

A METHOD FOR PRODUCING AND USING A COMPLEX FLUID

FIELD

The present disclosure relates to producing bubbly liquid with complex fluid properties that is used in additive manufacturing.

5 BACKGROUND

In fabrication of 3D printed objects with diversity of shapes and complex geometries there may be shapes, or part of shapes such as overhangs that may be critical overhangs, which cannot be balanced by the main body of the printable object and therefore printing material may collapse due to gravity. There are various attempts that may be used to
10 overcome this issue, for example, printing the material in supporting bath and multichannel plotting by co-extrusion of temporary supporting material together with the main printing material. When supporting path is used, the Newtonian and non-Newtonian type liquids and gels have physical properties which under shear-stress by the movement of the injection head of the 3D printing device cause movement of the
15 supporting material and stretching the printable material. This causes deformation and inaccuracy to the printable object. In addition, the liquid supporting material regardless of its possible high viscosity may not support the printable material enough against the effects of gravity when the density of the printable material is high for instance due to heavy filler particles. Change of the viscosity of the liquid supporting material at
20 different temperatures or different pH like with polyacrylic acid hydrogels (carbomer) causes also inaccuracy to the printing object. Furthermore, when the printing material is considered, the stability of the viscosity at various temperatures is a desired property.

It is a required property for the supporting material that it has liquid-like continuous
25 phase in which the printing head moves but at the same time the continuous fluid phase needs to demonstrate plastic behavior when shear stress is applied to the supporting material by movement of the printing head. Also temperature sweep stability of viscosity and biocompatibility are required properties for the supporting material and to the printing material.

30

BRIEF DESCRIPTION

The scope of protection sought for various embodiments of the invention is set out by the independent claims. The exemplary embodiments and features, if any, described in this specification that do not fall under the scope of the independent claims are to be
5 interpreted as examples useful for understanding various embodiments of the invention.

According to a first aspect there is a method for producing complex fluid of bubbly liquid material that is suitable for being used in 3D printing, the method comprising
10 producing to liquid material at least primary bubbles, and optionally secondary and/or tertiary bubbles, as a supporting material for printing a 3D object or for using as printing ink, wherein the liquid material comprises at least the primary bubbles.

According to a second aspect there is a system for 3D printing, wherein the system
15 comprises at least a printing head configured to inject printing material to form a 3D printed object, wherein the system further comprises controlling the 3D printing by a controlling unit, the system being configured to inject the printing material into supporting material that is produced using the method.

20 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the bubbly liquid system with primary bubbles and printable material. Figure 2 illustrates the bubbly liquid system with primary and secondary bubbles and printable material.

Figures 3A and 3B illustrates collapse and runoff of the additional material due to the
25 gravity and effect of bubbly liquid to resist the effect of gravity.

Figure 4 illustrates static flow of the liquid of same composition without and bubbles.

Figure 5 illustrates stability of the viscosity of the material with free-radical forming cross-linker at various temperatures.

Figure 6 illustrates stability of the viscosity of the material with calcium chloride cross-
30 linker at various temperatures.

DETAILED DESCRIPTION

The following embodiments are exemplifying. Although the specification may refer to “an”, “one”, or “some” embodiment(s) in several locations of the text, this does not necessarily mean that each reference is made to the same embodiment(s), or that a particular feature only as to a single embodiment. Single features of different
5 embodiments may also be combined to provide other embodiments.

A method and system is disclosed for producing bubbly liquid material where Newtonian or non-Newtonian liquid material may be transformed by jamming transition
10 to bubbly liquid material having plastic deformation properties of a complex fluid and stable temperature sweep properties. The bubbly liquid material produced may be used as supporting material for 3D printing in a 3D printing system or as a printing material (printing ink) in bioprinting.

15 In an example embodiment, the bubbly liquid material is formed by producing to liquid material primary bubble. This may be achieved for example by adding surfactant to the Newtonian liquid and forming the primary bubbles to the liquid by physical means with aerator or shaking for making the bubbly liquid complex fluid of the first type.

20 The primary bubble liquid material's viscosity may be changed by adding free radicals or molecular compounds to the continuous liquid phase after which chemical reaction forms secondary bubbles thus making the bubbly liquid complex fluid of the second type.

