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(54) Title: BIODEGRADABLE SACCHARIDE MICROCAPSULES, PROCESS FOR PREPARING THE SAME AND METHOD OF USE THEREOF

Microcapsules of Example 1 (226-83-1)

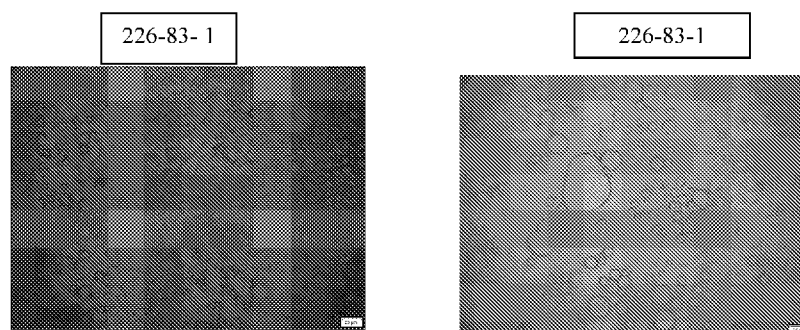


Fig. 1

(57) Abstract: The present invention relates to biodegradable microcapsules, that can encapsulate and retain cargoes such as, lipophilic, or hydrophobic core materials comprising fragrances, butters, essential or other oils; or oil solubilized ingredients, process of making said biodegradable microcapsules, and their applications in various industries. Present invention further relates to biodegradable microcapsule shell materials that comprise a natural or biobased component, specifically a saccharide or saccharide containing polymer or oligomer, and which show evidence of biodegradation or non-persistence in aquatic based and/or soil or compost based environments.



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**BIODEGRADABLE SACCHARIDE MICROCAPSULES, PROCESS FOR
PREPARING THE SAME AND METHOD OF USE THEREOF**

FIELD OF THE INVENTION

[0001] The present invention relates to biodegradable microcapsules, that can encapsulate and retain cargoes such as lipophilic, or hydrophobic core materials comprising fragrances, butters, essential or other oils; or oil solubilized ingredients, process of making said biodegradable microcapsules, and their applications in various industries. Present invention further relates to biodegradable microcapsule shell materials that comprise a natural or biobased component, specifically a saccharide or a saccharide containing polymer or oligomer, and which show evidence of biodegradation or non-persistence in aquatic based and/or soil or compost based environments.

BACKGROUND OF THE INVENTION

[0002] Conventionally, microcapsules: (a) provide protection and stability to actives or ingredients entrapped inside the microcapsule; (b) facilitate, trigger, or control release of the entrapped actives or ingredients, (c) extend the life of the actives, (d) reduce the threat of exposures or (e) enable easily handling of entrapped actives which are otherwise toxic in nature or difficult to handle.

[0003] The microcapsules of the invention have an inner core material comprising lipophilic/hydrophobic compounds surrounded by an outer polymeric shell. The release rate of the core material and the diffusion of the core material through the capsule wall can often be controlled by varying the wall composition and/or the degree of crosslinking of the wall (shell) material. Further, the degree of crosslinking of the wall material directly impacts the strength and nature of the microcapsule wall.

[0004] A highly beneficial use, for example, of microcapsules is for the prolongation of fragrances, essential oils, or other lipophilic or oil solubilized ingredients which have been encapsulated inside a polymer shell. Typically, the technologies or materials used for encapsulation of fragrances or similar molecules (cargoes) have included melamine formaldehyde, urea-formaldehyde, or poly-urea/urethane technologies or acrylate technologies, most often using classical interfacial or other oil-in-water polymerizations. Because such cargoes are often aggressively solvating or plasticizing for many polymers and/or are volatile or have low boiling components difficult to retain within polymeric shells, such polymer shell walls used for their encapsulation are typically crosslinked networks of such polymers for stability and durability in the formulations in which they are used, for example,

laundry/washing products, household cleaning products, hair care products skin care products among others. They are not typically designed to be biodegradable or non-persistent in the environments they may end up in. There are some known examples of biodegradable polymers used in microcapsule shell walls. They include polyesters or poly- β -amino-esters, for example. However, in most cases, they are typically not encapsulating fragrances or essential oils or other solvating or plasticizing lipophilic or oil solubilized components for use in such consumer products, and/or are not biodegradable in relevant end media and/or are not stable on storage in aqueous or formulated end products that may contain aggressive surfactants or other components, and which may be formulated at pH's significantly above or below neutral.

[0005] U.S. Patent US 8,287,849 (assigned to Massachusetts Institute of Technology) and scientific publication - "Degradable Poly- β -amino esters: Synthesis, Characterization, and Self-Assembly with Plasmid DNA" (written by Lynn, D.M, Langer, R.) published in J. Am. Chem. Soc. 2000, 122, 44, 10761–10768 disclose that poly- β -amino esters are typically unstable in solutions with wide pH range over hours to days, and are biodegradable in physiological or biomedical environments, comprising a compound prepared by reacting primary amine with bis-(acrylate ester).

[0006] European Patent Application EP 0517669 A1 (assigned to Sandoz) discloses process for microencapsulation of agrochemicals, obtained by microencapsulating an agrochemical in a crosslinked polymer capsule which is in part a polyester polymer, wherein such a process comprises the steps of (a) dissolving or suspending the agrochemical in a non-aqueous liquid mixture comprising unsaturated polyester resin and a vinyl monomer (preferentially styrene), (b) emulsifying said solution or suspension in water to a desired particle size; and (c) effecting crosslinking of the unsaturated polyester resin and vinyl monomer to produce the microcapsules.

[0007] PCT Publication WO 2017125395 (assigned to BASF SE) discloses 'biodegradable' (in soil) polyester capsules comprising an aqueous core and a pesticide, wherein the capsule shell comprises a polyester, and the capsule core comprises a water-soluble pesticide (so a hydrophilic core), and at least 10 wt. % of water based on the total weight of the capsule core. Further, acid chlorides are used for its practical application to enable moderate temperatures and short reaction times for formation of the *in-situ* polyester in the presence of the cargo.

[0008] US 116554410 (assigned to Gemminov) describes a method to prepare biodegradable microcapsules with lipophilic cores wherein the shell material is based on poly- β -amino-esters. The method described is an interfacial oil-in-water polymerization process wherein one reactant (an amine; donor) is added, at a significant excess of molar equivalents (of reactive

functional groups), to a pre-made oil-in-water emulsion containing the other reactant (an acrylate, acceptor). Secondary coatings based on polymers are optionally applied at the end of the interfacial polymerization as a water solution.

[0009] PCT Publication WO2023099610A1 (assigned to Droplet Genomics UAB, LT) discloses a composition, comprising a plurality of microcapsules each comprising a core surrounded by a shell, wherein: the shell is a hydrogel comprising a first polymer, wherein: the first polymer comprises a polysaccharide modified with a conjugated cross-linking moiety and optionally modified with a conjugated hydrophilicity /hydrophobicity-modifying moiety, and molecules of the cross-linking moiety of the first polymer are cross-linked in the hydrogel; and the core comprises a second polymer comprising a polysaccharide that does not include the cross-linking moiety and does not include the hydrophilicity /hydrophobicity-modifying moiety of the first polymer.

[0010] The Scientific publication - "Fragrance-containing microcapsules based on interfacial thiol-ene polymerization" (by Liao et al) published in J. Appl. Polym. Sci. 2016, 133,43905 doi: 10.1002/App.43905, discloses fragrance capsules with a poly- β -thio ester shell wall, made using a classical interfacial polymerization route wherein a water-soluble reactant is added in a water solution to a pre-made emulsion of an oil phase (containing the other reactant) and a water/stabilizer phase.

[0011] Such prior arts have numerous disadvantages wherein: (i) some are for water soluble actives and so not suitable for hydrophobic or lipophilic materials; (ii) few show or claim or are designed for biodegradability, or claim biodegradability in ambient aquatic environments or in related OECD tests, (iii) many use organic solvents to enable encapsulation which are problematic in removal and for use with volatile cargoes, (iv) some require the use of specifically modified saccharides with groups such as hydrophobic groups, or unsaturated (alkenyl) groups, or amine groups or others and (v) few, if any, show any ability to be stable on storage as made with fragrance or oils or other plasticizing cargoes inside, or show stability or utility after storage in end product formulations as are used in home or personal care applications, which may have pH extremes or surfactants or salts or solvents or other additives that may plasticize or attack the shell wall (vi) most do not contain any natural or biobased content or, in order to use biobased precursors for their encapsulation reactions it would be technically challenging or expensive.

[0012] There remains a significant challenge to encapsulate lipophilic or hydrophobic cargoes in a polymeric shell which can biodegrade in aquatic or other media, comprises natural or biobased content, and which is robust enough to hold the cargo (often in aqueous based

formulations of personal care or household or other products) until release is triggered or required and/or to release it in a gradual process or controlled way.

[0013] Current inventors aim to meet these criteria and so enable production of microcapsules that have a shell material that is biodegradable or non-persistent, particularly in aquatic media/waterways, and yet which can retain a hydrophobic or lipophilic cargo or a volatile or a plasticizing or oil solubilized cargo such as a fragrance or an essential oil or other oil, and which comprise at least one component which is natural, or nature derived or biobased.

SUMMARY OF THE INVENTION

[0014] We have discovered that volatile or plasticizing hydrophobic or lipophilic ingredients such as fragrances, oils and other lipophilic cargoes can be encapsulated within robust storage stable polymer shells made from saccharide units linked or crosslinked with ester, β -amino-ester or β -thio-ester based linking or crosslinking groups and, furthermore, in addition, that through the associated polymer shell precursors and polymer architectures, such polymer shell systems can meet important biodegradability criteria and in particular such criteria for biodegradability or non-persistence in ambient aquatic environments such as seawater, river/surface water, effluents, and/or other water treatment process streams (e.g. activated sludge). Such polymeric shells can be made from saccharides linked (co-reacted) with ester or β -amino-ester or β -thio-ester based linkers or crosslinkers can be made via addition or condensation reactions of functionalized saccharides. For example, the polymeric shells can be made from (a) amine or thiol functional saccharides co-reacted with polyfunctional conjugated alkenyl functional linkers or (b) from conjugated alkenyl functional saccharides co-reacted with polyfunctional amines or thiols.

