermoplastic matrix, mineral-containing fibers that are organized in 3-dimensional space wherein the biocomposite has anisotropic performance.

[0013] In an aspect, a disclosed biocomposite may have mineral-containing fibers integrated within the continuous thermoplastic matrix. In an aspect, a disclosed biocomposite may have a continuous thermoplastic matrix copolymer having at least one glass transition temperature of less than 60°C.

[0014] The present disclosure comprises articles made from disclosed biocomposite compositions or biocomposite materials. In an aspect, a disclosed biocomposite article may be made by additive manufacturing methods. In an aspect, a disclosed article may have a total article density that is within 10% of the biocomposite average density of the constituent components, or a disclosed article may have a total article density that is greater than 10% less than the composite average density of the constituent components. Disclosed articles include, but are not limited to, articles that are implantable medical devices. In an aspect, an article may comprise a continuous thermoplastic matrix that degrades in a buffered physiological environment more than 3 months faster than the microfibrinous degradable mineral-containing fibers.

[0015] Methods of making polymeric articles, such as those made with disclosed biocomposites, include known polymeric material manufacturing methods, including but not limited to, compression molding, injection molding, casting, pultrusion, extrusion, filament winding, composite flow molding, machining, weaving, electrospinning, additive manufacturing (3-D printing), and other known methods in the art. For example a method of additive manufacture of a biocomposite article, may comprise a) providing a fiber comprising the biocomposite disclosed herein to a fiber deposition additive manufacturing device, and b) depositing the fiber comprising the biocomposite of Claim 1 on a surface to form a biocomposite article. Such a 3-D printed article may be formed into medical device, such as an implanted medical device.

FIGURES

[0016] FIG. 1 is a scanning electron micrograph (SEM) of a biocomposite comprising degradable mineral-based glass fibers indicating the organized distribution of the mineral-based fibers throughout the biocomposite

DETAILED DESCRIPTION

[0017] Disclosed herein are methods and compositions comprising biocompatible bioresorbable and biodegradable polymeric biocomposites. For example, a disclosed biocomposite may comprise one or more types of resorbable polymers and a degradable fiber reinforcement, such as continuous glass fiber reinforcement. A disclosed biocomposite may comprise one or more types of resorbable polymers and continuous degradable fibers reinforcement, such as degradable continuous glass fiber reinforcement. A disclosed biocomposite may comprise one or more types of resorbable polymers and short and/or long fibers reinforcement, such as short and/or long degradable glass fiber reinforcement. A disclosed biocomposite may comprise one or more types of resorbable polymers and both continuous fibers reinforcement and short and/or long fibers reinforcement, such as degradable glass fibers reinforcement. Each of these and other disclosed biocomposite compositions may further comprise one or more additives.

[0018] As used herein, polymer includes polymers that are homopolymers or copolymers. In an aspect, polymers disclosed herein are absorbable, resorbable, bioabsorbable or bioresorbable, and the terms are interchangeable and refer to polymeric materials that are broken down under physiological conditions and are metabolized by living organisms. Such polymeric material may be used to form a thermoplastic copolymeric matrix. As used herein, continuous glass fibers means degradable or biocompatible glass in a fiber form, and may be referred to herein as degradable mineral-based fibers. Degradable or biocompatible glass, which terms may be used interchangeably, refers to mineral-containing fibers that are generally continuous and microfibrillar in structure. Biocompatible glass breaks down or degrades in physiological conditions, and is generally believed to be excreted from the body. As used herein, degradable mineral-based fibers may be referred to as fibers, fiber bundles, or a fiber which can be understood to mean a plurality of fibers, and is understood by those of skill in the art.

[0019] A fiber-reinforced biocomposite composition disclosed herein may be provided in physical forms such as a solid or a porous solid. In general, a disclosed biocomposite may be initially created as substantially a liquid polymer composition to which fibers, and optionally, additives, are bonded, blended and/or admixed. Fabrication of a medical device or component of a medical

device may comprise providing a liquid form of a disclosed biocomposite, e.g. applying a liquid biocomposite solution (at least one polymer dissolved in at least one organic solvent) coating that solidifies on a surface, or forming a solid form of a disclosed biocomposite, e.g., by molding, solvent casting, melt extrusion, additive manufacturing or other fabrication methods. As used herein, a biocomposite may comprise a liquid or solid physical form, and those of skill in the art can readily ascertain from the context what is intended.

[0020] Disclosed biocomposite compositions may be manufactured to provide desired characteristics to a medical device fabricated therefrom. Components and characteristics of disclosed biocomposites may include, but are not limited to, one or more polymeric components; one or more fiber components; one or more additive components; ratios of polymeric, fiber and optional additive components to one another in a biocomposite composition; ratios of two or more polymers comprising a polymeric component; fiber diameter; ratios of two or more fiber diameters in a fiber component; fiber length, ratios of fiber lengths in a fiber component; arrangement and number of fibers in bundles, filaments or yarns in a biocomposite composition or a fabricated medical device; fiber weight percentage, or ratios of two or more fiber weight percentages; fiber distribution within a biocomposite composition or within all or a portion of fabricated medical device; alignment of fibers within a fiber component or a fabricated medical device; orientation of fibers in a biocomposite or a fabricated medical device; random or no orientation of fibers in a biocomposite or fabricated medical device; pre-processing components; post-processing components or alterations; or combinations of one or more of these. Orientation of a fiber component may provide mechanical benefit by increasing the tensile strength of the matrix, increasing the tensile modulus of the matrix, increasing the bending modulus of the matrix, reducing the elasticity of the matrix, or other mechanical aspects. Measurement of the effect of fiber orientation is easily obtained through standard techniques such as tensile tests, bending tests, compression tests, and other test modes. Tensile testing can be performed in the direction of the fiber orientation, or in a different direction than the direction of fiber orientation. In an aspect, a tensile test to obtain the tensile strength and modulus is performed along the direction of the fiber orientation. In an aspect, a tensile test is performed in a direction orthogonally to the direction of the fiber orientation. In an aspect, the tensile strength and modulus in the direction of fiber orientation are significantly greater than the tensile strength and modulus in the direction orthogonal to the direction of fiber orientation. In an aspect, the tensile strength and modulus are

50% greater in the orientation direction compared to the orthogonal direction, or 100% greater, or 200% greater, or other measured percentages.

[0021] Preparation of a disclosed biocomposite and/or a fabricated medical device therefrom may comprise biocomposite components or processing steps that affect degradation rate; degradation products; device and/or local (close proximity to an implanted device) environmental pH and pH changes, including continuous, fluctuating or increasing/decreasing pH; ion release or attraction by the device and/or the local environment at any time point at implantation or afterwards; pre- and post-processing step effects, e.g. effect of sterilization, heating, rinsing, etc.; additive or other activities, including but not limited to, antimicrobial, anti-inflammatory, antineoplastic, angiogenic, neoplastic, attractant, antagonist, agonist, release rates of active agent(s), osteo- or cellular conductive properties resulting from the device, e.g., from additives or degradation products, and alterations in amounts thereof; surface features for all or a portion of one or more surfaces of a disclosed biocomposite and/or medical device, e.g. surface features or patterns, perforations, notches, indents, raised areas, patterns, etc.; and combinations thereof.

[0022] In an aspect, and optionally to provide specific characteristics in a medical device, a fiber-reinforced biocomposite composition may comprise continuous-fiber reinforcement. A fiber-reinforced biocomposite composition disclosed herein may comprise biocompatible glass fibers, that are continuous, long or short in length, or combinations thereof. A continuous glass fiber-reinforced biocomposite disclosed herein may comprise one or more types of resorbable polymers. A continuous glass fiber-reinforced biocomposite disclosed herein may further comprise one or more additives. In an aspect, a disclosed continuous glass fiber-reinforced biocomposite may have about all or at least a majority of the population of the continuous glass fibers aligned. In an aspect, a disclosed continuous glass fiber-reinforced biocomposite may have about all or at least a majority of the population of the continuous glass fibers randomly aligned, or almost entirely nonaligned. In a biocomposite, continuous glass fibers may be arranged in bundles of fibers or individually arranged, and can be oriented along one or more axes as aligned or not aligned. In a biocomposite, continuous glass fiber bundles can be organized along geometric paths, which can be co-planar with adjacent continuous glass fiber bundles or follow different geometric paths through the biocomposite. In a biocomposite, geometric paths can follow 1-dimensional paths, or 2-dimensional paths, or 3-dimensional paths. In a biocomposite, continuous glass fiber bundles can be organized and placed throughout the composite structure or continuous glass fiber bundles can be organized in regions throughout the biocomposite structure, where different regions contain

different densities of continuous glass fiber bundles. In a biocomposite, different regions can be measured to have different densities depending on the proportion of continuous glass fiber bundles within the region.

