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(54) **FIBER REINFORCED COMPOSITE MATERIAL**

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(57) **ABSTRACT**

The present disclosure relates to a fiber reinforced composite material. In an embodiment, the composite material includes a PLLA fiber material and a matrix material that does not have the same chemical element composition as the fiber material. Other fiber reinforced composite materials are also disclosed.

FIBER REINFORCED COMPOSITE MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a PCT International Application of U.S. Patent Application No. 60/867,978, filed Nov. 30, 2006, the disclosure of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present disclosure relates to bioresorbable composites and more specifically to a fiber reinforced polymer composite material that is used to make bioresorbable products,

[0004] 2. Related Art

[0005] Metal products have been used in fracture fixation due to their high strength. While these products perform well, there are a significant number of occurrences where these products can cause problems to the patient. In some cases the presence of the metal implant can cause irritation of the soft tissue around the implant, in severe cases this necessitates the removal of the implant. The procedure to remove the metal products exposes the patient to the risks associated with undergoing a major medical procedure and also adds to the overall cost of healing the original fracture. One potential solution to substantially reduce the need to remove fracture fixation hardware is to use bioresorbable devices to fix the fracture. However, the currently available bioresorbable materials and products do not have the required combination of initial strength and retention of this strength for suitable fracture healing to occur.

[0006] The currently marketed bioresorbable products include those products manufactured from injection molded polymers, polymer blends, and co-polymers. These products have been utilized in the areas of craniomaxillofacial implants and non-load bearing fracture fixation implants, such as pins and screws, for wrist and ankle applications and for reattaching soft tissues, such as ligaments and tendons, to bone. In addition, there are also some spinal products available that make use of the compressive properties of these polymers. Products including these materials are easy to process, but are limited by the mechanical properties of the materials. These materials have a tensile strength in the range of between about 50 MPa to about 100 MPa. Depending on the choice of polymer or co-polymer, products in this category retain the majority of their strength for less than about 12 weeks. Therefore, these materials are not suitable for fracture fixation applications beyond simple non-loaded pins and screws.

[0007] Other currently marketed bioresorbable products include self reinforced products that have improved strength due to orientation of the polymer during processing of the product. Even though these products have improved strength, their flexural strength is still only around 250 MPa. This limits the uses of this technology for fracture fixation to screws and pins.

[0008] Recently, devices have been manufactured from fiber reinforced polymer composites utilizing polyglycolic acid (PGA) fibers. These composites have a good initial strength, but suffer a rapid loss in strength due to the rapid hydrolysis of these fibers. Devices have been manufactured using PLLA fibers and PDLLA as the matrix material. Unfortunately, this matrix breaks down rapidly and results in the composites having a rapid loss in strength. Other attempts have used co-polymers containing PLLA as the reinforcing fiber, such as PLLA-co-PGA copolymers at a ratio of 82:18. However, there has been difficulty in finding a suitable polymer matrix material that can be processed into a composite without degrading or breaking this reinforcing fiber. Most recently, composites have been made where the matrix was a polymer with the same chemical composition as the fiber or where the matrix was a blend with the majority of the blend being a polymer with the same chemical composition as the matrix. These composites have an initial flexural strength of between 120 to 140 MPa, with most of this strength lost within about 12 weeks of use.

[0009] Attempts to slow down the degradation of the polymer matrix have included modifying the composition to increase the hydrophobicity of the polymer. However, this increases either the crystallinity of the polymer matrix, which is undesirable from a biological perspective, or it makes the polymer too ductile if a hydrophobic rubbery component, such as polycaprolactone (PCL), is added. Buffering materials, such as calcium carbonate, have also been added to polymers to slow degradation rates and improve the biological properties, such as osteoconductivity. However, in order to gain the beneficial effects of calcium carbonate it needs to be present at high levels, about 30% by weight of the composition. Since a fiber polymer composite contains at least 50% of fiber by volume, it would be anticipated that a calcium carbonate-containing matrix would interfere adversely with the interface between the polymer matrix and reinforcing fibers. This could result in the fiber-reinforced composite substantially weakening or even falling apart before complete healing of a fracture.