[0015] We have also discovered that volatile or plasticizing hydrophobic or lipophilic ingredients such as fragrances, oils and other lipophilic cargoes can be encapsulated within robust storage stable polymer shells can be made from saccharides linked with hydrolysable ester, β -amino-ester or β -thio-ester based linkers or crosslinkers and that such linked or crosslinked saccharide shells can be made by free radical reactions of a saccharide with alkenyl functional ester, β -amino-ester or β -thio-ester based linkers or crosslinkers. Furthermore, we have discovered that through the associated polymer shell precursors, polymer architectures, and via stoichiometry controls in the associated reactions, such polymer shell systems can meet important biodegradability criteria and in particular such criteria for biodegradability or non-persistence in ambient aquatic environments such as seawater, river/surface water, effluents, and/or other water treatment process streams (e.g., activated sludge). Such microcapsules can be made via free radical linking processes, typically interfacial or oil-in-water emulsion type

processes, wherein the saccharide reacts with (links to, or crosslinks with) alkenyl functional ester, β -amino-ester, or β -thio-ester linkers. Additionally in some embodiments we have discovered that robust microcapsules can be made without need for pre-modification of the saccharide such as necessarily being hydrophobic or bearing added alkenyl or amine or other functional groups not ordinarily present.

[0016] Some prior work has described hydrophobically modified polysaccharides also containing alkenyl (unsaturated or conjugated) bonds can be used to make capsules through free radical polymerizations (crosslinking) of such functionally modified polysaccharides with conventional multifunctional acrylates. There are serious drawbacks with that approach, in particular the requirement to use a hydrophobically modified polysaccharide which also bears unsaturated (alkenyl) bonds, and, when such precursors are reacted there is likely formation of some capsule content which is solely crosslinked acrylate (not linked to saccharide) and, as such leads to the presence of a non-biodegradable component, and the risk of a microplastic classification or association, which will be severely limiting in the future. Our discovery overcomes these two issues.

[0017] In one important aspect, the present application provides a microcapsule comprising: (i) a biodegradable polymeric microcapsule shell; and (ii) a lipophilic core; wherein, the polymeric microcapsule shell comprises saccharide units linked or crosslinked with one or more multi-functional linking groups selected from the group consisting of: (a) an ester, a β -amino-ester, or a β -thio-ester alone or combinations thereof, (b) a copolymer comprising two moieties selected from an ester, a β -amino-ester, and a β -thio-ester, or (c) a terpolymer of an ester, a β -amino-ester, and a β -thio-ester.

[0018] In another related aspect, the saccharide is crosslinked or reactively linked with a polymer, co-polymer or ter-polymer which is functionalized with acrylate or methacrylate or itaconate or maleate groups or other alkenyl groups, or mixtures thereof and which comprises hydrolysable or biodegradable bonds such as or ester, or β -amino-ester, or β -thio-ester.

[0019] In another important aspect, the present application provides a biodegradable composition of a plurality of microcapsules, the composition comprising at least two microcapsules selected from the group consisting of: (i) microcapsules comprising microcapsule shell material comprising saccharide units linked or crosslinked by reaction with β -amino ester having alkenyl functionality and/or β -thio ester having alkenyl functionality, (ii) microcapsules comprising microcapsule shell material comprising crosslinked β - amino ester having alkenyl functionality and/or β -thio ester having alkenyl functionality, (iii)

microcapsules comprising microcapsule shell material comprising saccharide or modified saccharide, and (iv) combinations or hybrids or interpenetrating networks of (i), (ii) or (iii).

[0020] In another important aspect, the present application provides a method for preparing a microcapsule, or a biodegradable composition of plurality of microcapsules, the method comprising: (a) preparing an oil phase, comprising at least one multifunctional alkenyl linker, at least one lipophilic core, and optionally adding at least one catalyst or initiator, and/or a diluent; (b) preparing a water phase comprising at least one saccharide or polysaccharide and an initiator or catalyst, and optionally a stabilizer, defoamer, and/or emulsifier; (c) mixing the two phases together and emulsifying to make an oil-in-water emulsion; (d) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by a reaction of the linker components with the saccharide component(s); and (e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0021] In another important aspect, the present application provides a method for preparing a microcapsule, or a biodegradable composition of plurality of microcapsules, the method comprising: a) preparing an oil phase, optionally with heating, comprising at least one multifunctional alkenyl linker, optionally with a diluent, and adding, after completion of any optional heating applied and allowing to cool, a catalyst or initiator and a lipophilic core; (b) preparing a water phase comprising at least one saccharide or polysaccharide, an initiator or catalyst, optionally a stabilizer, a defoamer, and/or an emulsifier and heating for a predetermined time until the point at which the oil phase and water phase are mixed; (c) mixing the two phases together and emulsifying to make an oil-in-water emulsion; (d) heating the oil-in-water emulsion of step (c) with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by a reaction of the linker components with the saccharide component(s); and (e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0022] In another important aspect, the present application provides a method for preparing a microcapsule, or a biodegradable composition of plurality of microcapsules, the method comprising: a) preparing a multifunctional alkenyl linker containing β -amino-ester and/or β -thio-ester groups by reacting, for a predetermined time to prior to the mixing of phases in step (c), in a Michael Addition reaction and optionally in the presence of a diluent, a multifunctional conjugated alkenyl functional ester acceptor with a multifunctional amine and/or thiol donor, wherein the alkenyl functionality of the acceptor is in stoichiometric excess compared to the total donor functionality of amine (primary and secondary) and/or thiol groups; (b) preparing

a water phase comprising at least one saccharide or polysaccharide and an initiator or catalyst, and optionally a stabilizer, defoamer, or emulsifier and heating and/or stirring for a predetermined time before the mixing of the phases in step (c); (c) after the predetermined times, mixing the two phases together and emulsifying to make an oil in water emulsion; (d) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by a reaction of the linker components with the saccharide component(s); and (e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Further embodiments of the present application can be understood with the appended figures.

[0024] **Figure 1** illustrates optical micrograph images of microcapsules of the invention, 226-83-1, where the microcapsule shell material is an ester linked polysaccharide, comprising Potato Starch (unmodified) and/or its components, linked with ester groups from Pentaerythritol tetraacrylate (PETA).

[0025] **Figure 2** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 226-90-1, where the microcapsule shell material is a P β AE (poly- β -amino-ester) linked saccharide comprising Potato Starch and/or its components, linked with β -amino-ester groups.

[0026] **Figure 3** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 226-90-2, where the microcapsule shell material is a P β AE (poly- β -amino-ester) linked saccharide comprising Potato Starch and/or its components, linked with β -amino-ester groups and where secondary crosslinking with tannic acid has been used.

[0027] **Figure 4** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 226-91-1, where the microcapsule shell material is poly- β -amino ester-co- β -thio-ester (P β ATE) linked polysaccharide, comprising Potato Starch and/or its components, linked with β -amino-ester-co- β -thio-ester groups.

[0028] **Figure 5** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 230-11-1, where the microcapsule shell material is poly- β - amino ester (P β AE) linked hydrophobically modified polysaccharide, comprising octenyl succinic anhydride modified starch (OSA starch) linked with β -amino-ester groups.

[0029] **Figure 6** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 230-12-1, where the microcapsule shell material is poly- β - thio-ester (P β TE) crosslinked hydrophobically modified polysaccharide, comprising octenyl succinic anhydride modified starch (OSA starch) linked β -thio-ester groups.

[0030] **Figure 7** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 230-13-1, where the microcapsule shell material is poly- β -amino ester-co- β -thio-ester (P β ATE) linked hydrophobically modified polysaccharide, comprising octenyl succinic anhydride modified starch (OSA starch) linked with β -amino- co - β -thio-ester groups.

[0031] **Figure 8** illustrates optical micrograph images of microcapsules of the invention, Microcapsules 230-20-1, where the microcapsule shell material is poly- β -amino ester-co- β -

thio-ester (P β ATE) linked hydrophobically modified polysaccharide, comprising octenyl succinic anhydride modified starch (OSA starch) linked with β -amino- co - β -thio-ester groups.

[0032] Figure 9 illustrates optical micrograph images of microcapsules of the invention, Microcapsules 226-24-3, where the microcapsule shell material is made from a saccharide with β - amino ester (P β AE) links and additional coating and/or crosslinking with tannic acid.

[0033] Figure 10 illustrates optical micrograph images of microcapsules of the invention, Microcapsules 229-74-1, where an initial microcapsule of the invention is overcoated with a protein.

[0034] Figure 11 shows sensory performance data (fragrance bloom test) from microcapsules from some of the examples.

DETAILED DESCRIPTION OF THE INVENTION

[0035] The present invention is directed to a biodegradable microcapsule, based on reactively linked (for example forming a copolymer) or crosslinked mono-saccharide, oligo-saccharide, or poly-saccharide with linker (or crosslinker) groups that are designed to be hydrolysable and selected from ester, β -amino-ester, β -thioester, or combinations thereof, to create a microcapsule shell wall which is biodegradable.

[0036] Compositions based on ester linked saccharides can be conceivably made by polycondensations but that requires high temperatures and as such will not be suited to volatile or sensitive cargoes. An alternative approach uses free radical polymerization of acrylates and is described below as one embodiment of this invention specifically where the saccharide is not modified to be hydrophobic saccharide also bearing alkenyl (unsaturated) bonds.

[0037] Compositions based on β -amino-ester or β -thio-ester linked saccharides can be conceivably made by pre-functionalizing the saccharide with amine and/or thiol donor groups, or with conjugated alkenyl (unsaturated) acceptor groups and then reacting the functionally modified polysaccharides in Michael Addition reactions with multifunctional acceptors or donors to form linked crosslinked saccharide.

[0038] In a preferred embodiment, the present invention is directed to a biodegradable microcapsule, based on reactively linked (for example forming a copolymer) or crosslinked mono-saccharide, oligo-saccharide, or poly-saccharide with specific acrylate, methacrylate, itaconate or maleate functional linkers which when reacted with the saccharide in an encapsulation process creates a microcapsules shell wall which is biodegradable.