25 Optionally, tertiary bubbles are produced to the bubbly liquid material by chemical reactions, physical means of injecting gas to the bubbly liquid material or by biological processes for making the bubbly liquid to be complex fluid of the third type (multi modal gas bubble system).

30 The bubbly liquid material may thus have a system of gas bubbles of one or several different size and gas compositions.

The gas bubbles may diminish buoyancy effect of the continuous liquid phase by the surface tension of the gas bubbles and hinders effect of the force of gravity to the printable object.

- 5 The complex fluid of the first, second or third type may diminish the effect of Archimedes' principle and holds the additional printing material vertically (y-direction) in the predetermined location.

- 10 The continuous liquid phase of the bubbly liquid i.e. the complex fluid of the first, second or third type, traps the gas bubbles inside of the bubbly liquid and hinders collapse and coalescence of the gas bubbles.

- 15 The complex fluid of the first, second or third type and the jamming transition of the bubbly liquid material influence firmness and stiffness of the bubbly liquid to be able to support additional materials in the bubbly liquid to be kept at desired x-y-z location and volumetric form.

- 20 The additional compounds in the complex fluid can transform their state of matter from fluid and fluid-like state to semi-solid. Additional compounds may be calcium chloride, isocyanates, epichlorohydrin, aldehyde derivatives like glutaraldehyde, urea derivatives or carboxylic acids or transition metals of III group of elements, and/or free radical forming compounds. Additional materials may also affect the behavior, function or state of matter of the printing material.

- 25 The viscosity and state of matter transformation of the bubbly liquid can be changed by the primary, secondary and tertiary types of the complex fluid by co-existing chemical reactions in the bubbly liquid and by addition of nanoparticles or molecules for emulsion, suspension, colloidal systems, proteins, microbes, yeast, or cells.

- 30 The bubbly liquid material as supporting material for the printing material it is not solidifying by polymerization but when the bubbly liquid material is used as printing ink it may contain solidifying cross-linker compounds.

The temperature sweep properties of the bubbly liquid material for its viscosity may be stable at different temperatures.

- 5 A non-Newtonian liquid is characterized by a viscosity that varies with motion. Most non-Newtonian liquids have a molecular chain structure and can be also complex fluids. Complex fluids are mixtures with two or several phases of solid-liquids (suspensions), solid-gas, liquid-gas (foams) or liquid-liquid (emulsions). Mechanical response of the complex fluid includes transitions between solid-like and fluid-like behavior including plastic deformation. Complex fluid with plastic deformation in shear can be for instance cut. Material of this kind is called Bingham plastic.

- Bubbly liquid of complex fluid, which may also be referred to as bubbly liquid material, comprises continuous liquid phase and gas bubbles at circa 50 percentage. High gas bubble volumetric loading the material becomes a foam. Bubbles modify the rheology of the liquid by resisting deformation and liquid's behavior is affected by the properties of the continuous liquid phase and size bubble volume fraction. Surface tension of the bubbles balances the outward force of air pressure and the weight of the material inside the bubbly liquid by Laplace pressure. Bubbles are formed to the liquid when the amount of dissolved gas exceeds the limit of its solubility in the liquid and gas molecules join in aggregates which forms gas bubbles. Gas bubbles are floating up because of their low density unless the physical properties of viscosity and plasticity of the continuous liquid phase is not hindering floating by trapping the bubbles and thus stabilizing the bubbly liquid. Trapping of gas bubbles in the liquid is also influenced by friction which is known as drag or fluid resistance.

- When additional material of object is placed to liquid the Archimedes' principle allows the buoyancy of the floating object which is immersed in the liquid. Buoyant effect for the material or object is equal to the weight of the displaced liquid. However, if the liquid is filled with gas bubbles, which weight is essentially less compared to liquid without gas bubbles, the buoyant effect is less. Balance between the buoyant effect, the effect of gravity and the surface tension of the gas bubbles holds the additional material

and object in steady location in the liquid. The buoyancy effect can also be explained by collisions of water molecules to the floating object rather than weight of the displaced liquid. Also in this case, gas bubbles diminish number of water molecules and floating in foamy liquid will be less. It is also noteworthy to highlight effect of surface tension
5 i.e. the density difference between the liquid and gas phases which typically is effective on the surface of liquid letting light object to float. The density difference exists also inside of the liquid when there are gas bubbles present.