[0010] In order to make a suitable fiber-reinforced composite material, the fiber and matrix material have certain requirements. The fiber needs to have both a high initial tensile strength, and the ability to retain the majority of this strength, for the fracture to heal. To have a high initial strength, the fibers need to be highly orientated and be present at about 40% by volume of the composite. In addition, the fibers should also have some crystallinity, as this imparts stability against relaxation of the orientation in the fiber.

[0011] The matrix material also needs to be able to retain the majority of its strength for a suitable time, approximately between about 6 to about 12 weeks, for the fracture to heal. In order to accomplish this, the matrix should have a sufficiently high initial molecular weight. As the polymers degrade, the molecular weight decreases and the polymers become brittle and lose their mechanical properties. Additives, such as calcium carbonate or other buffering materials, can be added to the matrix to control the degradation rate. The amount of the buffering material should be around 30% by weight of the matrix without adversely interfering with the interface between the polymer matrix and the reinforcing fibers.

[0012] In addition, the matrix material needs to be processable at a temperature which is low enough to not significantly affect the strength of the fiber and adhere well enough to the fiber to allow stress transfer from the matrix to the fiber. To accomplish this, both semi-crystalline and amorphous co-polymers can be used. Semi-crystalline co-polymers are typically composed of lactic acid and one or more additional monomer units whose function is to lower the melting point of the co-polymer matrix to a point where the strength of the fiber is not affected during the consolidation step. Amorphous or non-crystalline materials, such as poly (D-lactide) acid polymers, are suitable for processing with the fiber, as they soften at relatively low temperatures. However, these materials do not have a long strength retention time. This strength retention can be improved by incorporating a buffering material, such as calcium carbonate, into the matrix material. In this case, the calcium carbonate acts as both a buffer and also reduces the thermal sensitivity of the polymer to breakdown during processing. Taken together, the affect of the calcium carbonate is to both slow the rate of degradation of the polymer and help preserve the molecular weight during processing, without adversely interfering with the interface between the polymer matrix and the reinforcing fibers.

[0013] The present disclosure incorporates these requirements to produce a bioresorbable material which has a high initial strength and retains a significant proportion of this strength for a useful time.

SUMMARY OF THE INVENTION

[0014] In one aspect, the present disclosure relates to a fiber reinforced composite material including a PLLA fiber material, such as a continuous PLLA fiber material, and a matrix material that does not have the same chemical element composition as the fiber material. In an embodiment, the composite further includes a degradation controlling agent dispersed in the matrix material. In another embodiment, the degradation controlling agent includes a buffer material selected from a group including calcium carbonate, calcium hydrogen carbonates, calcium phosphates, tricalcium phosphates, dicalcium phosphates, magnesium carbonate, and sodium carbonate. In yet another embodiment, the degradation controlling agent includes a common salt. In an embodiment, the degradation controlling agent is selected from a group including a buffer material, a common salt, and combinations thereof. In a further embodiment, the degradation controlling agent is between about 0.1% to about 40% by weight of the matrix material. In yet a further embodiment, the composite further includes an accelerant dispersed in the fiber or matrix material. In a further embodiment, the PLLA fiber material is about 50% by volume of the composite. In an embodiment, the fiber material, which is bioabsorbable, has a tensile strength of between about 500 MPa to about 2000 MPa and a molecular weight of between about 290,000 g/mol and about 516,000 g/mol.