[0039] Such microcapsules can encapsulate and retain cargoes such as, lipophilic, or hydrophobic core materials comprising fragrances, butters, essential or other oils; or oil solubilized ingredients. The invention also relates to processes of making said biodegradable microcapsules and their applications in various industries. Before explaining at least one aspect of the disclosed and/or claimed inventive concept(s) in detail, it is to be understood that the disclosed and/or claimed inventive concept(s) is not limited in its application to the details of construction and the arrangement of the components or steps or methodologies set forth in the following description or illustrated in the drawings. The disclosed and/or claimed inventive concept(s) is capable of other aspects or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be regarded as limiting.

[0040] As utilized in accordance with the disclosure, the following terms, unless otherwise indicated, shall be understood to have the following meanings.

[0041] Unless otherwise defined herein, technical terms used in connection with the disclosed and/or claimed inventive concept(s) shall have the meanings that are commonly understood by those of ordinary skill in the art. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

[0042] The singular forms "a," "an," and "the" include plural forms unless the context clearly dictates otherwise specified or clearly implied to the contrary by the context in which the reference is made. The term "Comprising" and "Comprises of" includes the more restrictive claims such as "Consisting essentially of" and "Consisting of".

[0043] For purposes of the following detailed description, other than in any operating examples, or where otherwise indicated, numbers that express, for example, quantities of ingredients used in the specification and claims are to be understood as being modified in all instances by the term "about". The numerical parameters set forth in the specification and attached claims are approximations that may vary depending upon the desired properties to be obtained in carrying out the invention.

[0044] All percentages, parts, proportions, and ratios as used herein, are by weight of the total composition, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore; do not include solvents or by-products that may be included in commercially available materials, unless otherwise specified.

[0045] All publications, articles, papers, patents, patent publications, and other references cited herein are hereby incorporated herein in their entirety for all purposes to the extent consistent with the disclosure herein.

[0046] The use of the term "at least one" will be understood to include one as well as any quantity more than one, including but not limited to, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 100, etc. The term "at least one" may extend up to 100 or 1000 or more depending on the term to which it is attached. In addition, the quantities of 100/1000 are not to be considered limiting as lower or higher limits may also produce satisfactory results.

[0047] As used herein, the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

[0048] The term “core” and “cargo” as used throughout the specification are inclusive and refer to same ingredient forming part of the microcapsule encapsulation.

[0049] The term “each independently selected from the group consisting of” means when a group appears more than once in a structure, that group may be selected independently each time it appears.

[0050] The term “hydrophobic” as used herein refers to relatively water repelling, and hydrophobic groups are groups which inhibit the access of water molecules to the β -amino ester bond environment.

[0051] The terms “link”, “linker”, “crosslinker”, “linking group” as used herein singular or plural forms are same and interchangeable throughout the specification.

[0052] The term “polymer” as used herein, refers to a compound comprising repeating structural units (monomers) connected by covalent chemical bonds. Polymers may be further derivatized, crosslinked, grafted, branched, or end-capped. Non-limiting examples of polymers include copolymers, terpolymers, tetrapolymers, quaternary polymers, and homologues. The term “copolymer” refers to a polymer consisting essentially of two or more different types of monomers polymerized to obtain said copolymer.

[0053] The term “pre-polymer”, “precursor”, and “pre-modified” as used herein, refers to any polymer or oligomer pre-made prior to the encapsulation process stage, and which can undergo some form of further chemical or physical transformation during or after the process of encapsulation such as a reaction (chain extension, branching, molecular rearrangement, crosslinking, ionic, complexation, or other linking or molecular association).

[0054] The release rate of the core material and the diffusion of the core material through the capsule wall can, in many cases, be controlled by varying the wall composition and/or the degree of crosslinking of the wall (shell) material. Also, the degree of crosslinking of the wall material directly impacts the strength and nature of the wall of the microcapsule. Furthermore, if a material is encapsulated, its useful life can be significantly extended. Also, if a material is toxic and/or difficult to handle, encapsulation of the material can reduce the threat of exposures and/or allow for easier handling.

[0055] Fragrances and oils and other lipophilic ingredients are widely used in personal and household care products such as detergents, fabric softeners, shampoos, and shower gels to enhance the product performance and attributes. Long lasting release of fragrances is a key performance parameter in many personal and household care products, yet many fragrances or oils are volatile, and their aroma effects are quickly lost on application. Encapsulation of fragrances inside a solid shell can protect fragrances and enable longer lasting release. Among

the existing encapsulation systems, polymeric microcapsules made via interfacial polymerizations are widely used. These can be via oil-in-water (O/W) or water-in-oil (W/O) emulsions wherein typically, monomers react at the oil–water interface to form a polymeric shell. Most commercial fragrance microcapsules consist of poly(urea–formaldehyde), poly(melamine–formaldehyde), polyurethane, or polyurethane–urea shell materials or polyacrylates. Example References: U.S. Pat. 20080206291; WO2013092375; U.S. Pat. 20130337023; Chem. Eng. J. 2009, 149, 463; and WO 2017123965A1 are incorporated herein in its entirety.

[0056] These particular systems such as M-F systems, or U-F (urea -formaldehyde) or radically crosslinked acrylate or crosslinked urea or urethane systems, are chosen for their superior thermal and mechanical properties and are all rigid or highly crosslinked systems in order to retain volatile ingredients or ingredients that have a tendency to plasticize or dissolve away other shell walls or leach out through shell walls of other systems and also chosen for their stability in a wide range of end product formulations. They typically use low viscosity reactive monomers or reagents to enable interfacial or *in-situ* polymerization encapsulation processes to proceed smoothly to form rigid, highly insoluble, and highly crosslinked polymer systems. They are designed for durability, including long lasting stability in various formulations over a range of pH's with salts or surfactants or solvents or other additive s present which may compromise some other polymer shell walls, and have the feature of being friable meaning they are able to be crumbled or broken by application of pressure or friction such as in service or when required for release. This, for example is an attractive attribute in fragrance encapsulations for formulations or applications where a fragrance bloom (instant but long lasting or repeatable over time, release of cargo) can occur when shell walls are 'crumbled' or broken in service for example by rubbing or friction. Such durable polymeric shell materials are not claimed to be, nor would they be anticipated to be, biodegradable in aquatic environments, or indeed other environments such as soil or compost. Typically, such highly crosslinked or rigid polymer particles or capsules would be expected to be persistent or very slowly degrading in the environment and/or often use environmentally toxic or unfriendly materials such as formaldehyde or isocyanates in their production. Other routes such as coacervation do not make as robust a capsule and/or may require the use added undesirable solvents or use undesirable animal derived ingredients. There is a need for a robust microcapsule that can encapsulate, and retain until a triggered release, volatile or plasticizing cargoes and be biodegradable in the environments in which they end up in, which in many cases will be aquatic systems such as rivers, oceans, or water treatment plants.

[0057] We have surprisingly discovered that volatile or plasticizing hydrophobic or lipophilic ingredients such as fragrances, oils and other lipophilic cargoes can be encapsulated within robust storage stable polymer shells which are biodegradable and yet which can display a similar or acceptable degree of cargo retention and bloom (release) to some non-biodegradable robust polymer shell options, and can in some cases also show longer lasting release of cargoes such as fragrances or oils or other lipophilic cargoes. Such polymer shells can be made using linear polymers or branched polymers, or using lightly crosslinked or, highly crosslinked polymer systems incorporating specific saccharide moieties linked or crosslinked via radical reactions of specific alkenyl functionalized linkers, and preferably conjugated alkenyl (acrylate-, methacrylate-, itaconate-, maleate- functional) linkers, Furthermore, in addition to successful encapsulation and retention of potentially plasticizing or solvating lipophilic cargoes we have discovered that by selection of the polymer shell precursors and polymer architectures, such as linear or branched or crosslinked polymer shell systems, such polymer or copolymer shell materials can meet important biodegradability criteria and in particular such criteria for biodegradability or non-persistence in ambient aquatic environments such as seawater, river/surface water, effluents, and other water treatment process streams (e.g. activated sludge).

[0058] *Thus*, the invention encompasses a suite of microcapsule compositions, based on polymeric shell walls with specific saccharide which are linked with specific esters, including polyol- or polyether-esters, polyesters, β -amino esters, β -thio-ester or their various mixtures or combinations, which can be designed to be biodegradable according to criteria herein described, and all of which have encapsulated lipophilic cargoes and are able to be tailored to meet the difficult combination of biodegradability, stability in formulated products, and triggered performance release or bloom of cargo, which span a range of performance levels suited to different formulated end products or applications and/or different encapsulated cargoes for those end product formulations.

[0059] In one important embodiment, the present invention provides (i) a biodegradable polymeric microcapsule shell; and (ii) a lipophilic core; wherein, the polymeric microcapsule shell comprises saccharide units linked or crosslinked with one or more multi-functional linking groups selected from the group consisting of: (a) an ester, a β -amino-ester, or a β -thio-ester alone or combinations thereof, (b) a copolymer comprising two moieties selected from an ester, a β -amino-ester, and a β -thio-ester, or (c) a terpolymer of an ester, a β -amino-ester, and a β -thio-ester.

[0060] The capsules of the invention are also able to be dried and stored dried and subsequently redispersed into formulations. They may also be formulated, directly as a slurry

or after drying, into dry or 'waterless' formulated product forms such as tablets or soap bars or printed solid products other solid formats in various end applications, particularly, but not limited to, those used in personal and home care markets. In addition, in other embodiments the microcapsules may be overcoated and/or crosslinked via secondary crosslinking mechanism.

[0061] Biodegradation and non-persistence of materials which are in the environment are influenced by multiple factors. These include factors such as: (a) the environment in which the material finds itself either in use and/or after use, and the many factors therein such as, temperatures, humidity/water presence, pH, microbial populations, nutrients, etc., and (b) the timescale for monitoring or predicting biodegradation. Material composition, structure, morphology and physical size and form are also important factors, for a material of interest.