[0023] In an aspect, degradable mineral-based fibers are integrated within a thermoplastic copolymeric matrix. It is known in the art to use silane-based chemistries to create the potential for mineral-based fibers to incorporate with a matrix by physical or chemical means. Incorporation of increased amounts of continuous glass fibers within a matrix improves the performance, such as mechanical performance, of a biocomposite. In an aspect, the silane-based sizing on the surface of a mineral-based fiber may allow for integration of the fiber(s) with the copolymeric matrix so as to adhere the two material phases-mineral-based fiber(s) with copolymeric matrix. In an aspect, the silane-based sizing may integrate as part of a crystallite within a copolymeric matrix. In an aspect, the silane-based sizing is not cross-linked or chemically bonded to the copolymeric matrix.

[0024] Biocomposites can be defined by uniformity of structure. In an aspect, included components of a biocomposite can be distributed uniformly throughout the biocomposite structure. In an aspect, a biocomposite may have regions with variations in structure. In an aspect, a biocomposite may vary in regions defined by layers. In an aspect, a biocomposite may vary in regions defined by 3-dimensional volumes. In an aspect, a biocomposite may include regions with 50% included degradable mineral-based fiber components within a matrix and regions containing only polymeric matrix. In an aspect, biocomposite regions having different compositions are adjacent. In an aspect, a biocomposite may include regions defined by differences in degradable mineral-based fiber orientation. In an aspect, biocomposite regions having different degradable mineral-based fiber orientation are adjacent.

[0025] Biocomposite regions can be defined based on size. Micro-scale regions can be described with linear dimensions of between 0.1 and 100 μm , or with volumes between 0.001 μm^3 and 0.001 mm^3 . Meso-scale regions can be described with linear dimensions of between 100 μm and 10 mm, or with volumes between 0.001 mm^3 and 1 cm^3 . Macro-scale regions can be described with linear dimensions larger than 10 mm, or volumes larger than 1 cm^3 .

[0026] In an aspect, disclosed biocomposites comprise a polymeric component and glass fibers, such as degradable mineral-based fibers. Glass is traditionally defined as a random, amorphous material without long range order. As used herein, "glass" includes biocompatible and/or degradable glasses, and can also include glass-ceramic materials. Glass-ceramic materials, such as fibers of glass-ceramic materials, include formulations that through thermal treatment have a

portion of the morphological structure where constituents organize into crystallites. Glass compositions are based primarily on silica, boron, or phosphate network formers, whereby the silica composition is greater than 60% of the composition. The network former is combined with alkali or alkali earth network modifiers including, but not limited to, calcium, magnesium, potassium and sodium. The subject glass compositions are processable to fibers easily using historical techniques and technology of the standard art. As a function of the glass composition, biocompatible and degradable glass fibers can have variable degradation time and ion release profiles. As a consequence, biocompatible and degradable glass fibers, and the filaments that comprise them, can have varied levels of bioactivity. A biocompatible and biodegradable glass fiber was developed by Timo Lehtonen about 15 years ago.

[0027] As a function of the components of the glass composition, biocompatible and degradable glass fibers can have variable ion release profiles and different ion types can be released from the glass composition that can have therapeutic, antimicrobial, anti-inflammatory, and/or angiogenic effects for the surrounding tissues. For example, ions of some metals have been found to have anti-inflammatory effects on local tissue, e.g. lithium ions, +Li. Copper ions have been found to have angiogenic effects. Silver ions have been found to be antimicrobial, and are effective at infection prevention and resolution of an infection. These are sometimes referred to as “therapeutic ions”.

[0028] A disclosed biocomposite comprises a polymeric component, wherein the polymeric component forms a matrix for a fiber component. A matrix polymeric component's mechanical characteristics can comprise one or more polymers having chemical constituents resulting in a variety of stiff to compliant (more flexible) polymers. In an aspect, a disclosed biocomposite composition comprises a compliant absorbable polymer such that the polymeric matrix, comprising the compliant absorbable polymer, of the biocomposite composition does not significantly restrict the fabrication of a medical device capable of mating with or corresponding to one or more anatomical structures when implanted for the intended application. In an aspect, a disclosed biocomposite composition comprises a continuous matrix, where the matrix supports the general structure and geometry of the composition and retains the fiber components within the biocomposite structure. In an aspect, the matrix comprises a thermoplastic polymer.

[0029] A disclosed biocomposite, which may be referred to herein as a biocomposite composition, comprises a polymeric component, comprising one or more types of polymers. In an aspect, a disclosed biocomposite composition comprises a bioresorbable polymeric component, comprising

one or more types of bioresorbable polymers. Biocomposite compositions may comprise one or more bioabsorbable polymers. A bioresorbable polymer may be a homopolymer or a copolymer, wherein a copolymer includes two or more different monomers, including, but not limited to a random copolymer, a block copolymer, a graft copolymer, a linear polymer, a branched polymer, or a dendrimer. Bioresorbable polymers may be of natural or synthetic origin. Examples of bioresorbable polymers include, but are not limited to, polymers made from lactide, glycolide, caprolactone, valerolactone, carbonates (e.g., trimethylene carbonate, tetramethylene carbonate, etc.), dioxanones (e.g., 1,4-dioxanone), δ -valerolactone, 1,4-dioxepanones, e.g., 1,4-dioxepan-2-one and 1,5-dioxepan-2-one), ethylene glycol, ethylene oxide, esteramides, γ -hydroxyvalerate, β -hydroxypropionate, α -hydroxy acid, hydroxybuterates, poly (ortho esters), hydroxy alkanates, tyrosine carbonates, polyimide carbonates, polyimino carbonates such as poly (bisphenol A-iminocarbonate) and poly (hydroquinone-iminocarbonate), polyurethanes, polyanhydrides, polymer drugs (e.g., polydiflunisol, polyaspirin, and protein therapeutics, and copolymers and combinations thereof. Biologically-derived biodegradable polymers include, but are not limited to, collagen, chitin, chitosan, cellulose, poly (amino acids), polysaccharides, hyaluronic acid, gut, and copolymers, derivatives and combinations thereof.

[0030] A disclosed biocomposite composition may comprise bioresorbable polymers, including, but not limited to, polylactides (PLA), poly-L-lactide (PLLA), poly-DL-lactide (PDLLA); polyglycolide (PGA); copolymers of glycolide, glycolide/trimethylene carbonate copolymers (PGA/TMC); other copolymers of PLA, such as lactide/tetramethylglycolide copolymers, lactide/trimethylene carbonate copolymers, lactide/d-valerolactone copolymers, lactide/ ϵ -caprolactone copolymers, L-lactide/DL-lactide copolymers, glycolide/L-lactide copolymers (PGA/PLLA), polylactide-co-glycolide; terpolymers of PLA, such as lactide/glycolide/trimethylene carbonate terpolymers, lactide/ ϵ -caprolactone/trimethylene carbonate terpolymers, lactide/glycolide/ ϵ -caprolactone terpolymers, polydioxinone homopolymers and copolymers, glycolide/ ϵ -caprolactone/trimethylene carbonate terpolymers, PLA/polyethylene oxide copolymers; polydepsipeptides; unsymmetrically—3,6-substituted poly-1,4-dioxane-2,5-diones; polyhydroxyalkanoates; such as polyhydroxybutyrates (PHB); PHB/b-hydroxyvalerate copolymers (PHB/PHV); poly-b-hydroxypropionate (PHPA); poly-p-dioxanone (PDS); poly-d-valerolactone-poly- ϵ -caprolactone, poly(ϵ -caprolactone-DL-lactide) copolymers; methylmethacrylate-N-vinyl pyrrolidone copolymers; polyesteramides; polyesters of oxalic acid; polydihydropyrans; polyalkyl-2-cyanoacrylates; polyurethanes (PU); polyvinylalcohol (PVA);

polypeptides; poly-b-malic acid (PMLA); poly-b-alkanbic acids; polycarbonates; polyorthoesters; polyphosphates; poly(ester anhydrides); and mixtures thereof; and natural polymers, such as sugars; starch, cellulose and cellulose derivatives, polysaccharides, collagen, chitosan, fibrin, hyaluronic acid, polypeptides, silk, and proteins. A disclosed biocomposite composition may comprise mixtures, admixtures or combinations of synthetic and biologically-derived (i.e., natural) polymers, copolymers, and derivatives of the bioresorbable polymers disclosed herein and those known to those of skill in the art.

[0031] In an aspect, a disclosed biocomposite comprises a fiber component, wherein the fiber component is integrated, admixed, blended or bonded with at least a portion of the one or more polymeric component(s) of the biocomposite. A fiber component may be comprised of organic or inorganic material, or natural or synthetic material. A fiber component may be biodegradable glass, or fibers may be made from resorbable polymers such as those disclosed herein, natural polymers, such as sugars; starch, cellulose and cellulose derivatives, polysaccharides, collagen, chitosan, fibrin, hyaluronic acid, polypeptides, silk, and proteins. A function of a fiber component may be to provide strength and stiffness to a polymeric matrix.

[0032] In an aspect, a lactide-based copolymer may bioresorb or biodegrade, as measured by mass loss, over a period of 1 to 3 years. In an aspect, a polydioxanone polymer may bioresorb, as measured by mass loss, over a period of 6 to 12 months. In an aspect, a glycolide-based copolymer may bioresorb, as measured by mass loss, over a period of 2 to 6 months.