[0015] In an embodiment, the matrix material is bioresorbable and is selected from a group including a polymer, a copolymer, and a polymer blend. In another embodiment, when a polymer blend is used as the matrix, the blend includes at least two polymers and at feast one of the polymers has a chemical element composition that is different to that of the fiber. In yet another embodiment, the polymer having a chemical element composition that is different to that of the fiber comprises at least 50% of the polymer blend. In a further embodiment, the polymer having a chemical element composition that is different to that of the fiber comprises more than 50% of the polymer blend. In yet a further embodiment, the matrix material is bioabsorbable.

[0016] In yet a further embodiment, the composite has an initial tensile strength of at least 250 MPa and retains at least 75% of the initial tensile strength for at least 8 weeks. In an embodiment, the composite material includes a flexural strength of about 200 MPa and a shear strength of at least 140 MPa.

[0017] In another aspect, the present disclosure includes a fiber reinforced composite material having a matrix material, a glass fiber material, and a degradation controlling agent. In an embodiment, the matrix material is selected from a group including a polymer, a copolymer, and a polymer blend. In an embodiment, the matrix material is bioabsorbable. In another embodiment, the glass fiber material is bioabsorbable. In yet another embodiment, the glass fiber material includes a tensile strength between about 300 MPa and about 1200 MPa. In a further embodiment, the glass fiber material includes a hydrophobic material. In yet a further embodiment, the glass fiber material is about 50% by volume of the composite.

[0018] In an embodiment, the degradation controlling agent is dispersed in the matrix material. In another embodiment, the degradation controlling agent is coated on a surface of the fiber material. In yet another embodiment, the degradation controlling agent is between about 0.1% to about 40% by weight of the matrix material. In a further embodiment, the degradation controlling agent includes a buffer material selected from a group including calcium carbonate, calcium hydrogen carbonates, calcium phosphates, tricalcium phosphates, dicalcium phosphates, magnesium carbonate, and sodium carbonate. In yet a further embodiment, the degradation controlling agent includes a common salt. In an embodiment, the degradation controlling agent is selected from a group including a buffer material, a common salt, and combinations thereof.

[0019] In yet a further embodiment, the composite has an initial tensile strength of at least 250 MPa and retains the initial tensile strength for at least 8 weeks. In an embodiment, the composite includes an initial flexural strength of between about 250 MPa and about 400 MPa. In another embodiment, the composite includes an initial flexural modulus of between about 20-30 GPa. In yet another embodiment, the composite retains about 98% of an initial mass for at least 2 weeks.

[0020] In yet another aspect, the present disclosure includes a fiber reinforced composite material having a matrix material, a fiber material, and a degradation controlling agent.

[0021] In a further aspect, the present disclosure includes a fiber reinforced composite material having a matrix material and a glass fiber material, wherein the glass fiber material includes a tensile strength of between about 300 MPa and about 1200 MPa.

[0022] In yet a further aspect, the present disclosure includes a fiber reinforced composite material having a PLLA fiber material and a matrix material, wherein the fiber material includes a molecular weight of between about 290,000 g/mol and about 516,000 g/mol.

[0023] Further areas of applicability of the present disclosure will become apparent from the detailed description provided hereinafter. It should be understood that the detailed description and specific examples, while indicating the preferred embodiments of the disclosure, are intended for purposes of illustration only and are not intended to limit the scope of the disclosure.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0024] The following description of the preferred embodiment(s) is merely exemplary in nature and is in no way intended to limit the disclosure, its application, or uses.

[0025] In one aspect, the present disclosure relates to a fiber-reinforced composite material having a PLLA fiber material and a matrix material that does not have the same chemical element composition as the fiber material.

[0026] A continuous PLLA fiber is extruded and drawn to provide the fiber with a tensile strength of between about 500 MPa to about 2000 MPa and a molecular weight of between about 290,000 g/mol to about 516,000 g/mol. The extrusion and drawing process used to make the fiber may be any extrusion and drawing process known to one of ordinary skill in the art. The PLLA fiber material is about 50% by volume of the composite and is bioabsorbable.