[0062] Evidence of biodegradation or non-persistence may be achieved via demonstrating a certain level of degradation within a time and/or degradation at a rate that is indicative that ultimately the material will degrade and be non-persistent after a certain time. There are many testing standards or methods which specify certain tests and associated timescales. In use there are some applications which may desire certain levels of biodegradation within certain timescales and environments to be met for evidence of biodegradation. Of course, for some applications a certain level or percentage (%) of biodegradation may be desirable or even stipulated as evidence of more rapid biodegradation or of a certain minimum level of biodegradation. Others may specify evidence of non-persistence. As to what evidence of biodegradation and/or of non-persistence is required or desired depends on the details of the end-application, the expectations of the customers (often the final product manufacturers) or of the consumers (typically, the end-users) and can vary according to end use and end environments or regulatory body directives or guidelines, of which there may be many variations. OECD, ISO, ASTM, EN or other standards for testing are commonly used to measure biodegradation or compostability and can be used as evidence of non-persistence or, indeed, conversely, of any likely persistence in an environment. However, they are not the only methods available and many publications report on other methods or criteria, and which are peer reviewed or rational to those skilled in the art. Furthermore, different end use sectors (products) and different regions of the world have different specifications or guidelines such that there is no single universal definition.

[0063] In the case of polymers, biodegradation typically begins with breakdown of the polymer chains or backbone into smaller components which continues until they become small enough to be intracellularly metabolized by micro-organisms such as bacteria, yeast, or fungi. Often

the first steps of initial breakdown of polymers proceeds via hydrolysis or oxidation of the polymer backbone chains to generate smaller molecules suitable for intracellular consumption. Hydrolysis is a particularly common first step and may be facilitated, for example, by secreted extracellular enzymes (enzymatic hydrolysis; secreted by microorganisms in the end- or test-environment) and/or by the certain ambient conditions (pH, temperature, etc.).

[0064] Many polymers are resistant to biodegradation and persist in the environment for years or decades, for example many plastics, which are often used in applications for their long lasting durability. *Similarly*, many particles or microplastics are known to persist in the environments they end up in. This includes the many of the microcapsules of the prior art such as those based on M-F, U-F, crosslinked urea, or urethane, and crosslinked polyacrylates. This has become a concern for the global environment such that nations and organizations, such as ECHA, may implement bans or restrictions on the use of microplastics that persist in the environment in certain products. In some respects, depending on the materials used, and their characteristics, microcapsules may be considered as a form of microplastics. As noted above microcapsules are very convenient for protection of cargoes (entrapped actives or ingredients) and/or controlled release of cargoes. Thus, biodegradable microcapsules are sought after.

[0065] Biodegradable capsules are known and particularly in the fields of biomedical and pharma applications. Common polymers include polyesters among others. Biodegradation in such applications is in physiological human (or animal) body environments and typically are at 37°C and often with extremes of pH and/or a high presence of enzymes or nutrients that specifically facilitate breakdown of such polymers. Typically, the cargoes are solids, or water-soluble actives, and/or do not have volatile or reactive components. Also routes to manufacture such capsules involve undesirable solvents (such as dichloromethane) and/or processes such as microfluidics or freeze drying or evaporative processes, or extrusion methods, which are all impractical technically and/or commercially for encapsulating volatile fragrances and similar lipophilic cargoes or for applications in cosmetics or the personal care and household sector. Further, biodegradability in such biomedical/pharma environments (with their higher temperatures, enzyme presence, and more aggressive (for degradation) conditions etc.) is not indicative of, or comparable to, biodegradability in ambient aquatic waterways or seawater for example and, also, not reflective of the needs of the personal care or household sector, and other sectors (e.g., drilling/energy), where many of the products used will end in aquatic environments such as rivers, seas, surface water, water treatment plants/effluents - which are essentially ambient temperature (20°C or lower) waters, or in soils or sediments.

[0066] It is reported that some of the microcapsules or other ingredients which are used in the personal care and household sector today may potentially be considered persistent in the environment and that they may fall under the umbrella definition of microplastics, and as such are undesirable. All such products as may be classed as microplastics are likely to be restricted in their use in personal care and household, and other products at some stage in the future. ECHA has initiated proposed processes for that. Other bodies may develop similar or alternative guidelines or protocols. Thus, there is a need to develop polymer capsules that are biodegradable in environments where common personal care and household products may eventually end up in. Demonstrating reasonable biodegradability of an ingredient will likely such avoid restrictions assuming other factors are also favorable. OECD and ISO test methods are typically specified for biodegradation testing in some cases. Other test standards are also used and are likely to be relevant and including future new standards as may be developed or specified. Thus, there is a need to develop polymer capsules that are biodegradable in environments where common personal care and household products, and many other products, may eventually end up in, and which can be manufactured in commercially sensible processes for that sector (so not using solvents requiring evaporation or high temperature encapsulation processes, for example).

[0067] In some OECD biodegradation tests for aquatic media, which are typically in relatively short timescales such as 28 days, under certain test conditions, achieving 60% biodegradation within 28 days in certain OECD tests can lead to a classification of being readily biodegradable. Such a material would be considered as rapidly biodegradable. In some OECD tests achieving 20% biodegradation can indicate a classification of a material being inherently biodegradable or primary inherently biodegradable. This indicates the potential for a material to be biodegradable, which would be over longer timescales than for readily biodegradable materials. Although 28 day tests are the standardized duration in some OECD tests, for the inherent classifications, extended testing periods of up to 60 days and longer if biodegradation has started within 28 days and has not yet reached plateau (see for example Annex 1 of OECD document OECD Guideline for Testing of Chemicals: part 1 Principles and strategies related to the testing of degradation of organic chemicals available at <https://www.oecd.org/chemicalsafety/testing/34898616.pdf>, paragraphs 21 and 36).

[0068] Thus, for the purposes of this invention, evidence or data for biodegradability or evidence of non-persistence is tested in aquatic environments or media such as activated sludge, secondary effluent, river- or surface- or sea- water and the like according to OECD test standards but may be for longer than 28 days when biodegradation has started and not reach a

plateau. Typically testing of biodegradation herein is according to methods of OECD or ISO test protocols, such methods and their variants as described for OECD 301, 302, 306, 310 or EN ISO 14852:2018 or EN ISO14851:2004 or EN ISO 19679:2016 or EN ISO 18830:2006 or EN ISO 17556:2012) or analogous or other standards. If in using such tests, about 20% biodegradation has been attained within 28 days or, is attained within a longer time period if biodegradation has started within 28 days and not reached a plateau, then that is provided as evidence for being biodegradable or non-persistent. Such evidence for biodegradation can be demonstrated within 28 days or 40 days, or 45 days or 60 days or 90 days or 3 months, or within 6 months, or within 12 months, or longer when tested according to standards if no plateau is evident. Preferably for the purposes of this document 20% biodegradation will have been obtained within 60 days of such a standard OECD aquatic media and not shown a plateau in the biodegradation vs time plot. Thus, for testing purposes here, evidence or data for being biodegradable means evidence for inherently biodegradable or inherently primary biodegradable as per the OECD test methods and descriptions, including within longer timescale were allowed for to achieve 20% biodegradation with no plateau. It should be noted that not achieving such levels is not indicative of persistence - other tests can be applied to demonstrate non persistence or biodegradability in aquatic or other media. In addition, such OECD aquatic tests are typically at ambient conditions (20-25°C or lower) and it will be recognized that biodegradability in other media (compost, soil, and sediments) will also be likely attainable if biodegradation in aquatic media is demonstrated. Also, ready biodegradability is also covered should it be demonstrated. Furthermore, OECD methods are not the only relevant test methods, although in this document they have been used for test data. Other criteria can be accepted and are used by others and in certain regions or applications. Other standard test methods or justifiable variations can be used, and other data may be accepted by industry regulators or by experts or if showing a sensible or logical rationale and/or where other evidence of non-persistence may be presented and accepted by those skilled in the art. *For example*, molecular weight reductions or weight loss or other measurements as evidence of biodegradation or non-persistence particularly for more slowly degrading materials may be used. Degradation half-life determinations are also be used. All are potentially relevant depending on the circumstances. This document reports biodegradation data using OECD test methods, though it is recognized such other tests or criteria may also be applied in to show biodegradation or non-persistence. For the many samples or material types which are insoluble in water, dispersions or films, other approaches are used to achieve reliable sample forms for biodegradation tests. It is recognized that today's test methods (OECD or other) for

biodegradation of polymers in aquatic media are not necessarily representative, having not being designed or intended for testing such materials when originally conceived and especially for water-insoluble polymers and that refined or improved, or alternative test methods may in time be developed which are likely to be more relevant. (See for example: Kowalczyk, A. et al (2015) Refinement of biodegradation tests methodologies and the proposed utility of new microbial ecology techniques. *Ecotoxicology and Environmental Safety*, 111, 9–22. <https://doi.org/10.1016/J.ECOENV.2014.09.021> and: Timothy J. Martin, et al (2017) Environmentally Relevant Inoculum Concentrations Improve the Reliability of Persistent Assessments in Biodegradation Screening Tests. *Environ. Sci. Technol.* 2017, 51, 3065–3073, DOI: 10.1021/acs.est.6b05717). It would be expected that if a material is showing evidence of biodegradation or potential non-persistence in the OECD or ISO tests reported in this document then it will also be biodegradable or non-persistent in future test specifications, likely more suited to polymers and the environments of today or the future. Also, where testing of polymers in seawater (marine), or surface/river water or activated sludge has shown some, even low levels of, ongoing biodegradability then such materials will likely show greater rates or degrees of biodegradation in more active media such as soil or compost, or other in media where enzymes or microorganisms are present in greater concentrations or diversity. It is reasonable to assume, and generally understood, that if biodegradability is shown in the usual aquatic media tests for a material, then the material would also be expected to be compostable according to the various standard tests for compostability. *Furthermore*, and similarly, it would also be reasonable to assume biodegradability in soil or similar media if shown to biodegradable in aquatic media. The reverse, however, is not able to be stated. Thus, if a material is confirmed as compostable, it is understood that it is not an indication that it will degrade in waterways or other ambient aquatic media. Polylactic acid is a well-known example of a polymer (polyester) that is compostable but will not biodegrade in aquatic media or soil. Thus, the testing in this invention is based on aquatic media on the basis that if a material is showing biodegradability in ambient aquatic media, it will also be compostable and degradable soil, according to typical standard test methods.