[0033] A fiber component may comprise biodegradable glass fibers comprising silica-based mineral compound. An example of such a biodegradable glass may comprise the following ranges: (mol.%)

[0034] Na_2O : 11.0-19.0

[0035] CaO : 9.0-14.0

[0036] MgO : 1.5-8.0

[0037] B_2O_3 : 0.5-3.0

[0038] Al_2O_3 : 0-0.8

[0039] P_2O_3 : 0.1-0.8 and

[0040] SiO_2 : 67-73; or

[0041] Na_2O : 12.0-13.0

[0042] CaO : 9.0-10.0

[0043] MgO : 7.0-8.0

[0044] B_2O_3 : 1.4-2.0

[0045] P_2O_5 : 0.5-0.8, and

[0046] SiO_2 : 68-70.

[0047] In an aspect, biodegradable glass fibers may biodegrade, as measured by mass loss, over a period of between 1 and 4 years.

[0048] US Patent No. 10,869,954 references one such composition that is referenced as “NX-8” and cited as being disclosed in the article by Lehtonen (*Acta Biomaterialia* 9 (2013) 4868-4877). Glass fiber compositions processed by standard art techniques and technologies are known in the art, other glass fiber compositions are known in the art, and the present disclosure includes glass compositions known to those of skill in the art.

[0049] In an aspect, a disclosed biocomposite composition optionally comprises one or more additive components. An additive may be an active agent, including but not limited to, a pharmaceutical, one or more biologic molecules; osteoconductive material; osteoinductive material; osteogenic material; inorganic material; beta tricalcium phosphate (bTCP); calcium phosphate; hydroxyapatite; biphasic calcium phosphate; calcium sulfate; decellularized bone; bone morphological proteins; antimicrobial agents, antifungal agents; antineoplastic agents; antibodies; antibody fragments; agonists; antagonists; angiogenic agents; cellular attractants; ion releasing agents; ion absorbing agents; particulates such as bTCP, glass, salt; receptors; receptor blocking agents; other known active agents; and combinations and mixtures thereof. An additive may take the form of an insoluble particulate, which can remain as discrete dispersed particles that may or may not agglomerate when dispersed throughout a matrix. In an aspect, additives in the form of insoluble particulate can be defined by their shape and/or their size. In an aspect, particulate size can be defined in terms of apparent diameter and aspect ratio. Common analytical techniques to describe particulate are found in ASTM E2651 -- Standard Guide for Powder Particle Size Analysis. In an aspect, additive particle sizes are defined by apparent diameter, for example d50 (the length dimension of which half of the particulate is smaller), d90 (the length dimension of which 90% of the particulate is smaller), or d95 (the length dimension of which 95% of the particulate is smaller).

[0050] In an aspect, a disclosed biocomposite composition comprises physical properties. The density of a disclosed biocomposite composition may be from about 1 g/mL to about 5 g/mL, from about 1.3 g/mL to about 4 g/mL; from about 1.3 g/mL to about 3 g/mL; from about 1.3 g/mL to about 2.5 g/mL; from about 1.3 g/mL to about 2 g/mL; from about 1.3 g/mL to about 1.5 g/mL;

and all amounts thereinbetween. The wt% of inorganic material, for example glass fiber, glass-ceramic fiber, and/or ceramic additives, of a disclosed biocomposite composition may be 0%; in a range from about 0.5% to about 99.5%; from about 5.0% to about 99.5%; from about 10.0% to about 98%; from about 10% to about 95%; from about 20% to about 95%; from about 30% to about 95%; from about 40% to about 90%; from about 50%; and all amounts thereinbetween. A disclosed solid biocomposite composition may have porosity, for example porosity of less than 15%; no porosity (0%), or in a range of from about 0.1% to about 14.5%; from about 0.1% to about 12%; from about 0.1% to about 10%; from about 0.1% to about 5.0%; from about 0.1% to about 3.0%; from about 0.1% to about 2%; from about 0.1% to about 1.0%; from about 0% to about 75%; from about 0% to about 50%; from about 0% to about 95%; from about 0% to about 25%; and all amounts thereinbetween. A disclosed solid biocomposite composition may have porosity, for example porosity of 75% or less; no porosity (0%), or in a range of from about 0.1% to about 75%; from about 0.1% to about 70%; from about 0.1% to about 65%; from about 0.1% to about 60%; from about 0.1% to about 55%; from about 0.1% to about 50%; from about 0.1% to about 45%; from about 0.1% to about 40%; from about 0.1% to about 35%; from about 0.1% to about 30%; from about 0.1% to about 25%; from about 0.1% to about 20%; from about 0.1% to about 15%; and all amounts thereinbetween. A disclosed solid biocomposite composition may comprise at least one polymer having a molecular weight of greater than 0.6 dL/g; or in a range from about 0.6 dL/g to about 5 dL/g; from about 0.6 dL/g to about 4 dL/g; from about 1.0 dL/g to about 3 dL/g; from about 1.0 dL/g to about 5 dL/g; from about 2 dL/g to about 3 dL/g; and all amounts therein. Molecular weight can be measured by dilute solution inherent viscosity at a 0.10 mg/mL concentration in a suitable solvent, e.g., chloroform or hexafluoroisopropanol, at 20°C, according to ASTM D2857. In an aspect, molecular weight is useful to determine processability of a polymer. Polymers used as coatings or in sizing processes typically have a lower molecular weight, for example less than about 0.6 dL/g, and are easily applied through solvent-mediated or heat-mediated coating processes. Polymers having higher molecular weight, for example more than about 0.9 dL/g, are useful to create solid objects through extrusion or molding. Polymers having higher molecular weight exhibit relatively higher melting viscosity due to reduced chain mobility; however, increased process temperatures may be used to reduce the melt viscosity during processing. In general, high viscosity polymers are difficult to apply as fiber coatings due to their relatively high melt viscosity. In the case of absorbable polymers, thermal processes exhibit an

upper temperature limit above which the polymer degrades, and thereby limits the ability of a high viscosity absorbable polymer to be used in heat-mediated coating processes.

[0051] A fiber component of a disclosed biocomposite composition may be comprised of glass filaments. A glass filament may have a diameter in a range of from about 3 microns to about 50 microns; from about 5 microns to about 45 microns; from about 5 microns to about 30 microns; from about 10 microns to about 40 microns; from about 10 microns to about 20 microns; from about 5 microns to about 20 microns; and all amounts thereinbetween. A glass fiber component may have a glass fiber aspect ratio of the length to diameter aspect ratio of about 10:1; of about 100:1, of about 10,000 to 1; of about 50,000:1, or may be a continuous glass fiber. In an aspect, these lengths may be understood by those of skill in the art to be referred to as short, medium, long or continuous glass fibers. A fiber component of a disclosed biocomposite composition may be oriented. For example, a biocomposite composition may have continuous glass fibers that are oriented in at least a first direction, wherein at least 5 fibers are colinear along the path of the first direction; or wherein at least 100 fibers are colinear along the path of that first direction, or wherein at least 250 glass fibers are colinear along the path of the first direction, or wherein at least 500 glass fibers are colinear along the path of the first direction. A first or any other orienting directions may be linear, planar, helical, or hemispherical or the direction may be defined by a predetermined geometric path, for example, a 1) knit pattern of a textile product (knitted, woven) or 2) predetermined pattern or program to produce a braid (pics per inch, number of carriers) or 3) layup configuration for a 3D printed article or 4) a layup pattern for producing a solid body using an at least two-axis method of winding and bonding of the colinear pathways to produce a predetermined structural configuration. In an aspect, a biocomposite composition may have fibers that are oriented in a first direction, i.e. a primary direction of reinforcement, and in a second direction, i.e. a second primary direction of reinforcement, wherein at least 5 fibers are colinear along the path of the second direction; or wherein at least 100 fibers are colinear along the path of that second direction, or wherein at least 250 glass fibers are colinear along the path of the second direction, or wherein at least 500 glass fibers are colinear along the path of the second direction. There may be further and similar orientation of fibers in a third, fourth, fifth, and more orientation directions.

[0052] A disclosed biocomposite composition may have mechanical properties. In an aspect, a biocomposite composition may comprise tensile strength of greater than 500 MPa, or in a range from about 500 MPa to about 4.0 GPa; from about 600 MPa to about 3.5 Gpa; from about 500

MPa to about 3.0 GPa; from about 700 MPa to about 3.5 GPa; from about 800 MPa to about 3.5 GPa; from about 500 MPa to about 2.0 GPa; and all amounts thereinbetween. In an aspect, a biocomposite composition may comprise tensile modulus of greater than 10 GPa; or in a range from about 20 GPa to about 70 GPa; from about 10 GPa to about 70 GPa; from about 20 GPa to about 60 GPa; from about 10 GPa to about 50 GPa; from about 10 GPa to about 40 GPa; and all amounts thereinbetween. In an aspect, a biocomposite composition may comprise ultimate elongation of less than 15%; or in a range from about 0.5% to about 14.9%; from about 1.0% to about 10%; from about 0.5% to about 7%; from about 0.5% to about 5%; from about 1.0% to about 5%; and all amounts thereinbetween.