[0027] The matrix material, which is bioabsorbable and selected from a group that includes a polymer, a copolymer, and a polymer blend, is then made. For the purposes of this disclosure, a matrix material that does not have the same chemical element composition as the fiber material is defined as the following: If the matrix material is a polymer, then the polymer may not be a pure polylactide material. If the matrix material is a copolymer, then at least one of the monomeric species is not a lactone monomer. If the matrix material is a polymer blend, then at least one of the polymers has a chemical element composition that is different to that of the fiber. The polymer that has a chemical element composition different to that of the fiber comprises at least 50% or more of the polymer blend. Alternatively, a matrix material that has the same chemical element composition as the fiber material, which is also within the scope of this disclosure, is defined as the following: If the matrix material is a polymer, then the polymer is a pure polylactide material. If the matrix material is a copolymer, then both monomeric species are lactone monomers. If the matrix material is a polymer blend, then both polymers are pure polylactide materials.

[0028] The composite may further include a degradation controlling agent. For the purposes of this disclosure, the degradation controlling agent may include a buffer material, a common salt, and combinations thereof. The buffer material is selected from a group including, but not limited to, calcium carbonate, calcium hydrogen carbonates, calcium phosphates, tricalcium phosphates, dicalcium phosphates, magnesium carbonate, and sodium carbonate. The common salt is water soluble and may be organic or inorganic. In addition, the salt may be based on, without limitation, one of the following: a Group I metal, including but not limited to, lithium, sodium, and potassium; a Group II metal, including but not limited to, beryllium, magnesium, calcium, strontium, and barium; transition metals, including but not limited to, copper, zinc, silver, gold, iron, and titanium; a Group III metal, including but not limited to, aluminum and boron. Furthermore, the salt may include, without limitation, a carbonate, a hydrogen carbonate, a phosphate, a hydrogen phosphate, silicates, polyphosphates, and polysilicates. Finally, the salt may be a single element, a compound, or a mixture thereof.

[0029] The degradation controlling agent is dispersed in the matrix material and is used as a buffer agent and to slow the degradation of the composite. The degradation controlling agent is between about 0.1% to about 40% by weight of the matrix material. The composite may further include an accelerant, such as the tertiary butyl ester of lauric acid or the ditertiary butyl ester of fumaric acid, dispersed in the matrix material or fiber material. Other accelerants known to those of ordinary skill in the art may be used. Use of these accelerants accelerates the degradation rate of the fiber or matrix.

[0030] The composite material has an initial tensile strength of at least 250 MPa and retains at least 75% of this initial tensile strength for at least 8 weeks. For the purposes of this disclosure, an initial tensile strength is taken to mean the tensile strength of the composite material prior to degradation. In addition, the composite has a flexural strength of about 200 MPa and a shear strength of at least 140 MPa.

[0031] In another aspect, the present disclosure relates to a fiber-reinforced composite material including a matrix material, a glass fiber material, and a degradation controlling agent.

[0032] The matrix material may be any biodegradable polymer, polymer blend, copolymer, or other biodegradable material known to those skilled in the art. Examples of biodegradable polymers include alpha-polyhydroxy acids, polyglycolide (PGA), poly(L-lactide), poly(D,L-lactide), poly(.epsilon.-caprolactone), poly(trimethylene carbonate), poly(ethylene oxide) (PEO), poly(.beta.hydroxybutyrate) (PHB), poly(.beta.-hydroxyvalerate) (PHVA), poly(p-dioxanone) (PDS), poly(ortho esters), tyrosine-derived polycarbonates, polypeptides, polyurethane, and combinations thereof.