[0069] Thus in summary, it will be understood by those skilled in the art that for biodegradation testing the testing of biodegradability in aquatic media such as surface water or secondary effluent or activated sludge, as described by the aforementioned OECD tests, all carried out at temperatures around 20-25°C, is relatively mild and certainly less aggressive as a test for biodegradability compared to, for example, biodegradation testing in industrial composting facilities and via the test methods or standards developed for compostability testing such as

EN13243 or ASTM D-6400 or ASTM D-6868, and others. In such compostability testing usual temperatures are much higher, for example around 58-60 °C. It is understood that many polymers including polyesters such as polylactic acid which do show biodegradability in industrial composting tests are not able to show biodegradability in aquatic media tests (see for example: Bagheri, A.R., Laforsch, C., Greiner, A., Agarwal, S.: Global Challenges 2017, 1700048; DOI:10.1002/gch2.201700048). However, polyesters, or indeed other polymers, which do show evidence of biodegradation in such aquatic OECD tests would be confidently expected to be also compostable and able to pass tests for compostability.

[0070] It is also desirable for microcapsules to have a certain level of biobased or nature-derived content. Examples of sources of such biobased or natural contents are naturally occurring polysaccharides, oligo-saccharides mono-saccharides, protein or molecules derived from such naturally occurring resources, or other molecules derived or extracted from natural plant resources for example. It is particularly desirable in some applications for nature derived contents to be 50% or more.

[0071] A highly beneficial use of microcapsules is for the prolongation of fragrances or other ingredients which have been encapsulated inside a polymer shell. Typically, the technologies or materials used for encapsulation of fragrances or similar molecules (cargoes) have included melamine formaldehyde, polyurea/urethane technologies, or acrylate technologies. Most use crosslinked networks of these polymers for stability and durability in the formulations in which they are used (for example, laundry/washing products, household cleaning products, hair care products skin care products among others).

[0072] Thus, making microcapsules able to contain hydrophobic or lipophilic groups which may, also, optionally, be volatile and/or plasticizing, requires some alternative approaches to what is known in the prior art for making microcapsules suitable to encapsulate lipophilic or hydrophobic cargoes and yet which can also be storage stable and be biodegradable and especially biodegradable in aquatic environments such as seawater, rivers, surface water or in water treatment effluents, processes, or activated sludges.

[0073] It is an aim of this invention to meet these criteria and so enable production of microcapsules that have a shell material that is biodegradable or non-persistent, particularly in aquatic media/waterways, and yet which comprise a certain level of biobased or nature derived content, and which can retain a hydrophobic or lipophilic cargo or a volatile or a plasticizing or oil solubilized cargo such as a fragrance, an essential oil or any other oil, and is stable in a product form until use. Fragrances and oils are of prime interest since they are used in many end products and yet they typically have some volatile or low boiling components which can

evaporate quickly if not contained in some way and/or components which are plasticizing to many polymers.

[0074] In terms of prior art, there are many patents and publications on microencapsulation of actives which are lipophilic. There are many examples of microencapsulations, of hydrophilic and lipophilic components for pharmaceutical or biomedical applications which describe biodegradable shells for controlled release. Biodegradation in such physiological environments is not representative of biodegradation requirements in aquatic waterways and the like. Physiological environments are typically warm at 37°C, have mixtures of specific degrading enzymes do not present in aquatic waterways for example, and/or have local pH extremes, and/or have salts and many other chemical entities also present. Overall, they are relatively aggressive media for degradation for controlled release. Furthermore, the shell wall materials, many of which are polyesters, and/or the processes typically used in drug or pharma active delivery are typically not suited to volatile or plasticizing cargoes. Many processes use extrusion (high temperatures), or solvents (requiring evaporation to very low residual limits) and when they do use undesirable components or reactants for shell walls (e.g., isocyanates for urethane shells) they will require significant cleaning or work-up to ensure removal of trace amounts of such components. Much pharma based encapsulations using polylactide or polyglycolide or poly(glycolide-co-lactide) (PLGA) polyesters as capsule shells use, for example, dichloromethane as an enabling solvent for encapsulations and it is necessarily subsequently removed by evaporation. All such aspects are not suited to volatile or plasticizing cargoes and/or are prohibitively expensive in their work up or other process stages for applications outside of pharma. For developments that are biodegradable shells of capsules, excepting those for pharmaceutical or biomedical applications, where, as just described, end environmental conditions (pH, temperature and/or presence of special enzymes etc.) are quite different from those in waterways and soil and where processes for manufacture are not well suited to those in personal or home markets, there are fewer in number and all of which have drawbacks inhibiting their widespread practical applicability. Our invention overcomes such drawbacks while also meeting the criteria and desirable attributes described above.

[0075] In the existing prior art claiming microcapsules from polysaccharides for example many do not demonstrate biodegradability in ambient waterways, water treatment processes, soils. Although use in biomedical or physiological environments is often described the conditions experienced therein are substantially different from (more aggressive than) from those in rivers, water treatments plants, seawater, or soils for example. Few in crosslinked forms, which are desirable for stable microcapsules, have shown biodegradability in ambient aquatic

environments or in related OECD tests. This is a concern, and indeed a major obstacle for wide commercial deployment, if the microcapsules were to be used in a liquid laundry or cosmetic or personal care product formulation. Common processes to date to make polysaccharide capsules or polysaccharide-rich capsules are largely based on spray drying or fluidized bed processes. Such processes are wasteful and inefficient and are not suited to heat sensitive cargoes such as volatile oils or fragrances. Compared to emulsion or in-situ or interfacial polymerization approaches these processes are much less preferred or suited. There are few if any solutions to meet the requirements of a microcapsules shell which can encapsulate and retain lipophilic cargoes, especially volatile or sensitive lipophilic cargoes, until a triggered release (such as friction or rubbing) and which are biodegradable (via OECD tests in aquatic media) and which have a significant proportion of natural or nature derived or biobased content.

[0076] Natural or nature derived or biobased contents can be determined by calculations according to known standards such as ISO 16128 or ASTM D6866.

[0077] Biodegradable, nature derived microcapsules for fragrance or oil cargoes have not yet been widely described to show a combination of such biodegradation properties with a successful encapsulation of a fragrance or similar volatile lipophilic cargo with the attributes of imparting a noticeable bloom or release of cargo when triggered (e.g., when rubbed or application of pressure). Furthermore, few if any show any ability to be stable on storage as made with fragrance or oils or other plasticizing cargoes inside or show stability on storage in aqueous media or aqueous end product formulations, as are used in home or personal care applications which may have pH extremes or surfactants or salts or solvents or other additives that may plasticize or attack the shell wall.

[0078] In one embodiment, the present application provides a microcapsule comprising: (i) a biodegradable polymeric microcapsule shell; and (ii) a lipophilic core; wherein, the polymeric microcapsule shell comprises saccharide units linked or crosslinked with one or more multi-functional linking groups selected from the group consisting of: (a) an ester, a β -amino-ester, or a β -thio-ester alone or combinations thereof, (b) a copolymer comprising two moieties selected from an ester, a β -amino-ester, and a β -thio-ester, or (c) a terpolymer of an ester, a β -amino-ester, and a β -thio-ester.

[0079] The capsules of our invention show successful microencapsulation and subsequent triggered release of fragrance or other lipophilic cargoes with associated evidence for biodegradability or potential non-persistence, in aquatic media according to OECD test methods and are made via convenient interfacial or related oil-in-water polymerization processes at low to moderate temperatures suited to volatile ingredient encapsulations. As such

they do not require subsequent volatile solvent removal or the use of undesirable isocyanate or formaldehyde or acid chlorides or the use of high temperatures at the encapsulation stage.

[0080] Polyester, poly- β -amino ester, and poly β -thio ester homopolymer complexes, particles and capsules have been described. Polyester capsules are typically made by ring opening polymerizations of glycolide or lactides and via extrusion or solvent extraction process - neither of which are suited to volatile sensitive cargoes. β -amino ester and β -thio ester polymers are typically made by Michael Addition, or conjugate addition, reactions of a difunctional or multifunctional amine or thiol donor (bearing primary or secondary amines or thiols which is at least difunctional on available NH or SH groups), and a difunctional or multifunctional acceptor (e.g., an activated (electron deficient) conjugated double bond as in an acrylate or related molecules, well known in the field).

[0081] Solvent based processes have been applied to make polymers or capsules, e.g., with water as a solvent, typically making hydrogel based encapsulations. Other solvent mediated processes, or classical interfacial polymerizations (oil-in-water polymerizations wherein one reactant is one phase and another and/or a catalyst is another phase and the two mixed or emulsified, typically to make an oil in water emulsion, in which polymerization and microcapsule shell formation then progresses. It is desirable to introduce biobased or nature-derived content into such capsules while also overcoming some of the limitations of the homopolymer poly- β -amino- or poly- β -thio- esters based materials. Limitations for unmodified homo-poly- β -amino-esters may include susceptibility to premature hydrolysis and poor storage stability especially in formulations at high or low pH. Limitations for unmodified homo-poly- β -thio-esters may be slow biodegradation profiles (i.e., too stable for meeting OECD biodegradation criteria). Other limitations for these types of β -amino or β -thio- ester or of polyester based capsule materials can, in some cases, include the plasticization of shell materials by the oil soluble or lipophilic cargoes which can lead to leakage of the cargoes on storage. Thus, the known methods and materials associated with homo- poly- β -amino-esters and homo-poly- β -thio-esters, even when crosslinked, have disadvantages when trying to encapsulate polar or volatile or plasticizing cargoes in a robust, highly cross-linked, or rigid shell.

[0082] Polysaccharide capsules are also well known, typical methods for their preparation have included spray drying or fluidized beds processes, coacervations, or hydrogel capsules which all have limitations in terms of efficiency and, or effectiveness for retaining oil soluble or lipophilic cargoes. Crosslinked saccharides are preferred for many applications requiring particularly good retention of cargoes (cores) and good storage stability. However, if

polysaccharides are used in crosslinked forms in capsule shells, they are not necessarily able to be classified as biodegradable according to OECD tests methods. There are various other additional limitations in the known methods or approaches reported to make microcapsules from polysaccharides and crosslinking agents. *For example*, some methods report the use of isocyanates for crosslinking saccharides or proteins. These are highly undesirable since they are toxic and water sensitive reagents which are increasingly disfavored in industrial processes.