[0053] A disclosed biocomposite composition may have thermo-mechanical properties. In an aspect, a biocomposite composition may comprise a glass transition temperature (T_g) that is increased compared to a similar composition comprising no fiber component, e.g., comprising the same polymeric component without a fiber component, an unreinforced matrix polymeric component. The glass transition temperature increases at least 3°C compared to a composition comprising the same, but unreinforced matrix, polymeric component. The glass transition temperature increases at least 5°C compared to a composition comprising the same, but unreinforced matrix, polymeric component. In an aspect, a biocomposite composition may comprise a storage modulus plateau prior to the inflection point associated with the T_g . The storage modulus plateau below the T_g is at least 10% greater than a similar composition comprising no fiber component, e.g., comprising the same polymeric component without a fiber component, an unreinforced matrix polymeric component. The storage modulus plateau below the T_g is at least 15% greater than a similar composition comprising no fiber component, e.g., comprising the same polymeric component without a fiber component, an unreinforced matrix polymeric component. The storage modulus plateau below the T_g is at least 20% greater than a similar composition comprising no fiber component, e.g., comprising the same polymeric component without a fiber component, an unreinforced matrix polymeric component. The storage modulus plateau below the T_g is at least 25% greater than a similar composition comprising no fiber component, e.g., comprising the same polymeric component without a fiber component, an unreinforced matrix polymeric component. The storage modulus plateau below the T_g is at least 30% greater than a similar composition comprising no fiber component, e.g., comprising the same polymeric component without a fiber component, an unreinforced matrix polymeric component. In an aspect, a biocomposite composition may comprise minor shrinkage characteristics. In an aspect, a

biocomposite composition may exhibit a Tg of less than 60°C. In an aspect, an article prepared from a biocomposite composition may be shaped by heating the article above the Tg and forming into a shape, including shaping to approximate the curvature of a physiological or body structure. In an aspect, the shape is dimensionally stable at body temperature (37°C) after shaping. In an aspect, the physiological structure may include a bone such as the mandible, maxilla, cranium, vertebrae, phalanges, and others.

[0054] A disclosed biocomposite composition may have creep properties. In an aspect, a disclosed biocomposite composition may comprise constant stress linear deformation such that the application of a load that applies constant stress representing 20% of the yield strength results in less than 15% change in length after 48 hours, at temperatures above physiologic temperature (37°C). In an aspect, a disclosed biocomposite composition may comprise constant stress linear deformation such that the application of a load that applies constant stress representing 20% of the yield strength results in less than 15% change in length after 48 hours, at temperatures above physiologic temperature (37°C). In an aspect, a biocomposite may have creep performance that varies in different test directions. In an aspect, a biocomposite may exhibit lower creep along a primary direction of fiber reinforcement compared to higher creep in a direction that is not along a primary direction of fiber reinforcement.

[0055] A disclosed biocomposite composition may be manufactured or formed onto in a geometry suitable for use as an implanted medical device. In an aspect, the geometry may include, but is not limited to, plates, grafts, pins, rods, spacers, and fillers. In an aspect, the geometry of the device is defined in part by the outer surfaces of the device. In an aspect, continuous glass fiber(s) span the full length of the device geometry in a primary direction of reinforcement.

[0056] In an aspect, biocomposite compositions of the present disclosure may comprise

[0057] Round glass fiber

[0058] Round glass fiber coated with a resorbable polymeric matrix

[0059] Round glass composite fiber with resorbable polymeric matrix with one or more particulate additive, e.g. bTCP, glass, salt or other additives disclosed herein

[0060] Flat glass fiber

[0061] Flat glass fiber combined to form a round composite fiber bundle

[0062] Round composite fiber useful for additive manufacturing methods

[0063] 3D printed part having open, fully connected porosity

- [0064] Biocomposite composition comprising different porosity shapes, with pore size between 100 – 5,000 um
- [0065] 3d printed part having layers that have between 50 – 500 micron layer thickness
- [0066] Surface has fully open porosity that is the same as the contents of the 3d printed object
- [0067] Lightly coated material that is flexible, and braided into a suture, cerclage cable,
- [0068] Lightly coated material that is flexible, and used as a core in a suture, cerclage cable
- [0069] Lightly coated material that is flexible, and knit or woven into a mesh
- [0070] Coated material that is rigid, and woven into a composite reinforced mesh
- [0071] Mesh that is one layer or multiple layers, or flat or 3 dimensional.
- [0072] Monofilament fiber used as core for a polymeric braid
- [0073] Block spacer for vertebral fusion in standard sizes
- [0074] 3D printed plate flat plate with pre-drilled holes, strategically optimized and lightweighted to reduce total implanted mass based on FEA (finite element analysis)
- [0075] Overbraid wrapping of an article with glass fiber or coated glass fiber
- [0076] Stent made from biocomposite wherein the glass fiber is in a wrapped configuration about the perimeter of the stent in at least one primary direction
- [0077] Stent made from biocomposite wherein the biocomposite containing glass fiber forms the stent structure through a braiding process.
- [0078] Stent made from biocomposite wherein the biocomposite containing glass fiber is aligned primarily or in part in the direction of the stent axis
- [0079] Hernia mesh made from biocomposite composition
- [0080] Compositions of the present disclosure may include medical devices fabricated from disclosed biocomposite compositions.
- [0081] Medical devices may include, but are not limited to,
- [0082] 1) Load-bearing medical implant devices, including but not limited to, bone plates, rods, screws, tacks, nails, clamps, and pins for the fixation of bone fractures and/or to immobilize bone fragments, cervical wedges, lumbar cages, plates and screws for use in spinal surgery, bone fixation plates, intramedullary nails, joint (hip, knee, elbow) implants, spine implants, and other devices for such applications such as for fracture fixation, tendon reattachment, spinal fixation, and spinal cages,
- [0083] 2) mesh, woven mesh
- [0084] 3) tape

[0085] Methods of making biocomposite compositions are found in the Examples. Methods of fabricating articles, including but not limited to, medical devices from biocomposite compositions are known in the art, and may comprise compression molding, injection molding, casting, pultrusion, extrusion, filament winding, composite flow molding, machining, weaving, electrospinning, additive manufacturing (3-D printing), and other known methods in the art. A resulting article, or medical device, may be isotropic or anisotropic. For example, an article can be formed from a biocomposite composition, and that article may be referred to as a biocomposite. The article can be a medical device, such as an implantable medical device that is used in applications for treating subjects. A disclosed method herein comprises additive manufacturing methods wherein a biocomposite composition, shaped for filament deposition additive manufacturing, is "printed" or provided to a surface, to form an article comprising the biocomposite composition having predetermined characteristics, such as those disclosed herein.

Kits

[0086] The present disclosure comprises a kit comprising a biocomposite composition or components of a biocomposite composition disclosed herein, optionally, contained within a container and optionally, further comprising written instructions for its use or manufacture.

Definitions

[0087] As used herein, nomenclature for compounds, including organic compounds, can be given using common names, IUPAC, IUBMB, or CAS recommendations for nomenclature. When one or more stereochemical features are present, Cahn-Ingold-Prelog rules for stereochemistry can be employed to designate stereochemical priority, *EIZ* specification, and the like. One of skill in the art can readily ascertain the structure of a compound if given a name, either by systemic reduction of the compound structure using naming conventions, or by commercially available software, such as CHEMDRAW™ (Cambridgesoft Corporation, U.S.A.).

[0088] As used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a functional group," "an alkyl," or "a residue" includes mixtures of two or more such functional groups, alkyls, or residues, and the like.

[0089] References in the specification and concluding claims to parts by weight of a particular element or component in a composition denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of

component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0090] A weight percent (wt. %) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0091] As used herein, when a compound is referred to as a monomer or a compound, it is understood that this is not interpreted as one molecule or one compound. For example, two monomers generally refers to two different monomers, and not two molecules.

[0092] As used herein, the terms "optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0093] As used herein, the terms "about," "approximate," and "at or about" mean that the amount or value in question can be the exact value designated or a value that provides equivalent results or effects as recited in the claims or taught herein. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art such that equivalent results or effects are obtained. In some circumstances, the value that provides equivalent results or effects cannot be reasonably determined. In such cases, it is generally understood, as used herein, that "about" and "at or about" mean the nominal value indicated $\pm 10\%$ variation unless otherwise indicated or inferred. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about," "approximate," or "at or about" whether or not expressly stated to be such. It is understood that where "about," "approximate," or "at or about" is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0094] As used herein, the term "subject" can be a vertebrate, such as a mammal, a fish, a bird, a reptile, or an amphibian. Thus, the subject of the herein disclosed methods can be a human, non-human primate, horse, pig, rabbit, dog, sheep, goat, cow, cat, guinea pig or rodent. The term does not denote a particular age or sex. Thus, adult and newborn subjects, as well as fetuses, whether male or female, are intended to be covered. In an aspect, a mammalian subject is a human. The term "patient" includes human and veterinary subjects.

[0095] As used herein, the terms "administering" and "administration" refer to any method of providing a disclosed composition to a subject.