Gas bubbles can be produced using physical means, such as by using aerator or shaking
10 the liquid, or by chemical reaction in the liquid material to produce gas. Continuous liquid phase is typically made from Newtonian liquid of water and by adding surfactant like soap to the water surface tension of water is lowered which increases foaming. Normal foam is unstable system and bubbles will disappear by time. If the surfactant is simultaneously increasing the viscosity of water and making the liquid complex fluid
15 type decay time of the bubbles is prolonged or the bubbles are even trapped to the continuous liquid phase. One compound which is lowering the surface tension of water and enhancing formation of bubbles is methyl cellulose ($C_6H_7O_2(OH)_x(OCH_3)_y$), hydroxypropyl methyl cellulose ($C_{56}H_{108}O_{30}$) or chitin ($C_8H_{13}O_5N_n$). Methyl cellulose hydrogel can be aerated for air bubbles by aerator or shaking. For stabilization
20 of the methyl cellulose hydrogel and air bubbles, and to increase its viscosity and turning the liquid to be non-Newtonian, methyl cellulose macromolecules affinity to react with each other for cross-linking is enhanced by free radical forming compound in the methyl cellulose water liquid. Example of cross-link enhancing compounds are 4,4'-Azobis (4-cyanopentanoic acid) which forms hydroxyl radicals to the liquid after adding the cross-
25 link-enhancing compound to the liquid, thioxanthone-based hydrophilic cross-linkers (e.g. TX-MPEG350, TX-MPEG550, and TX-MPEG750) and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP). Other crosslinking agents for cross-linking methyl cellulose are epichlorohydrin, aldehyde-based reagents, urea derivatives and multifunctional carboxylic acids like citric acid and transition metals of the platinum
30 group. In cross-linking chain co-polymerization reactions with the vinyl group of the methyl cellulose takes place in the presence of water and hydrogel begins to form. Air bubbles produced by shaking or aerator in hydrogel is called as complex fluid of the first

type. Figure 1 illustrates as example of such primary bubbles 120 in bubbly liquid material 105 that is to be used produced to be used as supporting material for 3D printing. The primary bubbles 120 may be of diameter 0.1 to 1.0 mm for example (Figure 1). Quantity of methyl cellulose can be between 1 to 20 wt% of the weight of the water, preferably 5 wt%. Surface tension 125 of the air bubbles and the density difference of gas and liquid balances the outwards force of air pressure and supports the printable material extruding from the printing head 110, which is used for 3D printing in the 3D printing system 100, and forming the printable object 115 from run off by the force of gravity. Non-Newtonian type hydrogel can keep the air bubbles in the gel for a longer period of time than the Newtonian and water hydrogel is not trapping the gas bubbles and they will disappear by time when the hydrogel is used as supporting material for 3D printing material.

Thus, the overhangs will collapse by the force of gravity already less than one second after injecting of the resin material had started before becoming polymerized, which is illustrated in Fig. 2. In Fig. 2 there is a chart in which the y-axis illustrates runoff (mm) and the x-axis illustrates time from the start of printing. The printing may be performed using a 3D printing system such as the printing system 3D. In general, a 3D printing system comprises a printing head configured to inject the printing material into the supporting material, that may be bubbly liquid of complex fluid. The printing may be controlled by a controlling unit coupled to the printing head using any suitable mechanism for the coupling. It is also to be noted that controlling the printing may be performed, at least partly, using computer program instructions. In Fig. 2, the force of gravity 230 affects an overhang of the object 220 that is printed. In the scenario b), a printed object 220 has an overhang. In the scenario a), there are no gas bubbles in the hydrogel used as the supporting material and as a result, there is the runoff of the overhang. In the scenario b), the object 220 is printed and it has an overhang. In the scenario b) the hydrogel supporting material of the complex fluid of the first, second or third type with primary, secondary and tertiary gas bubbles provide a supporting effect for the overhang. To stabilize the bubble liquid to trap air bubbles additional compounds like cellulose nanocrystals (CNC) or other polysaccharides such as sucrose or fructose

can be added to the hydrogel. When sucrose is used for stabilization of the bubbles sugar content can be 10 – 150 weight percent of the weight of water, preferably 80 wt%.