[0033] The glass fiber material is bioabsorbable and represents about 50% by volume of the composite. The glass fiber material may be extruded and drawn by any extrusion and drawing process known to one of ordinary skill in the art. The fiber includes a tensile strength of between about 300 MPa and about 1200 MPa. In addition, the fiber material may include a hydrophobic material to slow down the degradation of the glass fiber material. The hydrophobic material may be a component of the composition of the glass fiber material or coated on a surface of the glass fiber material. Examples of hydrophobic materials include, without limitation, polycaprolactone, poly-para-xylylene (e.g. Parylene), isomers and co-polymers of polylactide, polypeptide, ceramic materials (i.e. hydroxyapatite and any form of calcium phosphate), and any other organic or inorganic hydrophobic material likely to slow down the penetration of water to the fiber. For the purposes of this disclosure, the glass fibers include about 50 mol % potassium oxide (P_2O_5), about 30 mol % calcium oxide (CaO), about 15 mol % sodium oxide (Na_2O), and 5 mol % iron oxide (Fe_2O_3). However, glass fibers of different compositions may be used.

[0034] The degradation controlling agent may be of the same type as the degradation controlling agents described above and may be dispersed in the matrix material or coated on a surface of the fiber material. The agent acts as a means to control the degradation of the composite and/or the glass fiber. Specifically, with regards to the glass fibers, it is believed that the common salt substantially reduces the release of ions from the fibers. Where the degradation controlling agent is dispersed in the matrix material, the agent represents between about 0.1% to about 40% by weight of the matrix material.

[0035] The composite has an initial tensile strength of at least 250 MPa and is able to retain this initial tensile strength for at least 8 weeks. In addition, the composite includes an initial flexural strength of between about 250 MPa and about 400 MPa. Furthermore, the composite retains about 98% of an initial mass for at least 2 weeks when it is placed in in-vivo conditions.

[0036] The reinforcing fibers of both composites, as described above, preferably have mechanical properties that are not substantially compromised when tested in a physiological (aqueous, 37° C.) environment. The fibers are preferably insoluble in the solvent used to dissolve the matrix polymer. In addition, the degradation controlling agent of both composites must be one that reads with the acid by-products that are generated during the degradation of the polymer fiber or matrix or the glass fiber, including, without limitation, lactic acid, glycolic acid, caproic acid, and different forms of phosphoric acid. Where the degradation controlling agent is in a particulate form, the particles may have a number of sizes, ranging from about 1 mm to about 10 nm, and geometries, such as needle, cubic, platelet, fibers, spheres, and other geometries known to one of ordinary skill in the art. It is important, but not required, that the particles have a shape that enhances the mechanical properties of the particles.

[0037] Biological agents, such as cells, growth factors, antibiotics, anti-microbials, or other such factors may be added to one or more components of the composites to promote healing of the fracture.

[0038] Further details may be derived from the examples below.

Example 1

[0039] PLLA fiber was first made by taking PLLA granules with a nominal intrinsic viscosity of 3.8 and extruding the granules into a fiber. A single screw extruder fitted with a gear pump and a 2 mm spinneret die was used. The extruder also had a provision for air cooling. The extruded fiber was batched on spools for the next processing step. Subsequently, the fiber was progressively stretched at elevated temperatures to produce a final diameter of ca. 100 microns and a draw ratio between about 8 and about 15. The final molecular weight of the drawn fiber was between about 290,000 g/mol^{-1} to about 516,000 $gmol^{-1}$. The resultant fiber had an average tensile strength of greater than about 800 MPa.

[0040] Composites were then made using an 85:15 co-polymer of PDLLA and PGA with a 35% weight addition of calcium carbonate ($CaCO_3$) as the matrix material. The drawn poly (L-lactide) fibers were then wound around a support frame of parallel bars that were held a constant distance apart. For each sample the fiber was wrapped 75 times around the support frame, resulting in 150 fibers in each composite. The matrix was dissolved in a solvent, methyl acetate, at 10% wt/vol of solvent. The solvent/polymer mixture was then coated onto the fibers. The composite was then placed in a vacuum oven at 40° C. for 12 hours to remove the solvent.