[0096] As used herein, the terms "comprises," "comprising," "includes," "including," "containing," "characterized by," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. The term "comprising" may also include the limitations associated with the use of "consisting of" or "consisting essentially of".

[0097] The transitional phrase "consisting of" excludes any element, step, or ingredient not specified in the claim, closing the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

[0098] The transitional phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps and those that do not materially affect the basic and novel characteristic(s) of the claimed invention. A "consisting essentially of" claim occupies a middle ground between closed claims that are written in a "consisting of" format and fully open claims that are drafted in a "comprising" format. Optional additives as defined herein, at a level that is appropriate for such additives, and minor impurities are not excluded from a composition by the term "consisting essentially of".

[0099] When a composition, a process, a structure, or a portion of a composition, a process, or a structure, is described herein using an open-ended term such as "comprising," unless otherwise stated the description also includes an embodiment that "consists essentially of" or "consists of" the elements of the composition, the process, the structure, or the portion of the composition, the process, or the structure.

[0100] The articles "a" and "an" may be employed in connection with various elements and components of compositions, processes or structures described herein. This is merely for convenience and to give a general sense of the compositions, processes or structures. Such a description includes "one or at least one" of the elements or components. Moreover, as used herein, the singular articles also include a description of a plurality of elements or components, unless it is apparent from a specific context that the plural is excluded.

[0101] The term "about" means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is "about" or "approximate" whether or not expressly stated to be such.

[0102] The term "or", as used herein, is inclusive; that is, the phrase "A or B" means "A, B, or both A and B". More specifically, a condition "A or B" is satisfied by any one of the following: A is true (or present) and B is false (or not present); A is false (or not present) and B is true (or present); or both A and B are true (or present). Exclusive "or" is designated herein by terms such as "either A or B" and "one of A or B", for example.

[0103] In addition, the ranges set forth herein include their endpoints unless expressly stated otherwise. Further, when an amount, concentration, or other value or parameter is given as a range, one or more preferred ranges or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether such pairs are separately disclosed. The scope of the invention is not limited to the specific values recited when defining a range.

[0104] When materials, methods, or machinery are described herein with the term "known to those of skill in the art", "conventional" or a synonymous word or phrase, the term signifies that materials, methods, and machinery that are conventional at the time of filing the present application are encompassed by this description. Also encompassed are materials, methods, and machinery that are not presently conventional, but that will have become recognized in the art as suitable for a similar purpose.

[0105] Unless stated otherwise, all percentages, parts, ratios, and like amounts, are defined by weight.

[0106] All patents, patent applications and references included herein are specifically incorporated by reference in their entireties.

[0107] It should be understood, of course, that the foregoing relates only to preferred embodiments of the present disclosure and that numerous modifications or alterations may be made therein without departing from the spirit and the scope of the disclosure as set forth in this disclosure.

[0108] The present disclosure is further illustrated by the examples contained herein, which are not to be construed in any way as imposing limitations upon the scope thereof. On the contrary, it is to be clearly understood that resort may be had to various other embodiments, modifications, and equivalents thereof which, after reading the description herein, may suggest themselves to those skilled in the art without departing from the spirit of the present disclosure and/or the scope of the appended claims.

EXAMPLES

[0109] Example 1: An intermediate of a mixed-fiber bundle that is consolidated to a strand comprised of glass filaments and absorbable polymer (I-1)

[0110] A consolidated mixed fiber strand intermediate can be produced by first physically mixing absorbable polymer multifilament fibers with a bundle of biocompatible and degradable glass fiber, consisting of a plurality of glass filaments. The glass filaments are treated with a 0.5% by weight of a silane based-sizing or coupling agent during glass fiber manufacturing. An absorbable polymer can be covalently linked to the coupling agent and acted as a compatibilizer. The absorbable fiber can be spun from a copolymer of polylactide, TMC, and caprolactone with a molar ratio of 74/15/11, respectively. The absorbable fiber may have a glass transition temperature below room temperature and a molecular weight the corresponded to an η_{sp}/c of 2.0 dL/g. The physical mixing of polymer and glass fibers is accomplished by combining 86 filaments of the absorbable polymer with approximately 190 glass filaments. Glass filaments with at least 60% silica network former are processable to fibers easily using historical techniques and technology of the standard art. The linear density of the absorbable polymer fibers and the glass fibers may be approximately 39 tex and 24 tex, respectively. The mixed fiber bundle is created by first spreading the polymer and glass fibers separately by dragging the fiber over several 15mm diameter pins under controlled tension conditions. Once the fibers are adequately spread to an approximate single layer of filaments, the two warps are combined into a single bundle. The mixed fiber bundle will be subsequently spread over pins and combined back into a bundle using a series of pins and eyelet guides until the two fiber types are homogenized and randomly oriented with respect to the cross-section. The fully homogenized bundle is wound up onto a spool.

[0111] In a subsequent operation, the mixed fiber bundle is unwound from the spool and pulled through a series of three dies. The dies are heated to melt the absorbable polymer and size the strand outer diameter. The round dies may consist of three different diameters, each with a

different temperature setting. The temperature of the first die is set to 20°C below the melt temperature of the polymer and may have a diameter of 0.45 mm. The second die is set to the melt temperature of the polymer and may have a diameter of 0.25 mm. The final sizing die is set to a temperature of 40°C above the melt temperature of the polymer and the diameter may be 0.18 mm. The mixed fiber bundle is fully consolidated with a high degree of wetting and low porosity. The consolidated composite strand may possess a loading of 38% glass fibers by weight and would be compliant due to its small diameter and the low glass transition temperature of absorbable polymer. The consolidated mixed fiber strand is then taken up onto a spool for storage. Storage conditions are at room temperature under reduced pressure.

[0112] Example 2: An intermediate of a monofilament comprised of glass filaments and absorbable polymer (I-2)

[0113] A consolidated glass fiber reinforced monofilament was produced by the pultrusion process, where biocompatible and degradable glass fibers were pulled through a crosshead die that is fed with an absorbable polymer melt. The glass filaments are oriented in a primary direction along the axis of the monofilament. The glass filaments were treated with a 0.8% by weight of a silane based-sizing or coupling agent during glass fiber manufacturing. An absorbable polymer was covalently linked to the coupling agent and act as a compatibilizer. The absorbable polymer was polydioxanone with a starting η_{sp}/c of 1.8 dL/g. The polymer and glass fibers entered the crosshead die through different entrance points. The glass fiber consisted of approximately 290 filaments. Glass filaments with at least 60% silica network former are processable to fibers easily using historical techniques and technology of the standard art. Inside the crosshead die the glass fibers were wetted by the molten polymer and exited the die through a sized circular opening. The die opening was 0.48mm in diameter. The glass fiber reinforced monofilament exited the crosshead die and was immediately cooled using a temperature-controlled water bath set to 10°C. The cooled monofilament was subjected to an air knife to remove surface water as it exited the water bath. The glass fiber to polymer ratio was approximately 30/70 by weight, respectively. The density of the monofilament was about 1.7 g/cm³. The monofilament was then taken up onto a spool for storage. Storage conditions were at room temperature under reduced pressure.

[0114] Example 3: An intermediate of a glass fiber coated with an absorbable polymer (I-3)

[0115] A coated glass fiber multifilament was produced by applying an absorbable polymer from solvent, where biocompatible and degradable glass filaments were simultaneously

pulled, spread, and immersed in a solvent/polymer solution. The solution consisted of 8 grams of polymer per 100 mL of solvent. The absorbable polymer was a copolymer of lactide, TMC, and caprolactone with a molar ratio of 74/15/11, respectively. The polymer had a molecular weight that corresponds to an IhV of 1.6 dL/g. The glass filaments were treated with a 0.7% by weight of a silane-based sizing or coupling agent during glass fiber manufacturing. An absorbable polymer was covalently linked to the coupling agent and acted as a compatibilizer. The absorbable copolymer was dissolved into a mixture of chloroform and acetone. The glass fiber consisted of 290 filaments with a tex value of about 75 grams/1000m. Glass filaments with at least 60% silica network former were processable to fibers easily using historical techniques and technology of the standard art. Glass filaments from the glass fiber were spread within the solvent/polymer solution to facilitate the complete wetting of polymer across the surface of each filament in the fiber. Solvent was extracted by passing the coated glass fiber through a series of heated, turbulent air tunnels. Within the air tunnels, the coated glass fiber was physically pulled through a series of sizing dies to further distribute the polymer solution and approximate a round cross-section. A total add-on of polymer to the glass fiber was approximately 6% by weight and the cross-section exhibited a good distribution of the glass fibers within the polymer coating. The polymer add-on was sufficient to bind the glass fibers together and prevent separation under typical handling and subsequent processing conditions. The coated glass fiber was then taken up onto a spool for storage and handling for construct manufacturing. Storage conditions are at room temperature under reduced pressure.

[0116] Example 4: Biocompatible and degradable high-strength and stiffness monofilament (C1)

[0117] Utilizing the intermediate produced in Example 2 (I-2), the monofilament was coated with a low molecular weight copolymer of mostly caprolactone. The lubricous coating was applied using a solution of 5 grams of polymer dissolved in 100mL of acetone, which resulted in a 2 % polymer add-on to the monofilament. After drying of the acetone using a heated air tunnel, the monofilament was again wound up on a spool for storage under reduced pressure to remove residual acetone.