Complex fluid properties and homogeneity of the hydrogel may be enhanced by
5 additional secondary gas bubbles which can be nitrogen gas (N_2) comprising bubbles of
for example 0.01 to 0.1 mm in diameter. The effect of primary and secondary gas
bubbles i.e. complex fluid of the first and second type for the static flow of 10 ml
hydrogel drop 300 on glass plate is demonstrated in an example illustrated in Figures
3A and 3B as measured of spreading the hydrogel drop at room temperature and pressure
10 (RTP) in 20 minutes time (Figure 3 A). Grouping A to D with the same composition of
methyl cellulose and sucrose refers the following: A: No primary, secondary and tertiary
bubbles (not complex fluid, control); B: with secondary bubbles; C: with primary and
secondary bubbles with arrowheads showing schematically the width of the drop
(spreading) after 20 minutes. Figure 3 B shows that spreading of hydrogel with same
15 composition but with different gas bubble structure behave differently in their flow
properties.

A source for the secondary gas bubbles, which may have a function of protection gas
like N_2 , argon (Ar) for enhancing free radical polymerization of the printable resin
20 material, is chemical reaction in the hydrogel. The secondary gas bubbles increase
homogeneity of the hydrogel and also fill the large size primary air bubbles. This is
illustrated in Fig. 4 in which there are secondary bubbles 425 comprised in supporting
material 405. The supporting material is used with the printing system 400, in which
there is a printing head 410, that injects printing material into the supporting material
25 405 to produce a 3D printed object 415 comprising an overhang. The supporting material
405 also comprises primary bubbles 420. The printing system in 400 in this example
embodiment may further comprise a control unit configured to control the movement of
the printing head 410 as well as injection of the printing material. The controlling may
be achieved using suitable mechanical structured and software to control the 3D printing
30 process. Having the secondary bubbles 405 improves surface smoothness of the
printable object 415 if the hydrogel is used as supporting material 405 for the 3D printed
object 415 with the overhang. The bubble system of the complex fluid with its

consistency and plastic deformation provides support for the resin material used as the printing material and which is 3D printed to the hydrogel used as the supporting material 405 and eliminates material runoff due to force of gravity, the effect of which was illustrated in Fig. 2.

5

Complex fluid of the first, second or third type, i.e. hydrogel supporting material of methyl cellulose and sugar with different bubble systems is stable for its viscosity at various temperatures (temperature sweep) which is not the case for other hydrogels like agar, alginate or gelatin hydrogels which shows lowering of the viscosity when the temperature is increased and illustrated in the Fig. 5. Viscosity of complex fluid hydrogel made of methylcellulose and sucrose of the first type with (510) or without (520) free radical forming chemical compound vary from 21 to 300 Pa·s. being e.g. 70 Pa·s. for the example hydrogel (530) and the viscosity is stable at temperatures from 5 to 60 °C and as 20 to 40 °C with the methyl cellulose sucrose hydrogel complex fluid of the first type in example (510, 520) whereas when the methylcellulose – sucrose hydrogel contains UV sensitive compound and it is UV radiated for 1 minute with wavelength of 360 - 400 nm and radiation power of 14 mW/cm² and total energy of 0.69 J/cm² for becoming complex fluid of the second type its viscosity increases to 145 Pa·s. (540) and still has the temperature sweep stability. For comparison, a commonly used hydrogel of agar and gelatin loses its viscosity from 175 to 5 Pa·s. when the temperature is increased from 20 to 40 °C (550).

Hydrogel of methyl cellulose – sucrose complex fluid of the first, second or third type can also be enlaced by additional cross-linking compounds such as calcium chloride (CaCl₂) for releasing Ca²⁺ ion which bind the methyl cellulose and sucrose units of the complex fluid by oppositely charged molecules and ionic complexes with Ca²⁺ ions. Other ions which can be used for crosslinking are Mg²⁺ and Ba²⁺. When CaCl₂ is used for releasing Ca²⁺ ions in methyl cellulose – sucrose complex fluid its concentration vary between 0.1 – 20 wt% of the water content of the complex fluid. Fig. 6 illustrates stability of the viscosity of the material with calcium chloride cross-linker at various temperatures. Hydrogel of methyl cellulose – sucrose complex fluid having cross-linker of CaCl₂ of 2.0 wt% retains its viscosity (610) stable (temperature sweep stability) at

