

Polycaprolactone having improved SLS 3D-printing sintering properties**Field of the invention**

The present invention refers to a compound particle for 3D printing obtained by hot melt extruding

5 50 to 90 wt.-% at least one polycaprolactone based polymer;

10 to 50 wt.-% of at least one filler; and

optionally up to 5 wt.-% of at least one additive into pellets, wherein

the total weight of the components is 100 wt.-%, and thereafter milling the pellets to obtain the compound particle. Furthermore, the present invention refers to a composition for 3D printing

10 comprising

a) 94 to 99 wt.-% of at least one compound particle according to the present invention;

b) 1 to 6 wt.-% of at least one filler; and

c) optionally up to 5 wt.-% of at least one additive; wherein

the total weight of a) to c) is 100 wt.-%. Moreover, the present invention refers to a 3D printing

15 method comprising the compound particle or the composition according to the present invention,

the article obtained by the 3D printing method and its use as a substitute for bones or a scaffold for broken bones.

Description of the related art

20 Polycaprolactone is commonly 3D-printed at bed-temperatures of around 50 to 65 °C via SLS 3D printing. However, most SLS printing devices can work at 50 °C, but perform and control temperature significantly better at higher bed temperatures, i.e., 100°C or higher. Furthermore, 50 to 65°C temperatures are not significantly higher than room temperature. The temperature control is therefore challenging and cannot be precisely controlled in common commercial available SLS printing

25 devices. The temperature control is in those devices at these temperatures not very precise, and thus can lead to hot spots. Common issues during printing of Polycaprolactone are thus hot-spots (the polymer agglomerates in certain small percentage resulting in some agglomerated powder with higher diameter). Powder with agglomerated slightly more % of agglomerated particles cannot be easily re-used, leading to defects during printing process and impairing the overall flowability of the

30 powder. Colder zones on the other side can lead to unsintered spots in the printed part.

In order to improve flowing of the powder and avoiding part defects, flowing-agents also referred to as flow aids or fillers have been added for improving flowability for example as disclosed in WO 2019/043137 A1. These flowing agents can be hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP), bioactive glass, other calcium phosphates among other materials. When Polymer and flowing

agents are blended, the amount of flowing agent in the blend should not exceed around 10 wt.-%. It was observed, that loads of 10 wt.-% or more and in several cases even 5% load of flowing agent can lead to segregation of flowing agent and thus inconsistent flowing properties. i.e. the flowing agent loses his characteristics as flowing aid and flow is not further improved. At loads above 10 wt.-%, not only segregation can be observed, but inhomogeneous flowing properties are commonly the result. This limits the real usage of flowing agent to a wt.% of 1 to 5% in the practice.

Furthermore, low amounts of flow agent, around 2 to 10 wt.-% have no significant improvement to a better laser absorption of the composition. Thus, the printing bed temperature needs to be as high as possible (around 60 and even 65 °C) and unwanted sintering of neighboring particles, poor flowing, black-spots, etc. can be observed.

Therefore, it was a need to provide printing compositions based on polycaprolactone polymers which can be printed below 60 °C and better at 58°C or lower and show sufficient sintering capability.

The inventors of the present invention surprisingly found one or more of the objects can be solved by using a compound particle which is obtained by hot melt extruding 50 to 90 wt.-% at least one polycaprolactone based polymer; 10 to 50 wt.-% of at least one filler; and optionally up to 5 wt.-% of at least one additive into pellets, wherein the total weight of the components is 100 wt.-%, and thereafter milling the pellets to obtain the compound particle. The use of these particles surprisingly leads to a more stable sinter process as well.

20 Summary

Therefore, in a first aspect the present invention refers to a compound particle for 3D printing obtained by hot melt extruding

50 to 90 wt.-% at least one polycaprolactone based polymer;

10 to 50 wt.-% of at least one filler; and

25 optionally up to 5 wt.-% of at least one additive into pellets, wherein

the total weight of the components is 100 wt.-%, and thereafter milling the pellets to obtain the compound particle.