[0118] In a subsequent step, the monofilament can be unwound from the spool and cut to a length of 800 mm. A curved needle can be swagged to one end of the cut monofilament to provide a cutting mechanism through tissue. The suture can be then coiled around a paperboard core and placed into a Tyvek headed foil pouch. The monofilament suture produced can be EtO

sterilized using a low-temperature cycle of 43°C to a SAL level of 10^{-6} . The following properties could be collected on the sterilized, high-strength and stiffness suture. For comparison, additional commercially available monofilament suture properties are provided.

Table 1

	EtO Sterilizati on SAL	Tensile Strength (MPa)	Modulus (MPa)	Ultimate Elongation (%)	<i>In vitro</i> * Tensile Strength (MPa)	<i>In vitro</i> * Modulus (MPa)
C1	10^{-6}	308	8596	6	289	8250
Matrix polymer only from C1	10^{-6}	37	899	356	--	--
PDS, Ethicon	10^{-6}	115	798	75	459	658
Maxon, Medtronic	10^{-6}	85	831	---	482	543

* after 10 days *in vitro* at 37C in SBF buffer media

[0119] Example 5: Biocompatible and degradable high-strength and stiffness multifilament braided suture (C2)

[0120] Utilizing the intermediate produced in Example 3 (I-3), the coated multifilament was braided to produce a suture. The braid was constructed using a 8 carrier braiding machine and utilizes four coated fibers (I-3) in the core and a single coated fiber for each of the 8 rotating carriers. The machine was set to braid at about 52 pics per inch. The multifilament braid was subsequently tightened by hot stretching to 2-5% of its original length at 90°C. To facilitate less drag through tissue, the multifilament braid had a lubricous absorbable polymer coating, based primarily on caprolactone, added from a solution of 5 grams of polymer dissolved in 100mL of acetone, which resulted in a 3 % polymer add-on to the multifilament braid. After drying of the acetone using a heated air tunnel, the braid was wound on a spool for storage under reduced pressure to remove any residual acetone. The processed braid resulted in a diameter of about 0.25 mm.

[0121] In a subsequent step, the coated multifilament braid can be unwound from the spool and cut to a length of 1 meter. A 16mm, ½ circle, reverse cutting needle can be swagged to one end of each cut braid to provide a cutting mechanism through tissue. The multifilament suture can be

then coiled around a paperboard core and placed into a Tyvek headed foil pouch. The pouch could be EtO sterilized using a low-temperature cycle of 43°C to a SAL level of 10^{-6} .

[0122] Example 6: Biocompatible and degradable glass fiber composite knitted surgical mesh construct (C3)

[0123] Utilizing the intermediate produced in Example 1 (I-1), the consolidated strand is warp knit into a surgical mesh. Knit constructions are produced using a two-step process of warping yarn onto beams and constructing meshes using a typical Raschel or tricot knitting machine. The knitting process utilizes two warped beams threaded on bars 1 and 2.

[0124] The knit pattern is a balanced sandfly knit or atlas knit of 18 gauge and threaded 1-in and 1-out. Mesh is knit using the following pattern at 30 courses per inch.

[0125] Knit Pattern at 30 Courses Per Inch

[0126] Bar 1—1-0/1-2/2-3/2-1//2x (1-in, 1-out)

[0127] Bar 2—2-3/2-1/1-0/1-2//2x (1-in, 1-out)

[0128] Rolls of knit mesh are heat set or annealed at 100° C under compression. for 1 hour while under constant strain in the wale and course directions. The stabilized knitted fabric is cut into individual surgical meshes of size 10x15cm and packaged in a paperboard folder. The paperboard folder is placed into a Tyvek headed foil pouch. The surgical mesh could be EtO sterilized using a low-temperature cycle of 43°C to a SAL level of 10^{-6} .

[0129] The knitted surgical mesh mechanical burst properties testing are conducted using a MTS Universal Tester equipped with a burst test apparatus as detailed in ASTM D3787-01 for fixture geometry (25.4 mm polished steel ball, 44.45 mm diameter inside opening). The mesh is clamped in the fixture without any tension applied and the ball is positioned in the center of the 44.45 mm opening. The ball is positioned down to the mesh such that a 0.1 N force was applied. The test is conducted at a speed of 2.54 cm/min until failure, characterized as the point of maximum load. In vitro conditioning is completed using 0.1M buffered sodium phosphate at 37°C under constant orbital agitation.

[0130] Example 7: Biocompatible and degradable glass fiber composite woven surgical mesh construct (C4)

[0131] Utilizing the intermediate produced in Example 3 (I-3), the coated multifilament was woven into a surgical mesh utilizing a simple weaving loom machine. The weaving pattern was a 1-by-1 plain weave and utilizes 30 ends per 25 mm. Woven sheets were calendared at 100°C

under slight tension to set the woven pattern and consolidate the connection points of the alternating coated multifilament fibers running in opposing directions. The stabilized woven sheets were cut into individual surgical meshes of size 10x15cm and packaged in a paperboard folder. The paperboard folder was placed into a Tyvek headed foil pouch and the woven surgical mesh was sterilized by EtO gas to an SAL level of 10^{-6} .

[0132] The woven surgical mesh mechanical burst properties testing were conducted using a MTS Universal Tester equipped with a burst test apparatus as detailed in ASTM D3787-01 for fixture geometry (25.4 mm polished steel ball, 44.45 mm diameter inside opening). The mesh was clamped in the fixture without any tension applied and the ball was positioned in the center of the 44.45 mm opening. The ball was positioned down to the mesh such that a 0.1 N force was applied. The test was conducted at a speed of 2.54 cm/min until failure, characterized as the point of maximum load. In vitro conditioning was completed using 0.1M buffered sodium phosphate at 37°C under constant orbital agitation. The following properties were collected on the sterilized, high-strength and stiffness woven surgical mesh. For comparison, the physical and mechanical properties of a commercially available woven surgical mesh are provided.

Table 2. *Largest load cell available limited to 5,000N maximum force

	EtO Sterilization SAL	Area Weight (g/m ²)	<i>Maximum Burst Force (N)</i>
C4	10^{-6}	240	> 5kN*
Vicryl Woven Mesh, Ethicon	10^{-6}	80	633

[0133] Example 8: Biocompatible and degradable tissue engineering scaffold for bone graft medical devices (C5)

[0134] Utilizing the intermediate produced in Example 1 (I-1), the consolidated strand is weft knit into a tubular mesh. The weft knit is constructed into a tube using a circular knitter (Lamb) utilizing a 30 gauge cylinder with every other needle removed. The knitting tensions for feed and pull-down are set to result in a weft knit tube with lay-flat width of approximately 22 mm. The tubular knit is then cut to lengths of approximately 150 mm and cleaned in isopropyl alcohol (IPA)

for 15 minutes under ultrasonic agitation. The cut tubular knits are then dried under ambient conditions for 2 hours with subsequent removal of residual IPA under reduced pressure for 24 hours.

[0135] To produce a bag from the tubular knit, one end can be sealed using a sealing bar (Fuji Impulse) set to 160°C for 3 seconds of applied pressure. After sealing one end, the knitted bag is heat set or annealed using a 25 x 200 mm mandrel. The mandrel with the tube fully inserted over the end is placed in an oven at 110°C for 30 minutes. The sealed and heat set bag is then filled with allograft demineralized bone and the open end is closed using the stealing technique described above. The constructed medical device is intended for spine applications where fusion of vertebrae is required for clinical treatment. As such, the device could be placed into a Tyvek headed foil pouch, dried under reduced pressure, and sterilized via gamma irradiation with a dosage of 25 kGy.

[0136] Example 9: 3D printing fully absorbable continuous glass fiber composites

[0137] Composite monofilament fiber was prepared, having compositions as set forth in Table 3. Lactoprene 7415 (Poly-Med, Anderson SC, USA), a linear segmented block copolymer of lactide, ϵ -caprolactone, and trimethylene carbonate had a molecular weight such that a dilute solution in chloroform (CHCl_3) had an inherent viscosity of 2.2 dL/g at a concentration of 0.1 mg polymer / mL solvent. The continuous degradable glass fiber was a multifilament having an average filament diameter of 12 μm . Tricalcium phosphate in the beta form (βTCP , CamBioceramics, Leiden, Netherlands) with a nominal diameter (D50) of 17 μm .

Table 3. Absorbable continuous mineral-based fiber composites for 3D printing

Filament	Composite monofilament Composition			Nominal Diameter (mm)
	Lactoprene 7415 (wt %)	Absorbable mineral-based fiber (wt %)	βTCP (wt %)	
A	60	40	0	0.35
B	80	10	10	0.35
C	60	0	40	1.75
D	100	0	0	1.75

[0138] FDM printing of Filament A and B was performed using a custom 3D printer equipped with a Bowden tube print head with a 0.35mm nozzle and a fiber cutting head and a nozzle temperature of 185°C with bed temperature of 45°C. Rectangular prisms were printed with a 50% rectilinear infill at a size of 10mm x 70mm x 2mm.