[0083] In other approaches using polysaccharides to form microcapsules including those using interfacial or in-situ or emulsion and related polymerization methods and including those using unmodified conventional acrylates as crosslinkers, the polysaccharide is typically modified with reactive groups to help participation in the crosslinking or polysaccharides are modified with hydrophobic groups again to aid their participation in the oil-water based polymerization-encapsulation process and/or to impart better end performance. We have surprisingly found that no such modifications to the polysaccharides are necessarily required in some circumstances and, also, that biodegradable microcapsules based on crosslinked saccharides can be made by certain combinations and approaches including capsule shells that are biodegradable according to OECD aquatic test method such as those test methods referenced in this document.

[0084] The microcapsule shells of our invention show successful encapsulation and subsequent triggered release of fragrance, and have storage stability in aqueous formulations, and can demonstrate associated evidence for biodegradability or non-persistence over time in aquatic media according to OECD test methods and will have biobased or nature derived contents. Furthermore, they are made via a convenient emulsion processes which can be conducted at low to moderate temperatures suited to volatile ingredient encapsulations in an oil-in-water process, and not requiring subsequent volatile solvent removal and not using undesirable isocyanate or other such reagents nor requiring high temperatures at the encapsulation stage. Furthermore, they show a combination of fragrance encapsulation, biodegradability and storage stability in aqueous media or various formulated products or pH ranges.

[0085] Present invention relates to biodegradable microcapsules containing a natural or nature derived polymer, particularly, microcapsules that: (a) can encapsulate and retain cargoes, which can subsequently be released by a trigger and/or released gradually, and particularly where such cargoes are, or contain, lipophilic or hydrophobic core materials such as fragrances, butters or essential oil or other oils or oil solubilized cargoes; and, (b) whose shell material(s) show evidence of biodegradation or non-persistence in the environment and in particular in environments that are aquatic based (waterways, rivers, surface waters, seawater, sludge,

treated waters, etc.) and/or soil or compost based and (c) which are storage stable as made or in one or more end-product formulations, and (d) which have as one component a saccharide or protein or a derivative thereof which has been crosslinked and (e) where in the crosslinking moiety is derived from an acrylate, methacrylate, maleate, fumarate or itaconate.

[0086] Present application further describes a route to make micron sized (and above) capsules (microcapsules) and can be used for encapsulating sensitive or plasticizing or volatile lipophilic or other hydrophobic ingredients or actives or such as oils, or fragrances or butters or oil solubilized ingredients. Said biodegradable microcapsule polymeric shell compositions can effectively be used in various applications including, but not limited to personal care products and home care products.

[0087] Our approaches have surprisingly found that polymeric shell capsules can be made to encapsulate fragrances, oils etc. and other cargoes which exhibit lipophilic tendencies, compatibilities, or behaviors and which are stable on storage in aqueous media such as 'as-made', or in aqueous formulations of various pH's and optionally containing surfactants or other additives, and yet which are able to biodegrade in common, ambient, water based environments after use. Insoluble materials can be encapsulated by dissolution or partial dissolution, or via dispersion or emulsification, in a lipophilic carrier or diluent additive.

[0088] Non-limiting examples of cargoes that can be encapsulated through any of the embodiments in addition to fragrances, perfumes, essential or natural oils and the like, including oil (ester or hydrocarbon) solubilized ingredients, liquids or low melting solids include lipophilic esters, chlorinated solvents, hydrocarbons, insect repellants, pesticides, phase change materials, pigments, colorants, dyes, vitamins, antioxidants, lipophilic natural extracts, or other actives which are oily or oil (ester or hydrocarbon) soluble, and some solids.

[0089] In another non-limiting embodiment, the present application provides various methods for preparing said microcapsules and for preparing microcapsules from any combination of a saccharide or protein or derivative thereof, and a multifunctional linking group based on acrylate, methacrylate, acrylamide, methacrylamide, itaconate, maleate or fumarate derivatives of a diol or polyol, or of an ester or, a β -amino-ester or a β -thio-amino-ester, or mixtures thereof.

[0090] In another non-limiting embodiment, the present application provides a method for preparing said microcapsules from an unmodified saccharide, and a multifunctional linking group based on acrylate, methacrylate, acrylamide, methacrylamide, itaconate, maleate or fumarate derivatives of a diol or polyol, or of an ester or, a β -amino-ester or a β -thio-amino-ester, or mixtures thereof, in all such embodiments the shell material of the microcapsules is

biodegradable in the chosen medium (such as seawater, river water, activated sludge, etc. or soil or compost) is synthesized, or pre-synthesized from saccharide(s) and precursor linker(s) with reactive groups either in-chain or at chain end(s). A prepolymer or oligomer or precursor may be designed and synthesized with free radical reactive groups, in particular groups selected from conjugated alkenyl groups including acrylate, methacrylate, maleate, fumarate, itaconate, acrylamide or methacrylamide functionality and is used to link to or crosslink with saccharides during the encapsulation process stage during which the reagents are transformed to form a microcapsule shell, and which is biodegradable or hydrolysable and which is also initially compatible with the heated cargo (or cargo diluent mixture) as described below. A designed linker may contain hydrolysable groups selected from ester, β -amino-ester, or β -thio-ester bonds, optionally with amide and/or ether and/or other ester and/or carbonate and/or urethane bonds, though ensuring its structure and composition is designed to be biodegradable according to criteria herein described. The linker may be a pre-polymer or oligomer or 'small molecule' and may also be a polymer containing one or more hydrolysable groups selected from β -thio-ester, ester, or β -amino-ester but designed to be biodegradable, with suitable reactive radical polymerizable functionality through alkenyl (C=C) double bonds and via α,β -conjugated unsaturated carbon-carbon double bonds (C=C) as in acrylate, maleate, itaconate and the like. Such functionality may be in chain or at chain ends, and able to react in free radical linking or crosslinking reactions with the saccharide or radical activated saccharide form crosslinked or copolymeric (linked) saccharide based microcapsules. The saccharide is monosaccharide or disaccharide or oligosaccharide or polysaccharide and is not required to be modified with hydrophobic or alkenyl double bonds for such reactions.

[0091] In one approach the linkers or crosslinkers (there may be more than one type) are melted or dissolved (with warming if needed) into the cargo (optionally with added diluent or carrier or oil), or into a carrier oil or diluent first, and so is, or becomes, compatible with the cargo or a diluent or a mixture of the cargo and diluent, if necessary, when heated. Optionally co-reactive reagents (that may react with the reactive groups, in-chain or at chain ends and/or aid solubilization) or free radical initiators and/or other catalysts or accelerators may also be incorporated and/or additives to aid transformation during the capsule shell formation process. An inert (that is not necessarily co-reacting) biodegradable polymer additive may also be incorporated as an option, so making a polymer shell wall with a blended mixture of polymers.

[0092] The linker or crosslinker which contains hydrolysable groups as described also contains functional reactive groups which are free radically polymerizable. These reactive groups are alkenyl groups and are preferably selected from acrylate, methacrylate, maleate,

fumarate, itaconate, acrylamide or methacrylamide groups. The linkers or crosslinker is preferentially an acrylate methacrylate, maleate, fumarate, itaconate, derivative of a diol or polyol or of a polyester-diol or polyol, a β -amino-ester, or a poly- β -amino-ester, or of a β -thio-ester or a poly- β -thio-ester or a combination of these. Such derivatives, such as multi (di- or more) functional acrylates, methacrylates, maleates, and itaconates are well known and readily available or can be synthesized as meth(acrylic) or maleic or itaconic acid esters of diols or polyols, and others can be synthesized as esters of polyester-polyols or urethane-polyols or ester-urethane polyols. β -amino-ester or poly- β -amino-ester, or β -thio-ester or poly- β -thio-ester linkers with acrylate or methacrylate or maleate, fumarate or itaconate functionality are readily synthesized by known methods via Michael Addition reactions of amines, diamines, or polyamines or of thiols with polyfunctional acrylates, methacrylates, maleates or itaconates, or with acrylamides or methacrylamides. Via specific selected stoichiometries of the reactants in the Michael Addition reactions one can ensure that the desired proportion of residual (remaining) reactive unsaturation (C=C double bonds) are present in the linkers. The β -amino-ester or β -thio-ester, and other linkers as described, will thus contain reactive unsaturated groups, at chain ends or distributed along the chain, which can be used for co-reactions (linking or crosslinking) with the saccharide or activated saccharide to form a microcapsule shell wall. Non-limiting examples of reactive unsaturation functionality include acrylate, methacrylate, acrylamide, methacrylamide, itaconate, citraconate, maleate, fumarate, crotonate, and combinations thereof.

[0093] The linker (or crosslinker) cargo mixture (oil phase, with optional diluent, added catalyst or initiator) may be mixed with an aqueous phase which comprises the saccharide, dissolved or dispersed in water, optionally with added stabilizers, initiator, catalyst, or other additives. Optionally co-reactive reagents (that may react with the reactive groups, in-chain or at chain ends) or other free radical or crosslinking initiators are also incorporated into either phase and/or additives that may enable formation of complexes, salts, or other forms of interactions with the linker. The mixture is homogenized or stirred vigorously to form an emulsion, which may be while warm or heated and then reacted.

[0094] The capsules are formed during the reaction with stirring or homogenization. An insoluble polymer (insoluble in the cargo and insoluble in water) shell wall is made via crosslinking or linking or chain extension or branching reactions between the unsaturated linker molecules and the saccharide or activated saccharide and any (optional) added co-reactive reagents. In a preferred embodiment the linker (or crosslinker) is mixed with the cargo (oil phase, with optional diluent) together with a free radical initiator. In a parallel set up or vessel

the saccharide is mixed with (dissolved or dispersed in) water optionally with pre-heating or via a process of pre-dissolution such as through heating and stirring. This aqueous phase comprises the saccharide, dissolved or dispersed in water, and a initiator such as a persulfate or redox initiator system, is then incorporated with stirring and optional heating for a time which may be 1 minute, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 10 minutes, 12 minutes, 15 minutes, 30 minutes, 45 minutes, 1 hour, 2 hours or longer at about room temperature or at a defined temperature with heating at 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, or 80 °C or higher to generate radical or other activated or oxidized sites on the saccharide molecule. Other additives may be incorporated. *Optionally*, co-reactive reagents (that may react with the reactive groups, in-chain or at chain ends) or other free radical or crosslinking initiators are also incorporated into either phase and/or additives that may enable formation of complexes, salts, or other forms of interactions with the linker. The two phases are mixed after completion of the respective times for their pre- (or parallel) -reactions or -dissolutions and the mixture of the two phases is homogenized or stirred vigorously to form an emulsion, which may be while warm or heated and then the shell formation (linking or crosslinking) reaction occurs preferably with heating at 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, or 80 °C or higher, or via light or UV radiation, until shell or capsule formation is complete.