30 In a second aspect the present invention refers to a composition for 3D printing comprising or consisting of

- a) 94 to 99 wt.-% of at least one compound particle according to the present invention;
- b) 1 to 6 wt.-% of at least one filler; and
- c) optionally up to 5 wt.-% of at least one additive; the total weight of a) to c) is 100 wt.-%.

In a third aspect the present invention refers to a 3D printing method comprising the composition according to the present invention.

5 In a fourth aspect the present invention pertains to an article obtained by the 3D printing method according to the present invention.

In a fifth aspect the present invention refers to the use of the article according to the present invention as a substitute for bones or a scaffold for broken bones.

10 These and other aspects, embodiments, features, and advantages of the invention will become apparent to a person skilled in the art through the study of the following detailed description and claims. Any feature from one aspect of the invention can be used in any other aspect of the invention. Furthermore, it will readily be understood that the examples contained herein are intended to describe and illustrate the invention but not to limit the invention and that, in particular, the invention is not limited to these examples.

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Brief description of the drawings

Detailed description

20 Numerical ranges that are indicated in the format "from x to y" also include the stated values. If several preferred numerical ranges are indicated in this format, it is self-evident that all ranges that result from the combination of the various endpoints are also included.

"One or more", as used herein, relates to at least one and comprises 1, 2, 3, 4, 5, 6, 7, 8, 9 or more of the referenced species. Similarly, "at least one" means one or more, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9 or more. "At least one", as used herein in relation to any component, refers to the number of
25 chemically different molecules, i.e. to the number of different types of the referenced species, but not to the total number of molecules. For example, "at least one filler" means that at least one type of molecule falling within the definition for a filler is used but that also two or more different types of fillers falling within this definition can be present but does not mean that only one or more molecules of one type of filler are present.

30 All percentages given herein in relation to the compositions or formulations relate to wt.-% relative to the total weight of the respective composition, if not explicitly stated otherwise.

"Essentially free of" according to the present invention with regard to compounds means that the compound can only be present in an amount, which does not influence the characteristics of the composition, in particular the respective compound is present in less than 3 wt.-%, preferably 1 wt.-%, more preferably 0.01 wt.-%, based on the total weight of the composition or is not present at all.
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The weight average molecular weight M_w and the number average molecular weight M_n can be determined by GPC employing polystyrene standards, if not explicitly stated otherwise.

The term "osteoconductive filler" refers to a material which can be added to compositions to increase the biological response and bone tissue growth promotion of the resultant compositions.

- 5 "Osteoconductivity" is measured by histological, imaging or spectroscopical methods of new bone formation from in vivo tests or proliferation of bone forming cells (osteoblasts) to the material with producing bone specific proteins or substances known to the skilled person.

10 In particular, the present invention refers to a compound particle for 3D printing obtained by hot melt extruding

50 to 90 wt.-% at least one polycaprolactone based polymer;

10 to 50 wt.-% of at least one filler; and

optionally up to 5 wt.-% of at least one additive into pellets, wherein

15 the total weight of the components is 100 wt.-%, and thereafter milling the pellets to obtain the compound particle.

The at least one compound particle contains at least one polycaprolactone based polymer.

In one embodiment, the polycaprolactone based polymer can be a poly(caprolactone) or a poly(lactide-co-caprolactone).

- 20 In one embodiment, the polymer can be a poly(lactide-caprolactone), preferably can be 95:5 poly(lactide-co-caprolactone), 85:15 poly(lactide-co-caprolactone), 75:25 poly(lactide-co-caprolactone), 65:35 poly(lactide-co-caprolactone), or 50:50 poly (lactide-co-caprolactone), where the ratios are mole ratios.

25 In one embodiment the at least one polycaprolactone based polymer has a weight average molecular weight of 5.000 to 140.000 g/mol, measured via GPC using polystyrene standards.

In one embodiment the at least one polycaprolactone based polymer has an inherent viscosity of 0.1 to 2.5 dL/g, preferably 0.5 to 2.5 dL/g or 0.8 to 2.0 dL/g in CHCl_3 at 25 °C measured with a Ubbelohde size 0c glass capillary viscometer.

30 In one embodiment the at least one polycaprolactone based polymer has a melting temperature of 50 to 70 °C, preferably 55 to 65 °C.