[0139] FDM printing of Filaments C and D was performed using a direct drive 3D printer with a 0.4mm nozzle. A nozzle temperature and bed temperature of 185°C and 45°C respectively. Rectangular prisms were printed with a 50% rectilinear infill at a size of 10mm x 70mm x 2mm. The pore size targeted was between 100 - 500µm.

[0140] Printed parts were assessed for properties according to Table 4. Percentage solids, comprising glass fiber and/or β TCP, was calculated by soluble loss technique comparing pre- and post-dissolution dry weights with CHCl_3 as a solvent. Polymer composition was obtained by ^1H -NMR (400MHz JEOL) using CDCl_3 as a solvent. Polymer molecular weight was determined using GPC (Waters, Milford, MA) with a DCM mobile phase. Residual monomer was analyzed by GC (Perkin-Elmer Clarus, Shelton, CT). Thermal profile was measured by DSC (Perkin-Elmer Pyris 6, Shelton, CT), including melting temperature (T_m) and heat of fusion (ΔH_f).

Table 4

Material	% Solids	Polymer Composition	Polymer IV	Residual Monomer	T_m	ΔH_f
A	40	Poly(l-lactide)	1.8	<0.5	181°C	74
B	20	Poly(l-lactide-co-caprolactone-co-trimethylene carbonate)	2.4	<0.5	172°C	42
C	40	Poly(l-lactide-co-caprolactone-co-trimethylene carbonate)	2.4	<0.5	172°C	42
D	0	Poly(l-lactide-co-caprolactone-co-trimethylene carbonate)	2.4	<0.5	172°C	42
E	20	Polycaprolactone	1.5	<0.5	56°C	65
F	20	Polyglycolide	1.2	<0.5	212°C	81

[0141] Morphology was assessed by scanning electron microscopy (SEM) at multiple magnifications by first embedding printed samples in resin to create a cut and ground section. Prepared samples were sputter coated with platinum. Pore size was measured related to the largest circle that can be created in the pore. Percent porosity is calculated as the ratio of pore space to total image area. Distribution of particles and fibers were assessed by visual assessment. Percent volume porosity is calculated by mercury porosimetry.

[0142] FIG. 1 provides an SEM image of glass indicating the organized distribution of mineral-based fibers throughout the biocomposite.

[0143] Mechanical performance was evaluated in tensile and compression using an MTS Synergie 200 Universal Test Frame with vice-style and flat platen grips, respectively. 3-point bend analysis was performed using a 3-point bend fixture having frictionless rollers with a span of 50mm.

[0144] FDM printing of Filament A and B was performed using a custom 3D printer equipped with a Bowden tube print head with a 0.35mm nozzle and a fiber cutting head and a nozzle temperature of 185°C with bed temperature of 45°C. Rectangular prisms were printed with a 100% infill at 0°, +30°, and -30° from the long axis a size of 12mm x 70mm x 4mm.

[0145] FDM printing of Filaments C and D was performed using a direct drive 3D printer with a 0.4mm nozzle. A nozzle temperature and bed temperature of 185°C and 45°C respectively. Rectangular prisms were printed with a 100% infill at a size of 12mm x 70mm x 4mm.

[0146] 3 point bend assessment of rectangular prisms using a 64mm span indicate a bending strength and bending modulus of 284MPa and 14.2GPa, respectively, for parts printed from Filament A. Bending strength and bending modulus of Filament D, containing no reinforcing mineral-based fiber, is 30MPa and 1.2GPa, respectively.

[0147] Example 10 Sterilization of 3D printed parts

[0148] Printed parts made in Example 9 were sealed in Tyvek (Dupont Tyvek 1073B) pouches, one part per package. Materials were sterilized using standard conditions according to Table 5.

Table 5. Sterilization techniques and subsequent sterility level of 3D printed composite parts

Printed parts	Sterilization technique	Temperature / Exposure	Sterilization Assurance
A, B, C, D	Ethylene Oxide	40°C	SAL6
A, B, C, D	γ Radiation	RT, 25kGy	SAL6
A, B, C, D	NO gas	25°C	SAL6
A, B, C, D	scCO ₂	34°C	SAL6
A, B, C, D	H ₂ O ₂ Plasma	50°C	SAL6

[0149] Note: Some services, like Ethylene Oxide and γ sterilization require shipment to an outside vendor and larger shipping lots to distribute cost per device, while local sterilization

options like NO, scCO₂ and H₂O₂ Plasma allow for local, just-in-time sterilization of medical devices.

[0150] Example 11: Implantation of 3D printed Inlay / Onlay grafts

[0151] To study the potential of glass fiber composite parts, samples were prepared into rivet shapes. Skeletally mature female New Zealand White rabbits were implanted with experimental and control materials to study biocompatibility and bone ingrowth. First, circular unicortical diaphyseal defects were created at 3 places along the proximal femur bilaterally. Next, defects were closed by implanting either experimental grafts, particulate β TCP as a control, or no implant. Implants projected into the bone marrow cavity, through the cortical bone, and extended above the cortical plane, representing both an inlay as well as onlay graft. Implants were covered with a collagen membrane to protect from soft tissue infiltration and then the implant site closed in layers. Implants and surrounding bone was retrieved at 4, 8, and 16 weeks for analysis by x-ray, μ CT, and histology.

[0152] Example 12: Mineralization in SBF

[0153] To determine the mineralization potential of 3D printed materials, EtO sterilized parts were submerged in SBF according to ISO 23317 (2014), prepared by dissolving NaCl, NaHCO₃, KCl, K₂HPO₄•3H₂O, MgCl₂•6H₂O, HCl, CaCl₂, Na₂SO₄, and (HOCH₂)₃CNH₂ to create a 7.4pH buffer having ionic concentrations similar to human blood plasma. FDM printed parts were submerged in buffer and incubated at 37°C. At predetermined timepoints, including 7, 14, 21, and 28 days, samples were removed from buffer and dried. Mineralization potential was evaluated by staining with Alizarin Red to selectively stain for the presence of calcium. Controlled light images were used to assess sample colors on the RGB scale at each timepoint to calculate red shifts, which are associated with apatite formation. SEM with EDX was used to determine surface atomic composition, specifically for changes in calcium and phosphate concentrations. An increase in apatite concentration is correlated with the mineralization potential of different composites.

Table 6

Part	Composite monofilament composition			
	Lactoprene 7415 (wt %)	Absorbable glass fiber (wt %)	β TCP (wt %)	Mineralization potential
A	60	40	0	Yes
B	80	10	10	Yes

C	60	0	40	Yes
D	100	0	0	No

[0154] Example 13: IVT Degradation Study

[0155] Samples were evaluated for degradation rate by submersion in (1) 7.4pH 100mM phosphate buffer, (2) 7.4pH 100mM TRIS-SBF, and (3) 7.4pH 100mM SBF at 37°C and tested at predetermined timepoints below. The presence of different buffering chemicals and TRIS influenced degradation rate and conversion of glass degradants into mineralized components on the sample surface, including apatite formation, and therefrom the degradation rate of the sample. Ideally, the polymeric components of the composite hydrolytically degrade into soluble elements that are metabolized and ultimately excreted from the body, while constituent elements of the glass fiber support apatite formation and bone tissue development. Mass retention of the polymer and glass components of the composite we measured by weight loss, ash testing, NMR, and atomic composition. Time points included

[0156] Mass (% mass retention) – 1, 3, 6 12, 18, and 24 months

[0157] Molecular Weight, IV – 1, 2, 3 months

[0158] Tensile Strength, Modulus, Elongation – 1, 4, 8, 12, 16 weeks

[0159] Example 14: Creation of Patient-Matched Alveolar Ridge Scaffold

[0160] Vertical alveolar ridge deficiency remains a significant issue and obstacle for permanent dental implants. Current approaches involving the use of autograft or allograft tissues, or in some cases xenograft tissues, or synthetic approaches often including particulates of β TCP as scaffolding. In some instances, biologic agents such as bone morphogenic protein (Infuse®, Medtronic) or patient-derived components such as platelet-rich plasma (PRP) are used to encourage a strong biologic response. These approaches are historically successful with void filling in confined spaces like 4-wall defect filling of a tooth root or in increasing the width of alveolar bone (Cologne Classification System: Class I defect), but have not successfully and predictably increased the vertical gain in Class II and III defects of the alveolar ridge greater than about 2 mm.

[0161] To design a rigid, stable, tight-fitting, space maintaining degradable scaffold to support vertical alveolar ridge grafting, patients are first scanned by computer tomography (CT) with scan spacing at 1.25mm or less, and more preferably 1mm or less into a DICOM format. Scans are segmented by software to create a digital model of the bone defect surface and surrounding bone margins. A virtual repair is then designed to tightly conform (0.0mm surface

offset) to the bone surface, with the exterior defined by the contour of the desired future alveolar ridge surface. This defines the boundary of a repair implant. As an option, retaining screw holes can be included in 1 – 4 places to tighten the gap between the implant and existing bony surface and improve implant stability. Screw holes are predetermined in angle and diameter to align with adequate bone purchase for fixation, while at the same time avoiding adjacent teeth roots, arteries, and nerve bundles. The boundaries of the implant, including screw locating holes, are exported in an .stl file format.