temperatures of 20 to 40 °C. Ca^{2+} ions affect the state of matter of the printed material like bioink. Bioink of nanofibrillated cellulose – sodium alginate hydrogel can be printed to the hydrogel complex fluid with Ca^{2+} ions. By printing the nanofibrillated cellulose – sodium alginate hydrogel to the complex fluid of the first type which contains 0.1 – 18.0 wt% calcium chloride, preferably 2 wt% the printable hydrogel cross-links and changes its state of matter upon becoming in contact to the complex fluid. Cross-linking stabilizes form of the printable object even with complex forms of overhangs and enables cells to grow and form tissues according to the shape of the printable object in the 3D cell culture. By printing the bioink to the hydrogel complex fluid which contains cross-linker of Ca^{2+} ions, separate process for using cross-linking agent into which the printable object (cell-laden construct) is submerged after printing is not needed. The hydrogel complex fluid also supports the geometry of the cell-laden construct even in the complex tissue engineering scaffold forms and designs. Other compounds which are used to modify rheology of the hydrogel complex fluid and effect the state of matter of the printed material are aldehyde derivatives like glutaraldehyde, urea derivatives, carboxylic acids and isocyanates.

Other hydrogels than methyl cellulose can also be adjusted for becoming complex fluid by shaking or by aerator, or by adding sucrose molecules or some other molecules required for the complex fluid. Non-ionic polyacrylamide (PAM) ($(\text{C}_3\text{H}_5\text{NO})_n$) – water hydrogel (PAH), polyethylene glycol (PEG) – water hydrogel, polyacrylic acid, cellulose micro fibrils, cellulose nanocrystals, potassium salt, chitosan, alginate, polyvinyl alcohol, starch, gelatin water hydrogels and methacrylated galactoglucomannan can be used for the application of 3D printing supporting material or printable material of bioink. Biodegradable hydrogels are natural-based hydrogels like polysaccharides (e.g. chitosan) and proteins (e.g. collagen), or synthetic such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and polypropylene fumarate (PPF).

There are also other types of hydrogels which can be printed to the complex fluid hydrogel supporting material of the first, second or third type for changing its state of matter to semisolid or solid state. Example of the photo-curable printable hydrogel is

PEG-DA = polyethylene glycol diacrylate – water (40/60%) with 0.2 % 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophene
($\text{HOCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{COC}(\text{CH}_3)_2\text{OH}$) (IRGACURE) photoinitiator with additional calcium carbonate filler of 33 wt%. Presence of free radicals by the reaction of
5 photoinitiator in the printing material or supporting material may be harmful for the living cells and therefore complex fluid without and free radical forming compounds for printing material and for the supporting material are preferred for maintaining viability of human or animal origin stem cells, bone cells, endothelial cells, neutral cells, chondrocytes, blood cells and fibroblasts. Calcium chloride cross-linker is
10 preferred when the hydrogel complex fluid is as bioink and it contains living cells for tissues engineering or drug development purposes. Primary bubbles of air with oxygen enhance conditions of living cells to survive in the printing process of bioink

For silicone (organopolysiloxanes) elastomers cross-linking compound can be
15 photoinitiator such as thioxanthenes. The complex fluid of the first, second or third type which contains silicone's polymerization enhancing compounds of thioxanthone-based hydrophilic visible photoinitiators (TX-MPEG350, TX-MPEG550, and TX-MPEG750) can be used in 3D printing. Complex fluid can be enlaced with catalyst of transition metals of palladium, rhodium, germanium and platinum, their salts or
20 complexes typically of the Group III of elements (e.g. Karstedts's catalyst) for enhancing polymerization of silicone elastomers. With the complex fluid of the first, second or third type the transition metal (Group III) ions or complexes for silicone polymerization are water or DMSO (dimethyl sulfoxide) soluble compounds like cisplatin ($\text{cis}-(\text{Pt}(\text{NH}_3)_2\text{Cl}_2)$) or chloroplatinic acid. Other suitable catalysts are
25 platinum vinylsiloxane complexes and platinum phosphine complexes.

The hydrogel complex fluid of the first, second or third type can also be used to print metal or ceramic filled materials to their green stage for being sintered after the printing process, plaster and concrete. For this, the metal or ceramic particles are
30 mixed to the photo or chemical curing resin matrix, printed to the hydrogel complex fluid and after cross-linking be free radicals the object is sintered at the fusion temperature of the metal or ceramic fillers.