The at least one compound particle comprises at least one filler.

In one embodiment the at least one filler is an osteoconductive filler.

In one embodiment the at least one filler is selected from hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP), bioactive glass, biphasic calcium phosphate (BCP) and implantable alloys according to DIN EN ISO 5832-1:2019-12 or mixtures thereof. In one preferred embodiment the at
5 least one filler is selected from hydroxyapatite (HA), beta-tricalcium phosphate (β -TCP), bioactive glass, biphasic calcium phosphate (BCP) or mixtures thereof, more preferred is hydroxyapatite.

The hydroxyapatite can be a single type of hydroxyapatite or a mixture of different hydroxyapatites, for example sintered and unsintered hydroxyapatites.

In one embodiment the at least one filler has a particle size $dv(50)$ of at most 200 μm , preferably at
10 most 100 μm , the particle size is preferably determined via laser diffraction.

In one embodiment the at least one filler can have mono-modal or bi-modal or multimodal particle size distribution.

The at least one compound particle can further comprise at least one additive. The at least one additive is different from the at least one filler. All additives suitable for 3D printing and known to the
15 skilled person can be used.

In one embodiment the at least one additive is selected from flow aids, bioactive agents, and pigments or mixtures thereof.

In one embodiment the flow aid includes but is not limited to calcium phosphate and its doped variants (e.g. strontium, zinc, magnesium, fluoride, carbonate), calcium sulphate, and calcium
20 carbonate. Calcium phosphates include but are not limited to octacalcium phosphate, dicalcium phosphate, or a mixture thereof. Furthermore, salts like magnesium sulphate, sodium sulphate, potassium chloride, sodium chloride, sodium sulphate, aluminium potassium sulphate, magnesium chloride, and magnesium chloride hexahydrate are included as well.

Such flow aids are typically in the range of 0.1 micrometres to 1 mm, 0.1 micrometres to 500
25 micrometres, 0.1 to 250 micrometres, 0.1 to 100 micrometres, or 0.1 to 50 micrometres, 0.1 to 40 micrometres, 0.1 to 30 micrometres, 0.1 to 20 micrometres, 0.1 to 10 micrometres, 0.1 to 5 micrometres, or 0.1 to 1 micrometre.

A wide variety of bioactive agents can be used in the present invention. In one embodiment, the
30 bioactive agent can be a releasable bioactive agent, i.e., a bioactive agent that can be released from the controlled release system into adjacent tissues or fluids of a subject. In certain aspects, the bioactive agent can be in or on the controlled release system.

Various forms of the bioactive agent can be used, which are capable of being released from the controlled release system into adjacent tissues or fluids. To that end, a liquid or solid bioactive
35 agent can be incorporated into the controlled release system described herein. The bioactive agents are at least very slightly water soluble, and preferably moderately water soluble. The

bioactive agents can include salts of the active ingredient. As such, the bioactive agents can be acidic, basic, or amphoteric salts. They can be non-ionic molecules, polar molecules, or molecular complexes capable of hydrogen bonding. The bioactive agent can be included in the compositions in the form of, for example, an uncharged molecule, a molecular complex, a salt, an ether, an ester, an amide, polymer drug conjugate, or other form to provide the effective biological or physiological activity.

Examples of bioactive agents that incorporated into systems herein include, but are not limited to, peptides, proteins such as hormones, enzymes, antibodies and the like, nucleic acids such as aptamers, iRNA, DNA, RNA, antisense nucleic acid or the like, antisense nucleic acid analogs or the like, low-molecular weight compounds, or high-molecular-weight compounds.