[0095] Mixtures of stabilizers may be used (and incorporated at various points) and mixtures of stabilizers with added polymers to complement them and/or aid control viscosity or stability.

[0096] Non-limiting examples of stabilizers used alone or as part of a mixture, include polyvinyl alcohols, polyvinylpyrrolidones, hydroxyethyl celluloses, hydroxypropyl celluloses and other cellulosic derivatives, guar, guar derivatives including cationic guar, gums including xanthan gum and the like, starches, and starch derivatives, and/or any known emulsifier or dispersing aid and including particles such as silicas. Particle stabilized (Pickering emulsion) approaches are also able to be used.

[0097] Non-limiting examples of defoamers may also be used which may include liquid hydrocarbons, oils, hydrophobic silicas, fatty acids, alkoxylated compounds, polyethers, polyalkylene glycols, and nonionic emulsifiers.

[0098] This process outline and its incorporated variations can be applied to produce a microcapsule which has a shell wall which is biodegradable in the chosen medium and yet can encapsulate and retain a lipophilic cargo and have natural derived or biobased content.

[0099] Non-limiting examples of a diluent or solvent is selected from the group consisting of hydrocarbon oil, alkanes, an ester oils, a fatty acid esters, an aliphatic esters, and alkylene carbonates.

[0100] A microcapsule with a biodegradable shell wall is produced according to any of the above methods, wherein such a polymer shell is formed around the cargo. Accordingly, the lipophilic core is selected from the group comprising agrochemicals, aliphatic esters, anti-microbial agents, anti-fungal, anti-fouling agents, antioxidants, anti-viral agents, biocides, catalysts, cosmetic actives, dyes, colorants, detergents, edible oils, emollient oils, essential oils, fats, fatty acids, fatty acid esters, food additives, flavors, fragrances, hair care actives, halogenated compounds, hydrocarbons, insecticides, insect repellants, lipids, lipophilic scale inhibitors, mineral oil, oral care actives, organic solvents, organic esters, chlorinated solvents, pesticides, perfumes, preservatives, skin care actives, UV absorbers, vegetable oils and combinations thereof. Accordingly, the core is a fragrance, a perfume, or an essential oil.

[0101] In some cases, the products may be particles with entrained or absorbed or adsorbed cargo rather than fully formed capsules or may be capsules which function in both aspects. Entrained or absorbed cargoes are still retained though typically for shorter times compared to fully encapsulated cargoes in shell walls. A combination of entrained, absorbed, or adsorbed cargo together with encapsulated cargo is also able to make in some cases. Also, the capsules or particles may form films on drying or casting or other processing which also contain and retain the cargo for certain times, all still being biodegradable. In one embodiment, microcapsules that are formed in a slurry (typical initial reaction product mixture) with encapsulated cargo which can dry as capsules and then, if desired, be re-dispersed in water or aqueous media or formulations and retained as capsules which are biodegradable.

[0102] In some embodiments, the polymer shells are built up during oil-in water reactions of selected reactants, or mixtures thereof, chosen to introduce specific attributes or features. Other methods to make the polymeric shells with the specific attributes or features targeted are also able to be used. In some other embodiments the polymer shell, made by any method, is modified post (after the) encapsulation reaction to introduce specific attributes or features. This may include additional crosslinking after the formation of the initial shell (post -crosslinking) or may also involve spray drying or overcoating.

[0103] In all the embodiments described above, the polymeric shells are based on a saccharide which is linked or crosslinked with linkers that contain ester, or β -amino-ester or β -thio-ester bond or mixtures of such linker groups. The initial linking or crosslinking reactions are preferably via free radical reactions. Post crosslinking can be via free radical or other routes for example using aldehydes or polyphenols such as tannic acid for secondary (additional) crosslinking.

[0104] The polymeric microcapsule shell is formed by a reaction between (a) the saccharides units and (b) one or more multi-functional linking group selected from the group consisting of an ester having alkenyl functionality, a β -amino-ester having alkenyl functionality and a β -thio-ester having alkenyl functionality.

[0105] The polymeric microcapsule shell is formed by a reaction between (a) the saccharide units and (b) a multi-functional linking group having alkenyl functionality and β -amino-ester, a β -thio-ester groups, or their combinations or mixtures. The reaction is a free radical reaction, a conjugate addition reaction, or a Michael addition reaction. Preferably it is a free radical reaction.

[0106] The alkenyl functionality of the ester, β -amino-ester or β -thio-ester is selected from the group consisting of an acrylate, a methacrylate, a maleate, a fumarate, an itaconate, a crotonate, a citraconate, a maleimide, an acrylamide, a methacrylamide and combinations thereof.

[0107] The β -amino ester or β -thio-ester linkers or their mixtures or copolymers may be made via Michael Addition reactions and are designed to have reactive unsaturation for radical reactivity to be able to reactively link with the saccharide. Alternatively, or in addition, the introduction of the modifying group can be via an overcoating step applied to the polymeric capsule shell. The saccharide is a mono-saccharide, a di-saccharide, oligo-saccharide, or a poly-saccharide.

[0108] Non limiting examples of saccharides may be mono- di-, oligo- poly-saccharides and include one or more selected from glucose, galactose, fructose, sucrose, maltose, lactose, xylose, trehalose, dextran, pullulan, guar gum, locust bean gum, other galactomannans, other saccharide based gums, pectin, starches, potato starch, corn starch, pea starch, hyaluronic acid, depolymerized celluloses, and variants or derivatives of such saccharides, including sugar alcohols or related derivatives including xylitol, sorbitol, and isosorbide, and all non-hydrophobically modified saccharides. Depolymerized higher molecular weight saccharides are also included, including depolymerized celluloses, gums, and starches among others. More particularly, the saccharide is selected from the group consisting of (i) unmodified starch, potato starch, corn starch, wheat starch, pea starch, guar gum, cassia gum, lactose, maltose, sucrose, fructose, trehalose, or oligomers thereof, or (ii) a degraded or depolymerized cellulose, cellulose ether, starch, or guar; or (iii) combinations of (i) and (ii).

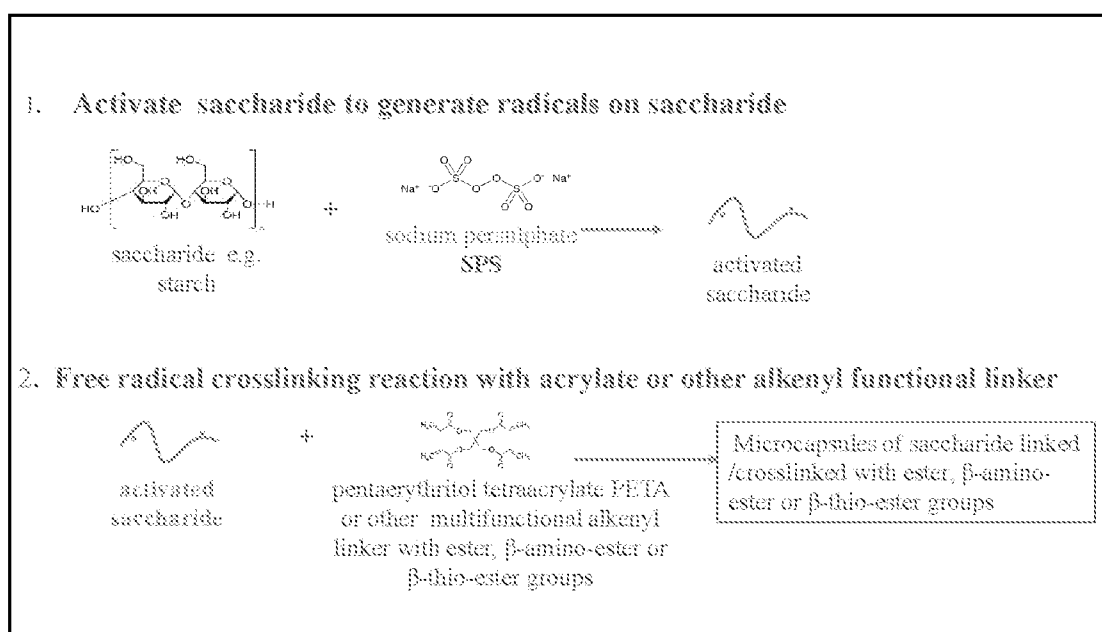
[0109] For embodiments using ester based alkenyl linkers such as acrylate methacrylate esters of diols or polyfunctional alcohols (polyols), used in the absence of β -amino ester or β -thio-ester linkers, the saccharide is not modified with an alkenyl, a hydrophobic or an amine group or is an unmodified saccharide.

[0110] For embodiments using β -amino ester or β -thio-ester linkers any saccharide or polysaccharide - modified or unmodified may be used. In some embodiments, the saccharide is not modified with an alkenyl, a hydrophobic or an amine group or is unmodified. In some embodiments, the saccharide is either modified with hydrophobic or alkenyl or amine functional group or other groups.

[0111] This includes hydrophobic or alkenyl functional saccharides such as octenyl succinate modified starch or dodecenyl succinate modified starch or any other modified saccharides. It also includes all unmodified saccharides and sugar derivatives.

[0112] For embodiments using conventional acrylate linkers only unmodified saccharides or polysaccharides may be used - that is saccharides that do not contain hydrophobic or alkenyl functional groups. Scheme 1 below illustrates an example of the process of the invention.