[0162] To manufacture a rigid, stable, tight-fitting, space maintaining degradable scaffold to support vertical alveolar ridge grafting, the .stl file is imported into 3D print slicing software (CURA) and oriented such that the superior/inferior plane (typically the sagittal view) is along the build plate axis. The printing profile is designed assuming a 0.35mm diameter nozzle with a 0.25mm slice thickness, having no outlines and a rectilinear infill at 40%. The software generates a printing file which is in turn transferred to a custom 3D printer suitable for processing continuous glass fiber-filled composite filaments comprising 45% biodegradable glass fiber (12µm diameter) in a matrix of 50% Poly(l-lactide-co-caprolactone-co-trimethylene carbonate) and 5% βTCP microparticles. After part printing, the implant is inspected for size tolerance, pore continuity, correlation with predicted weight, and material composition. Implants are cleaned in an ultrasonic bath in isopropanol, dried under reduced pressure, and sealed in a Tyvek envelope for sterilization.

[0163] The sterilized implant can be provided in a kit containing the graft, cortical lag screws that match the pre-planned fixation holes, and a drill guide.

CLAIMS

What is claimed is:

1. A biocompatible biodegradable biocomposite, comprising,
 - a. a continuous thermoplastic matrix, the matrix comprising an absorbable segmented block copolymer comprising at least a majority repeat unit derived from cyclic monomers selected from glycolide, lactide, caprolactone or dioxanone,
 - b. a plurality of microfibrinous degradable mineral-containing fibers, wherein the mineral-containing fibers exhibit tensile elongation of less than 5%.
2. The biocomposite of Claim 1, further comprising one or more discrete bioceramic additives.
3. The biocomposite of Claim 2, where the discrete bioceramic additive is selected from β TCP, biphasic calcium phosphate, hydroxyapatite, allograft bone particulate, xenograft bone particulate, calcium phosphate, calcium sulfate, whitlockite, and bioactive glass, or combinations thereof.
4. The biocomposite of Claim 3, wherein the discrete bioceramic additive has a d90 of less than 100 μ m diameter.
5. The biocomposite of Claim 3, wherein the discrete bioceramic additive has a d90 of less than 50 μ m diameter
6. The biocomposite of Claim 3, wherein the discrete bioceramic additive has a d90 of less than 20 μ m diameter.
7. The biocomposite of Claim 3, wherein the discrete bioceramic additive has a d90 of less than 10 μ m diameter.
8. The biocomposite of Claim 1, wherein the continuous thermoplastic matrix copolymer has an inherent viscosity of greater than 0.9 dL/g.
9. The biocomposite of Claim 1, wherein the continuous thermoplastic matrix copolymer has an inherent viscosity of greater than 1.2 dL/g

10. The biocomposite of Claim 1, wherein the continuous thermoplastic matrix copolymer has an inherent viscosity of greater than 1.5 dL/g.
11. The biocomposite of Claim 1, wherein the continuous thermoplastic matrix copolymer has a melting temperature as measured by DSC of between 50°C and 225°C.
12. The biocomposite of Claim 1, wherein the continuous thermoplastic matrix copolymer has a density of between 0.8 g/cm³ and 1.6 g/cm³.
13. The biocomposite of Claim 1, wherein the microfibrinous degradable mineral-containing fibers increase the tensile strength of the biocomposite by more than 50% in at least one test orientation.
14. The biocomposite of Claim 1 wherein the microfibrinous degradable mineral-containing fibers increase the tensile modulus of the biocomposite by more than 50% in at least one test orientation.
15. The biocomposite of Claim 1, wherein the microfibrinous degradable mineral-containing fibers increase the bending modulus of the biocomposite by more than 50% in at least one test orientation.
16. The biocomposite of Claim 1, wherein within the continuous thermoplastic matrix the mineral-containing fibers are organized in 3-dimensional space.
17. The biocomposite of Claim 16, wherein the mineral-containing fibers are organized into at least two primary directions.
18. The biocomposite of Claim 17, wherein the mineral-containing fibers are organized into 2-dimensional planes, where each plane comprises mineral-containing fibers organized in at least one primary direction.
19. The biocomposite of Claim 18, comprising more than 2 stacked planes.
20. The biocomposite of Claim 17, where the mineral-containing fibers comprise bundles of mineral-containing fibers.

21. The biocomposite of Claim 20, wherein the bundles of mineral-containing fiber comprise between 5 and 5,000 fibers.
22. The biocomposite of Claim 21, wherein the mineral-containing fiber bundles are in the form of a woven, knit, or braided structure.
23. The biocomposite of Claim 21, wherein the fiber bundles are organized to follow a geometric path.
24. The biocomposite of Claim 23, where the geometric path varies in 3 dimensions.
25. The biocomposite of Claim 1, further comprising variations in density in adjacent meso-scale volumes of greater than 25%.
26. The biocomposite of Claim 1, further comprising variations in density in adjacent meso-scale volumes greater than 50%.
27. The biocomposite of Claim 1, further comprising meso-scale volumes exhibiting density of between 0 g/cm³ and 0.5 g/cm³.
28. The biocomposite of Claim 1, further comprising meso-scale volumes exhibiting density of between 0.5 g/cm³ and 1.5 g/cm³.
29. The biocomposite of Claim 1, further comprising meso-scale volumes exhibiting density of between 1.5 g/cm³ and 3 g/cm³.
30. The biocomposite of Claim 17, where a primary direction exhibits tensile strength at least more than 100% of a tensile strength in a non-primary direction.
31. The biocomposite of Claim 17, where a primary direction exhibits tensile modulus of at least more than 100% of a tensile modulus in a non-primary direction.
32. The biocomposite of Claim 17, wherein a primary direction exhibits bending modulus of at least more than 100% of a tensile modulus in a non-primary direction.
33. The biocomposite of Claim 17, having less than 10% creep in a primary direction at 37°C with 15% breaking stress applied for 24 hours.

34. The biocomposite of Claim 17, having less than 10% creep in a primary direction at 37°C with 15% breaking stress applied for 1 week.
35. The biocomposite of Claim 17, having anisotropic mechanical performance.
36. The biocomposite of Claim 23, further comprising continuous mineral-containing fibers continuously spanning the geometric boundaries of the biocomposite along the geometric path.
37. The biocomposite of Claim 1, wherein the mineral-containing fibers are integrated within the continuous thermoplastic matrix.
38. The biocomposite of Claim 1, wherein the continuous thermoplastic matrix copolymer has at least one glass transition temperature of less than 60°C.
39. An article made from the biocomposite of Claim 1.
40. The article of Claim 39, wherein the article is produced by additive manufacturing.
41. The article of Claim 39, wherein the total article density is within 10% of the biocomposite average density of the constituent components.
42. The article of Claim 39, wherein the total article density is greater than 10% less than the composite average density of the constituent components.
43. The article of Claim 39, wherein the article is an implantable medical device.
44. The article of Claim 39, wherein the continuous thermoplastic matrix degrades in a buffered physiological environment more than 3 months faster than the microfibrillar degradable mineral-containing fibers.
45. A method of additive manufacture of a biocomposite article, comprising,
a) providing a fiber comprising the biocomposite of Claim 1 to a fiber deposition additive manufacturing device, and
b) depositing the fiber comprising the biocomposite of Claim 1 on a surface to form a biocomposite article.

46. The method of Claim 44, wherein the biocomposite article is an implantable medical device.

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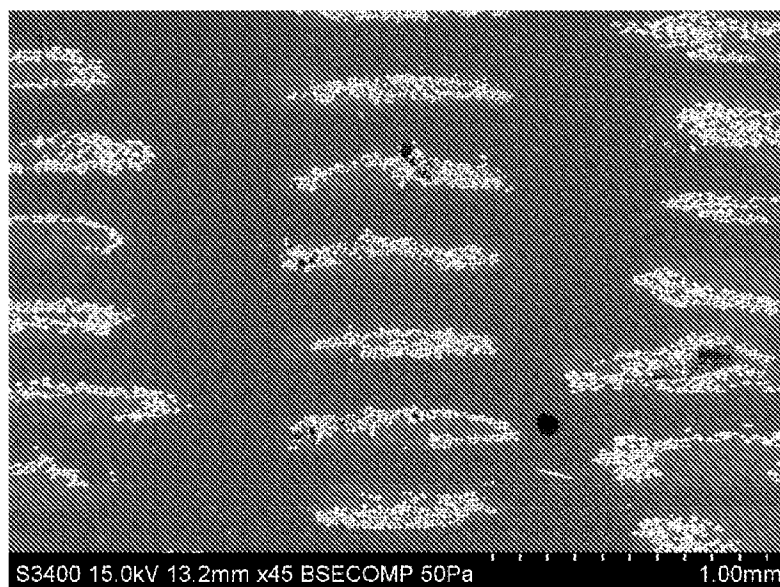


FIG. 1