Bioactive agents contemplated for use in the disclosed implantable composites include anabolic agents, antacids, anti-asthmatic agents, anti-cholesterolemic and anti-lipid agents, anti-coagulants, anti-convulsants, anti-diarrheals, anti-emetics, anti-infective agents including antibacterial and antimicrobial agents, anti-inflammatory agents, anti-manic agents, antimetabolite agents, anti-nauseants, anti-neoplastic agents, anti-obesity agents, anti-pyretic and analgesic agents, antispasmodic agents, antithrombotic agents, anti-tussive agents, anti-uricemic agents, anti-anginal agents, antihistamines (e.g., terfenadine), appetite suppressants, biologicals, cerebral dilators, coronary dilators, bronchodilators, cytotoxic agents, decongestants, diuretics, diagnostic agents, erythropoietic agents, expectorants, gastrointestinal sedatives, hyperglycemic agents, hypnotics, hypoglycaemic agents, immunomodulating agents, ion exchange resins, laxatives, mineral supplements, mucolytic agents, neuromuscular drugs, peripheral vasodilators, psychotropics, sedatives, stimulants, thyroid and anti-thyroid agents, tissue growth agents, uterine relaxants, vitamins, or antigenic materials.

Other bioactive agents include androgen inhibitors, polysaccharides, growth factors (e.g., a vascular endothelial growth factor-VEGF), hormones, anti-angiogenesis factors, dextromethorphan, dextromethorphan hydrobromide, noscapine, carbetapentane citrate, chlophedianol hydrochloride, chlorpheniramine maleate, phenindamine tartrate, pyrilamine maleate, doxylamine succinate, phenyltoloxamine citrate, phenylephrine hydrochloride, phenylpropanolamine hydrochloride, pseudoephedrine hydrochloride, ephedrine, codeine phosphate, codeine sulphate morphine, mineral supplements, cholestyramine, N-acetylprocainamide, acetaminophen, aspirin, ibuprofen, phenyl propanolamine hydrochloride, caffeine, guaifenesin, aluminium hydroxide, magnesium hydroxide, peptides, polypeptides, proteins, amino acids, interferons, cytokines, and vaccines.

Representative drugs that can be used as bioactive agents include, but are not limited to, peptide drugs, protein drugs, desensitizing materials, antigens, anti-infective agents such as antibiotics, antimicrobial agents, antiviral, antibacterial, antiparasitic, antifungal substances and combination thereof, antiallergenics, androgenic steroids, decongestants, hypnotics, steroidal antiinflammatory agents, anti-cholinergics, sympathomimetics, sedatives, miotics, psychic energizers, tranquilizers,

vaccines, estrogens, progestational agents, humoral agents, prostaglandins, analgesics, antispasmodics, antimalarials, antihistamines, cardioactive agents, nonsteroidal antiinflammatory agents, antiparkinsonian agents, antihypertensive agents, p-adrenergic blocking agents, nutritional agents, and the benzophenanthridine alkaloids. The agent can further be a substance capable of acting as a stimulant, sedative, hypnotic, analgesic, anticonvulsant, and the like.

Other bioactive agents include but are not limited to analgesics such as acetaminophen, acetylsalicylic acid, and the like; anaesthetics such as lidocaine, xylocaine, and the like; anorexics such as dexadrine, phendimetrazine tartrate, and the like; antiarthritics such as methylprednisolone, ibuprofen, and the like; antiasthmatics such as terbutaline sulphate, theophylline, ephedrine, and the like; antibiotics such as sulfisoxazole, penicillin G, ampicillin, cephalosporins, amikacin, gentamicin, tetracyclines, chloramphenicol, erythromycin, clindamycin, isoniazid, rifampin, and the like; antifungals such as amphotericin B, nystatin, ketoconazole, and the like; antivirals such as acyclovir, amantadine, and the like; anticancer agents such as cyclophosphamide, methotrexate, etretinate, and the like; anticoagulants such as heparin, warfarin, and the like; anticonvulsants such as phenytoin sodium, diazepam, and the like; antidepressants such as isocarboxazid, amoxapine, and the like; antihistamines such as diphenhydramine HCl, chlorpheniramine maleate, and the like; hormones such as insulin, progestins, 17-alpha-hydroxyprogesterone caproate, iso-allo-pregnanolonetestosterone, prenisolone, prednisone, dexamethasone estrogens (e.g., estradiol), corticoids, glucocorticoids, androgens, and the like; tranquilizers such as Thorazine, diazepam, chlorpromazine HCl, reserpine, chlordiazepoxide HCl, and the like; antispasmodics such as belladonna alkaloids, dicyclomine hydrochloride, and the like; vitamins and minerals such as essential amino acids, calcium, iron, potassium, zinc, vitamin B12, and the like; cardiovascular agents such as prazosin HCl, nitroglycerin, propranolol HCl, hydralazine HCl, pancrelipase, succinic acid dehydrogenase, and the like; peptides and proteins such as LHRH, somatostatin, calcitonin, growth hormone, glucagon-like peptides, growth releasing factor, angiotensin, FSH, EGF, bone morphogenic protein (BMP), erythropoietin (EPO), interferon, interleukin, collagen, fibrinogen, insulin, Factor VIII, Factor IX, ENBREL®, RITUXAM®, HERCEPTIN®, alpha-glucosidase, Cerazyme/CEREDOSE®, vasopressin, ACTH, human serum albumin, gamma globulin, structural proteins, blood product proteins, complex proteins, enzymes, antibodies, monoclonal antibodies, and the like; prostaglandins; nucleic acids; carbohydrates; fats; narcotics such as morphine, codeine, and the like, psychotherapeutics; anti-malarials, L-dopa, diuretics such as furosemide, spironolactone, and the like; antiulcer drugs such as ranitidine HCl, cimetidine HCl, and the like, and calcium channel antagonist such as nimodipine and the like, lumenfantine, cilengitide, 3-hydroxy-3-methylglutaryl-coenzyme A reductase inhibitors such as lovastatin and the like.