[0041] The composite was then placed in a cylindrical mold and heated to 165° C. This temperature is used to melt the matrix material to allow it to flow and consolidate the composite. Once thermal equilibrium was reached, slight tension was applied to the fibers to align them in the mold. The mold was then closed completely to consolidate the fibers and the matrix. The closed mold was then maintained at 165° C. for up to 5 minutes and then removed from the heated press and placed between cool metal blocks to cool the composite down to room temperature to allow tension to be released from the fibers.

[0042] Samples of the composite were aged in phosphate buffer solution (PBS) at 37° C. The average diameter of the samples was about 1.7 mm. The composites were removed from the aging solution, dried, and tested using a 3-point bend test method. As shown in Table 1, the samples were tested for their initial tensile strength and their tensile strengths after 6, 10, 12, and 16 weeks. Compared to the initial tensile strength, the tensile strength of the composite during the succeeding weeks remained high.

TABLE 1

Week	Tensile strength/ MPa
0	325
6	319
10	338
12	291
16	315

Example 2

[0043] Composites were made using the method described in Example 1, with and without $CaCO_3$ mixed in the matrix, and with a range of different matrix materials. The resultant composites were tested for their flexural strength in 3 point bending. The pins were 2 mm in diameter and tested using a 16:1 span to diameter ratio. The results are given in Table 2. It is clear that the mechanical properties of the composites containing a degradation controlling agent are not significantly compromised by the presence of the material.

TABLE 2

Matrix material	Composite flexural strength/ MPa
PLLA-co-PGA (85:15)	342
PLLA-co-PGA (82:18)	299
PLLA-co-PGA (82:18) + 30 wt % $CaCO_3$	311
PDLA-co-PGA (85:15) + 35 wt % $CaCO_3$	323

Example 3

[0044] Composites were made that included poly-L-lactic acid (PLLA) fibers and a co-polymer matrix of poly-L-lactic acid (PLLA) and polyglycolic acid (PGA) (PLGA 85:15) using the method described in example 1. The composite did not include calcium carbonate or other degradation controlling agents. The flexural and shear properties of the resultant pins were tested, via a 3-point bending test, after aging in PBS at 37° C. The results are given in Table 3.

TABLE 3

Week	Flexural Strength/MPa	Shear Strength/MPa
0	251	192
6	261	187
12	172	190
18	185	173
24	87	158

Example 4

[0045] 40 g of poly(D,L-lactide-co-glycolide) were dissolved in 360 ml of $CHCl_3$ to produce a clear solution and 61.54 g of calcium carbonate ($CaCO_3$) filled poly(D,L-lactide-co-glycolide) were dissolved in 360 ml of $CHCl_3$ to produce a suspension of $CaCO_3$ particles in polymer solution. 1 m long skeins of glass fiber, having the properties shown in Table 4 and weighing between 4.56 g and 7.32 g, were then dipped in the solutions and suspended in a fume cupboard to allow the solvent to evaporate. The resulting coated fiber strips were vacuum dried at 80° C. below 1 mbar to constant mass. The weights and compositions of the dried skeins are shown in Table 5.

TABLE 4

Fibre	A	B	C
Number of specimen	n = 15	n = 16	n = 11
Diameter (μm)	18 ± 5	36 ± 6	24 ± 5
Tensile strength at break (MPa)	1 200 ± 320	560 ± 190	313 ± 280
Tensile Chord Modulus (GPa) (0.1% to 0.3% strain)	101 ± 18	82 ± 24	39 ± 15

TABLE 5

Coating solution	Skein (g)	Coated skein (g)	Fibre (% v/v)
Filled Poly(D,L-lactide-co-glycolide)	5.75	9.45	53.7
	7.32	9.95	67.5
Poly(D,L-lactide-co-glycolide)	4.56	6.31	58.0
	6.68	8.58	65.1

[0046] The coated fiber strips were cut into 120 mm lengths and compression molded at 160° C. to produce composite bars with nominal measurements of 10×3×120 mm. The bars were accurately measured and weighed to calculate their compositions. The flexural mechanical properties of the composites were tested using a 3 point bend test method. The length/distance ratio of the composites was 32 and the test speed was 4.74 min/min. The moduli were determined from 3 measurements and the strength/strain to failure from 1 specimen. The compositions and mechanical properties results are shown in Table 6. The table shows that the glass fiber composites have substantially similar flexural strengths to the polymer fiber composites in Table 2. For the purposes of this disclosure, the modulus is a quantity that expresses the degree to which a substance possesses a property, such as elasticity.