The method and the complex fluid system can be used in 3D printing supporting material or printing ink of several other applications which benefit of complex spatial or omnidirectional printing. These include aviation and automotive vehicles and their parts, soft robots, electronics, pneumatic and fluidic elastomer actuators and sport equipment, printed textiles, tools, customized industrial products, furniture and interior appliances and decorations, and architecture and engineering applications. Due to biocompatibility and non-toxicity the hydrogel complex fluid can be also used for everyday goods like in food and packing industry, in cosmetic products and in production of medical and dental devices for humans and animals, art objects and testing platforms for drug development. The complex fluid system is also utilizable as cleaning foam or moisturizing agent for skin products including pharmaceutical compounds for skin diseases and drug delivery for iontophoretic therapy.

A method for producing complex fluid of bubbly liquid material that is suitable for being used in 3D printing, may comprise producing to liquid material primary bubbles as a supporting material for printing a 3D object or for using as printing ink. Optionally, secondary and/or tertiary bubbles are produced to the liquid material as the supporting material for printing the 3D object or for using as the printing ink. The liquid material may comprise at least the primary bubbles, and optionally the secondary and/or tertiary bubbles.

The method may further comprise causing rheology transition of a liquid phase to viscous liquid and temperature sweeping stability of viscosity between 20.1 – 300.0 Pa·s. The producing of the primary bubbles may comprise adding surfactant to the liquid material and the liquid material is Newtonian or non-Newtonian liquid material, and shaking the liquid material or using an aerator.

The method may comprise stabilizing the primary bubbles by adding free radicals, ions, molecular compounds, nanofillers or function of cells in continuous liquid phase of the liquid material. The compounds of the complex fluid bubbly liquid material may

change a state of matter of the printing ink upon becoming in contact with the liquid material.

5 The method may comprise producing to the liquid material secondary bubbles by a chemical reaction. The method may further comprise producing to the liquid material tertiary bubbles by injecting gas to the liquid material or by a chemical reaction.

10 The bubbles may be comprised in a bubble system, and the bubble system and the bubbles in the bubble system are of one or several different gas compositions. The secondary and/or tertiary bubbles may comprise air or nitrogen gas.

The liquid material may be hydrogel and may contain cross-linking compounds and living cells.

15 A system for 3D printing may comprise at least a printing head configured to inject printing material to form a 3D printed object, wherein the system further comprises controlling the 3D printing by a controlling unit, the system being configured to inject the printing material into supporting material that is produced using said method.

CLAIMS

1. A method for producing complex fluid of bubbly liquid material that is suitable for being used in 3D printing, the method comprising producing to liquid material primary bubbles, and optionally secondary and/or tertiary bubbles, as a supporting material for printing a 3D object or for using as printing ink, wherein the liquid material comprises at least the primary bubbles.
2. A method according to claim 1, wherein method further comprises causing rheology transition of a liquid phase to viscous liquid and temperature sweeping stability of viscosity between 20.1 – 300.0 Pa·s.
3. A method according to claim 1 or 2, wherein producing the primary bubbles comprises:
- adding surfactant to the liquid material and the liquid material is Newtonian or non-Newtonian liquid material; and shaking the liquid material or using an aerator.
4. A method according to any previous claim, comprising stabilizing the primary bubbles by adding free radicals, ions, molecular compounds, nanofillers or function of cells in continuous liquid phase of the liquid material.
5. A method according to any previous claim, wherein compounds of the complex fluid bubbly liquid material change a state of matter of the printing ink upon becoming in contact with the liquid material.
6. A method according to any previous claim, comprising producing to the liquid material secondary bubbles by a chemical reaction.
7. A method according to any previous claim, wherein the method further comprises producing to the liquid material tertiary bubbles by injecting gas to the liquid material or by a chemical reaction.

8. A method according to any previous claim, wherein the bubbles are comprised in a bubble system, and the bubble system and the bubbles in the bubble system are of one or several different gas compositions.

5

9. A method according any previous claim, wherein the secondary and/or tertiary bubbles comprise air or nitrogen gas.

10. A method according to any previous claim, wherein the liquid material is hydrogel and contains cross-linking compounds and living cells.

11. A system for 3D printing, wherein the system comprises at least a printing head configured to inject printing material to form a 3D printed object, wherein the system further comprises controlling the 3D printing by a controlling unit, the system being configured to inject the printing material into supporting material that is produced using a method according to any of claims 1 to 10.

20