Bioactive agents include fibrin, fibrinogen, cellulose, starch, collagen, and hyaluronic acid as well.

A wide variety of pigments can be used in the present invention. In one embodiment, the pigments are carbon black and violet 2.

In one embodiment the at least one compound particle has a size (Dv50) of at most 200 μm , preferably at most 120 μm , more preferably at most 50 μm . The particle size can preferably be determined via laser diffraction.

- 5 The at least one compound particle is obtained by hot melt extruding of the compounds. The skilled person knows how to perform hot melt extrusion of the compounds.

In one embodiment the hot melt extrusion is performed at 60 to 100°C, preferably 60 to 80°C.

After the hot melt extrusion pellets are obtained, which are thereafter milled to obtain the at least one compound particle, which forms compound a) of the composition.

- 10 In one embodiment the pellets have an average diameter of less than 4 mm.

In one embodiment the milling is performed by micronizing or cryogenic milling, preferably at process temperatures below -50 °C, preferably below -60 °C.

In one embodiment the milling is performed with a pin mill or counter-rotating pin-mill.

- 15 The at least one compound particle can be present as powder or can come in many particle forms as a result of the milling method. These forms include but are not limited to, porous, hollow, solid, spherical, or irregular shapes.

The compound particle, preferably in powder form, can be sieved or dried.

- 20 The characterization of the different powders can be done on a standard test machine such as a laser scattering machine for particle size determination (commercially available from the company Beckmann Coulter or Malvern). The DSC tests were performed with a heating rate of 10°C/min and a cooling rate of 20°C/min using a TA instruments machine. SEM was performed on a desktop machine (commercially available from the company Hitachi). BET measurements were done on a Micromeritics instrument.

The compound particle can be preferably used in 3D printing composition.

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Furthermore, the present invention refers to a composition for 3D printing comprising or consisting of

- a) 94 to 99 wt.-% of at least one compound particle according to the present invention;
b) 1 to 6 wt.-% of at least one filler; and
30 c) optionally up to 5 wt.-% of at least one additive; the total weight of a) to c) is 100 wt.-%.

The composition according the present invention comprises at least one filler b). The at least one filler b) is the same or different to the at least one filler used in the compound particle, preferably is the same filler.

- 5 The embodiments and preferred embodiments described above for filler of the compound particle apply for filler b) as well.

The composition can further optionally comprise at least one additive c). The at least one additive c) is the same or different to the at least one additive used in the compound particle, preferably is the same filler.

- 10 The embodiments and preferred embodiments described above for additive of the compound particle apply for additive c) as well.

The composition according to the present invention can be used in 3D printing.

- 15 In one embodiment the 3D printing method is preferably a SLS 3D printing method. SLS 3D printing methods are known in the art.