TABLE 6

Matrix polymer	Fibre (% v/v)	Modulus (Gpa)	Strength (Mpa)	Strain to faliure (%)
Filled Poly(D,L-lactide-co-glycolide)	60.6	26.6 ± 1.1	297.4	1.1
Poly(D,L-lactide-co-glycolide)	61.6	25.9 ± 0.3	297.1	1.2

Example 5

[0047] Solutions of 10% w/w of poly (D-L-lactide-co-glycolide) 85:15 and 35% w/w (of the polymer weight) CaCO3 in CH_2Cl_2 were prepared. Approx. 50 cm lengths of glass fiber (50 mol % P_2O_5, 30-40 mol % CaO, 5-15 mol % Na_2O, 5 mol % Fe_2O_3) weighing between 1.5 and 7 g were weighed, dipped in the polymer solution, and hung up to dry in a fume cupboard over night. The fibers were then vacuum dried at 80° C. and re-weighed. The composite strips were cut into 12 mm lengths and randomized.

[0048] The composites were compression moulded in an aluminium mould with a cavity measuring 120×3×10 mm. The mould was lined with a strip of PTFE impregnated glass cloth to allow the product to be removed more easily. The moulding was done at 160° C. under 100 kN pressure. The mould was pre-heated and then strips were loaded into the cavity by hand one or two at a time. Once the mould was full, the pressure was applied for a few seconds, the mould was then re-opened, and further strips added. This was repeated until no further strips could be forced into the mould. The mould was then cooled to room temperature under pressure. The composite bars were trimmed and then capped with a layer of filled matrix to seal the ends. The weights and compositions of the fibers are shown in Table 7.

TABLE 7

Composite type	n	Weight (g) Before end-capping Mean	Weight (g) Before end-capping Standard Deviation (SD)	Volume (mL) Mean	Volume (mL) Standard Deviation (SD)	Density (g/mL) mean	Density (g/mL) Standard Deviation (SD)	Fiber fraction (% v/v) Mean	Fiber fraction (% v/v) Standard Deviation (SD)	Fiber fraction (% v/v) Max	Fiber fraction (% v/v) Min
15% Na2O	11	7.1146	0.2102	3.34	0.06	2.13	0.06	69.9	5.8	76.2	57.4
5% Na2O	13	6.9774	0.1987	3.30	0.09	2.12	0.03	67.9	3.5	74.3	63.6

[0049] All samples were tested to assess flexural stiffness and tested to failure. Tests were performed in a 3 point bending test set-up, with a testing span of 90 mm and thickness and width measured for each sample. For modulus measurements, deflection was performed at a crosshead displacement of 4.74 mm/min using a 100N load cell. Strength was measured using a 10 kN load cell. The compositions and mechanical properties results are shown in Table 8.

TABLE 8

Composite type	Flexural strength (MPa)	Flexural modulus (GPa)
15% Na2O	272.2 ± 31.0	26.8 ± 1.7
5% Na2O	334.6 ± 22.5	27.3 ± 1.9

Example 6

[0050] Glass fiber composites, as prepared in Example 5, with and without CaCO3 filler mixed in the matrix, were immersed individually in bottles containing 300 ml of phosphate buffer saline (PBS) and placed in an incubator at 37° C. The samples were removed for analysis after 14 days, and their dry mass was recorded. The samples containing CaCO3 had retained 98% of their initial dry mass, while those without CaCO3 had only retained 63% of their initial dry mass