- Selective laser sintering (SLS) can be performed on a blade based (e.g. EOS P series) machine. The technique produces physical parts through a selective solidification of a variety of fine powders. SLS builds up parts layer by layer using powders which are selectively bonded when a laser beam scans the powder across each layer's cross-sectional area. Typical laser energy densities are anywhere from 7 kJ/m² to 60 kJ/m² SLS fuses thin layers of powder (typically ~0.1 mm thick) which have been spread across the build area using a blade. The part building takes place inside an enclosed chamber filled with an inert gas. Preferably nitrogen gas, to minimize oxidation and degradation of the powdered material. The powder in the build platform is maintained at an elevated temperature just below the melting point (for semi-crystalline polymer only) of the powdered material.
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The article obtained after 3D printing is preferably a medical implant.

The 3D printed article can be used as a substitute for bones or a scaffold for broken bones.

Examples

- 30 RESOMER® C 212 is a commercially available semi-crystalline polycaprolactone polymer from Evonik Operations GmbH.

General procedure for the examples:

The polymer and the fillers are compounded via hot-melt-extrusion and thus very well homogenized. The particles of the fillers are distributed statistically around the polymer chains. In the extrusion process, polycaprolactone and a ceramic filler such as calcium phosphate or bioglass are combined to form a physical mixture or composite. The extruder applies heat and pressure to melt the polycaprolactone and mix it with the filler. The ceramic filler does not chemically react with the polymer, but is simply dispersed throughout the melted polycaprolactone to form a homogeneous mixture. This physical mixture can then be extruded into various shapes and forms, such as rods or sheets, depending on the desired application. The addition of the ceramic filler can improve the mechanical properties of the polycaprolactone, such as its strength and stiffness, making it more suitable for certain biomedical applications. Polymer and filler(s) were extruded with a twin-screw extruder with a temperature profile of 60 to 90°C. The strand can be cooled with a water bad and afterwards pelletized or the polymer can be direct pelletized with i.e. an underwater pelletizer.

General procedure for the comparative examples:

Polymer and filler were blended in a Somakon MP-LB Labormischer Speedmix and mixed utilizing three iterations of 300 rpm for two minutes. The obtained blends were SLS 3D printed.

Selective laser sintering

Selective laser sintering (SLS) was performed on a blade based (e.g. EOS P series) machine. The technique produces physical parts through a selective solidification of a variety of fine powders. SLS builds up parts layer by layer using powders which are selectively bonded when a laser beam scans the powder across each layer's cross-sectional area. Typical laser energy densities are anywhere from 7 kJ/m² to 60 kJ/m² SLS fuses thin layers of powder (typically ~0.1 mm thick) which have been spread across the build area using a blade. The part building takes place inside an enclosed chamber filled with an inert gas. Preferably nitrogen gas, to minimize oxidation and degradation of the powdered material. The powder in the build platform is maintained at an elevated temperature just below the melting point (for semi-crystalline polymer only) of the powdered material.

#	Amount Polymer	Polymer	Amount filler 1	Type filler 1	Amount filler 2	Type filler 2	IR Absorption at 10,600 nm
	[%]		[%]		[%]		[%]
C1	100	RESOMER® C 212	0	n.n.	-	n.n.	7.3
C2	91	RESOMER® C 212	9.0	unsintered hydroxyapatite (1µm)	-		-
C3	80	RESOMER® C 212	20.0	unsintered hydroxyapatite (1µm)	-		-
1	70	RESOMER® C 212	30.0	β-tricalciumphosphate	-	n.n.	18.4
2	70	RESOMER® C 212	30.0	Bioglas 58 S	-	n.n.	21.4
3	70	RESOMER® C 212	30.0	unsintered hydroxyapatite (1µm)	-	n.n.	18.0
8	81	RESOMER® C 212	9.0	unsintered hydroxyapatite (1µm)	10	hydroxyapatite (50µm)	11.5
9	76	RESOMER® C 212	9.0	unsintered hydroxyapatite (1µm)	15	hydroxyapatite (50µm)	12.5
10	71	RESOMER® C 212	9.0	unsintered hydroxyapatite (1µm)	20	hydroxyapatite (50µm)	14.1
11	51	RESOMER® C 212	9.0	unsintered hydroxyapatite (1µm)	40	hydroxyapatite (50µm)	21.9
12	90	RESOMER® C 212	10.0	β-tricalciumphosphate	-	n.n.	12.2

Table 1. Examples and Comparative examples (indicated with C). Comparative examples are commonly used blends, while the examples refer to the compound particles obtained via hot melt extrusion.

3D SLS printing of the comparative examples C2 and C3 did not produce desirable results.

An significant increase in the IR absorption depending on the amount of filler can be seen by examples 8 to 11. The compound is less transparent and thus absorbs better the light and can be better sintered.

The compositions according to the present invention, obtained by extrusion are still semi-crystalline and the fillers are well distributed within the polymer. When the laser of the SLS machine scatters the compound particles, the absorption is better and therefore the sintering process is improved. The laser time, scattering profile and the bed temperature can be optimized leading to a more stable process. SLS 3D printing with the compounds of the examples lead to very good results.

Claims

1. A compound particle for 3D printing obtained by hot melt extruding
50 to 90 wt.-% of at least one polycaprolactone based polymer;
5 10 to 50 wt.-% of at least one filler; and
optionally up to 5 wt.-% of at least one additive into pellets, wherein
the total weight of the components is 100 wt.-%, and thereafter milling the pellets to obtain the
compound particle.
- 10 2. The compound particle according to claim 1, wherein the at least one polycaprolactone based
polymer
 - i) has a weight average molecular weight of 5.000 to 140.000 g/mol, measured via GPC using
polystyrene standards; and/or
 - 15 ii) is selected from poly(caprolactone) or a poly(lactide-co-caprolactone) or mixtures thereof;
and/or
 - iii) has an inherent viscosity of 0.1 to 2.5 dL/g in CHCl₃ at 25 °C measured with a Ubbelohde size
0c glass capillary viscometer.
- 20 3. The compound particle according to any of the preceding claims, wherein the at least one filler
is
 - i) an osteoconductive filler; and/or
 - ii) selected from hydroxyapatite, beta-tricalcium phosphate, bioactive glass, biphasic calcium
phosphate, and implantable alloys according to DIN EN ISO 5832-1:2019-12 or mixtures
thereof; and/or
 - 25 iii) has a particle size Dv(50) of at most 200 µm, preferably determined by laser diffraction.
4. The compound particle according to any of the preceding claims, wherein the at least one
additive is selected from flow aids, bioactive agents, and pigments or mixtures thereof.
- 30 5. The compound particle according to any of the preceding claims, having a size (Dv50) of at
most 200 µm, preferably at most 100 µm, more preferably determined via laser diffraction.

6. The compound particle according to any of the preceding claims, wherein the hot melt extrusion is performed at 60 to 100°C.
7. The compound particle according to any of the preceding claims, wherein milling is performed by micronizing or cryogenic milling.
8. A composition for 3D printing comprising or consisting of
 - a) 94 to 99 wt.-% of at least one compound particle according to any of the preceding claims;
 - b) 1 to 6 wt.-% of at least one filler; and
 - c) optionally up to 5 wt.-% of at least one additive; the total weight of a) to c) is 100 wt.-%.
9. The composition according to claim 8, wherein the at least one filler is
 - i) the same or different to the at least one filler contained in the compound particle; and/or
 - ii) an osteoconductive filler; and/or
 - iii) selected from hydroxyapatite, beta-tricalcium phosphate, bioactive glass, biphasic calcium phosphate, and implantable alloys according to DIN EN ISO 5832-1:2019-12 or mixtures thereof; and/or
 - iv) has a particle size $Dv(50)$ of at most 200 μm , preferably determined by laser diffraction.
10. The composition according to claim 8 or 9, wherein the at least one additive is
 - i) the same or different to the at least one additive contained in the compound particle; and/or
 - ii) selected from flow aids, bioactive agents, and pigments or mixtures thereof.
11. 3D printing method comprising the compound particle according to any of claims 1 to 7 or the composition according to any of claims 8 to 10.
12. Article obtained by the 3D printing method according to claim 11.
13. Use of the article according to claim 12 as a substitute for bones or a scaffold for broken bones.