[0051] The polymer fiber composite material of the present disclosure includes a polylactic acid fiber of high strength and a matrix material that is suitable for working with this fiber. The matrix allows for a good interfacial strength between the fiber and the matrix, which provides the composite with a high mechanical strength and a decreased degradation rate. Also disclosed are polymer and glass fiber composite materials having a concentration of buffering material that has been shown to not adversely interfere with the interface between the polymer matrices and the fiber materials. Rather, the testing results show that the buffering material works to provide the composite with the ability to retain a majority of its initial strength over a longer period of time by slowing the rate of degradation of the polymer matrix and, in the glass fiber composite, the degradation rate of the glass fiber.

[0052] A composite material containing a matrix material and a mixture of the above-described glass and polymer fibers, with or without a degradation controlling agent, is also within the scope of this disclosure. The matrix and the glass and polymer fibers may be of the same type and made by the same processes as the above-described matrices and polymer/glass fibers. In addition, the degradation controlling agents may be of the same type as described above. Furthermore, the processing conditions for making the composite may be the same as the processing conditions for making the above-described polymer fiber composites.

[0053] As various modifications could be made to the exemplary embodiments, as described above with reference to the corresponding illustrations, without departing from the scope of the disclosure, it is intended that all matter contained in the foregoing description and shown in the accompanying drawings shall be interpreted as illustrative rather than limiting. Thus, the breadth and scope of the present disclosure should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims appended hereto and their equivalents.

1-22. (canceled)

23. A fiber reinforced composite material comprising:
a matrix material;
a glass fiber material; and
a degradation controlling agent.

24. The composite material of claim **23**, wherein the matrix material is selected from the group consisting of polymers, copolymers, and polymer blends.

25. The composite material of claim **23**, wherein the matrix material is bioabsorbable.

26. The composite material of claim **23**, wherein the glass fiber material is bioabsorbable.

27. The composite material of claim **23**, wherein the glass fiber material has a tensile strength between about 300 MPa and about 1200 MPa.

28. The composite material of claim **23**, wherein the glass fiber material comprises a hydrophobic material.

29. The composite material of claim **23**, wherein the composite material comprises the glass fiber material in an amount of about 50% by volume.

30. The composite material of claim **23**, wherein the degradation controlling agent is dispersed in the matrix material.

31. The composite material of claim **23**, wherein the degradation controlling agent is coated on a surface of the fiber material.

32. The composite material of claim **30**, wherein the composite material comprises the degradation controlling agent in an amount of between about 0.1% and about 40% by weight of the matrix material.

33. The composite material of claim **23**, wherein the degradation controlling agent comprises a buffer material selected from the group consisting of calcium carbonate, calcium hydrogen carbonates, calcium phosphates, dicalcium phosphates, tricalcium phosphates, magnesium carbonate, and sodium carbonate.

34. The composite material of claim **33**, wherein the degradation controlling agent comprises a common salt.

35. The composite material of claim **23**, wherein the composite has an initial tensile strength of at least 250 MPa.

36. The composite material of claim **35**, wherein the composite retains the initial tensile strength for at least 8 weeks.

37. The composite material of claim **23**, wherein the composite has an initial flexural strength of between about 250 MPa and about 400 MPa.

38. The composite material of claim **23**, wherein the composite has an initial flexural modulus of between about 20 GPa and about 30 GPa.

39. The composite material of claim **23**, wherein the composite retains about 98% of an initial mass for at least 2 weeks.

40. (canceled)

41. A fiber reinforced composite material comprising:
a matrix material; and
a glass fiber material, wherein the glass fiber material has a tensile strength of between about 300 MPa and about 1200 MPa.

42. (canceled)

43. The composite material of claim **23**, wherein the degradation controlling agent is selected from the group consisting of buffer materials, common salts, and combinations thereof.

44. (canceled)

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