Scheme 1 : Illustration of an example process of one embodiment of the invention



[0113] In one embodiment, the present application provides various routes to prepare capsules (microcapsules) of the invention, which can contain, retain, or entrain a hydrophobic or lipophilic cargo, such as a fragrance or oil, and wherein such microcapsules can also be biodegradable in aquatic or other environments. In some embodiments, β -amino-ester or β -thio-ester linkers are used to tailor biodegradability performance. Such linkers are derived, either in a separate or in an integrated (continuous or semi-continuous) process step within the overall methods for the invention, from a Michael or conjugate Addition reaction of at least one amine or thiol donor and at least one acceptor, wherein one acceptor component will have

a reactive functionality of at least two and wherein the total acceptor functionality (unsaturated alkenyl, -C=C- groups) is in excess of the donor (amine or thiol) functionality to ensure multifunctional (two or more) alkenyl or free radical reactivity of the linker molecules. Thus, the β -amino-ester or β -thio-ester linkers are alkenyl functional and preferably with alkenyl functionality that is selected from acrylate, methacrylate, maleate, fumarate, itaconate, crotonate, citraconate, maleimide, acrylamide, methacrylamide based and which is multifunctional with an average alkenyl functionality of more than one and preferably at least two or more.

[0114] In other embodiments at least, for the β -amino-ester or β -thio-ester linkers made by Michael Addition reactions of donors and acceptors, at least one alkenyl functional acceptor component has a reactive functionality of at least two and preferably both donor and acceptor components have a reactive functionality of two or more, but always in ratios that ensure the total acceptor functionality (unsaturated -C=C- groups) is in excess of the donor (amine or thiol) functionality to ensure multifunctional free radical reactivity of the linker molecules.

[0115] In a non-limiting embodiment a linker can be derived from a donor-acceptor combination selected from the group containing: (i) a difunctional, trifunctional, tetrafunctional, pentafunctional or hexafunctional amine; and (ii) a difunctional, trifunctional, tetrafunctional, pentafunctional or hexafunctional acrylate or methacrylate, and wherein (ii) the acceptor is in a stoichiometric excess in terms of total reactive functionality – for example the mole equivalents of all acrylate or methacrylate groups (as examples) in the acceptors exceeds the total mole equivalents of all NH or SH groups in donor molecules. By tailoring this stoichiometry (to control the eventual reactive alkenyl (C=C) functionality in the linker and by controlling the relative proportions of ester, β -amino ester and β -thio ester in the linker it becomes feasible to impart and tailor the biodegradability of the linked (copolymeric) or crosslinked saccharide shell material.

[0116] In embodiments where a β -amino-ester or β -thio-ester is pre-synthesized (for the subsequent reaction with saccharide), via Michael Addition reaction, the donor is an amine or a thiol or is a mixture of amines and thiols. The donor can be a mixture of at least one difunctional amine or thiol and/or multifunctional amine or thiol. An amine donor can be a difunctional primary amine, a multifunctional primary amine, a difunctional secondary amine, a multifunctional secondary amine, or combinations thereof. Accordingly, one or more of the amine or thiol ester components has $\text{C}_2\text{-C}_{20}$ aliphatic chain functionality, a $\text{C}_4\text{-C}_7$ cyclic ring functionality or a $\text{C}_4\text{-C}_7$ heterocyclic ring functionality.

[0117] In another non-limiting embodiment, the amine donor (for a pre-synthesis of an β -amino-ester based alkenyl linker) is selected from the group consisting of any primary alkylamine or primary cyclo-alkylamine, 4,4'-trimethylenepiperidine (TMPP), isophorone diamine (IPD), bis-(aminomethyl) cyclohexane, cyclohexane diamine, piperazine, aminoethyl piperazine, bis-amino-norbornane, ethylene diamine, diethylene triamine, diethylene diamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine (PEHA), tris(2-aminoethyl) amine, bis(3-aminopropyl) amine, spermine, hexamethylene diamine (HMDA), diamino-propane, diamino-butane, diamino-pentane, diamino-octane, diamino-decane, diamino dodecane, amino-ethanol amino-propanol, amino-butanol, amino pentanol, any polyfunctional amine, and polyethyleneimine or any derivatives of such di- or multi-functional amines with available amine groups for reaction with acceptors.

[0118] Similarly, thiol donors (for β -thioester containing alkenyl linkers) will have poly- or multi- (2 or more) functionality in respect of SH (thiol) groups and will typically comprise a C2-C20 aliphatic chain, a C4-C7 cyclic ring or a C4-C7 heterocyclic ring.

[0119] Acceptors useful in synthesizing a linker functionalized with radically polymerizable alkenyl bonds include acrylates or methacrylates, maleates, fumarates, itaconates, crotonates or acrylamides. More particularly, the acceptor is selected from the group consisting of: (a) an itaconate containing polyester, (b) an acrylate, diacrylate, or multifunctional acrylate of a polyester; (c) an acrylate, diacrylate, or multifunctional acrylate of an epoxide; (d) an acrylate, diacrylate, or multifunctional acrylate of a urethane; (e) an acrylate, diacrylate, or multifunctional acrylate of a polyether or a diol or a polyol; (f) an acrylate, diacrylate, or multifunctional acrylate of an amine; (g) methacrylate analogue of (b) to (f) components, and combinations thereof.

[0120] Non-limiting examples of acrylates, used in the Michael or conjugate Addition reactions, as precursors for making alkenyl functional β -amino-ester or β -thio ester linkers, can be selected from the group consisting of butanediol diacrylate, trimethylol propane triacrylate, pentaerythritol triacrylate, pentaerythritol tetra-acrylate, dipentaerythritol penta-acrylate, and dipentaerythritol hexa-acrylate, any other multifunctional acrylate including acrylate derivatives of polyols, polyesters, epoxy functional precursors or urethanes - and methacrylate analogues thereof. The alkenyl functional acceptor component is used in a measured excess to ensure alkenyl functionality in the resulting linker, and so preferentially imparts multifunctional alkenyl functionality to the β -amino-ester or β -thio ester linkers.

[0121] These acrylates or methacrylates listed, and indeed other alkenyl functional esters, are also able to be used as linkers themselves in some embodiments, as *ester based* linkers, in

particular in combination with saccharides not modified with alkenyl, amine or hydrophobic groups.

[0122] In another non-limiting embodiment for the synthesis of the designed alkenyl functional β -amino-ester or β -thio ester linkers, the present application provides donor-acceptor combination comprising difunctional amine or thiol, trifunctional amine, or thiol, tetrafunctional amine or thiol, pentafunctional amine or thiol or hexafunctional amine or thiol. These may be primary or secondary amines. The relative acceptor (alkenyl) functionality is always used in excess of total donor (NH_2 , NH and/or SH) functionality to impart alkenyl functional groups to the designed linkers. As an example, a multifunctional amine such as PEHA is reacted with a multi-functional (two or more) acrylate or methacrylate at a stoichiometry which leaves multiple acrylate groups attached to former N-H groups which are available for subsequent free radical linking or crosslinking reactions. Any polyfunctional amine or thiol may be used in these or similar ways.

[0123] Accordingly, in some embodiments the polymeric shell comprises a saccharide, pre-modified or unmodified, which is linked or crosslinked with a poly β -amino-ester, a poly- β -thio ester or a copolymer, poly- β -amino-ester-co- β -thio ester.

[0124] Preferably the saccharide to linker reactants weight ratio will be such that 50 *wt.*% or more is saccharide in the reaction feed. Preferably the saccharide to linker reactants weight ratio will be 60 *wt.*% saccharide - 40 *wt.*% linker, 70 *wt.*% saccharide - 30 *wt.*% linker, 80 *wt.*% - 20 *wt.*% linker, or 90 *wt.*% saccharide - 10 *wt.*% linker, or in *wt.*% ratios in between these limits - provided that 50 *wt.*% or more of the saccharide-linker reactant feed is saccharide.

[0125] Accordingly, the ratio of total saccharide to total functional linking group having alkenyl functionality in the reactant feed, on a weight ('solids') % basis is 51:49, 60:40, 65:35, 70:30, 75:25, 80:20, or 90:10.

[0126] In another non-limiting embodiment, the present microcapsule further comprises an added biodegradable polymer.

[0127] In another non-limiting embodiment, the present microcapsule has a lipophilic core, wherein the lipophilic core is selected from the group comprising agrochemicals, aliphatic esters, anti-microbial agents, anti-fungal, anti-fouling agents, anti-perspirant, antioxidants, anti-viral agents, biocides, catalysts, cosmetic actives, colorants, dyes, detergents, edible oils, emollient oils, essential oils, fats, fatty acids, fatty acid esters, food additives, flavors, fragrances, hair care actives, halogenated compounds, hydrocarbons, insecticides, insect repellants, lipids, lipophilic scale inhibitors, mineral oil, oral care actives, organic solvents, organic esters, chlorinated solvents, pesticides, perfumes, preservatives, skin care actives, UV

absorbers, vegetable oils and combinations thereof. Preferably, the lipophilic core is a fragrance, a perfume, or an essential oil.

[0128] In one embodiment, the present application provides a method for preparing a microcapsule, the method comprising: (a) preparing an oil-in-water emulsion of (i) an oil phase comprising at least one multifunctional linker, and at least one lipophilic core; and (ii) a water phase comprising at least one saccharide, optionally with at least one initiator or activating catalyst, stabilizer, defoamer, or emulsifier, (b) optionally adding at least one catalyst or initiator, at least one diluent to the oil phase; (c) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and so forming the polymeric microcapsule shell by an oil-in-water or interfacial free radical polymerization reaction of the linker with the saccharide; and (d) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0129] *Thus*, there are described below non-limiting generic routes or embodiments for the practical application and implementation of the polymeric shell microcapsules of the invention which are able to encapsulate and retain lipophilic cargoes including aggressive cargo examples such as fragrances or volatile oils, while concomitantly such polymeric shells also being biodegradable according to the criteria described herein, and which are made via processes which, at the encapsulation stage avoid the need for high temperatures, and/or avoid the need to use or remove volatile or otherwise undesirable solvents or reagents.

[0130] In another non-limiting embodiment, the present application provides a method comprising: (a) making a linker in-situ by pre-reacting at least one multifunctional amine or thiol donor with a multifunctional (in terms of unsaturated alkenyl double bonds) acceptor, present in molar equivalent excess to form a linker with a radical polymerizable (alkenyl) groups ; (b) preparing an oil-in-water emulsion of (i) an oil phase comprising the product of the linker reaction (a), and at least one lipophilic core, optionally with added diluent and/or initiator ; and (ii) a water phase comprising a saccharide and, optionally, at least one initiator or activating catalyst, stabilizer, defoamer, or emulsifier, (c) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C to form the polymeric microcapsule shell by an oil-in-water or interfacial polymerization reaction; and (d) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0131] The diluent will preferably be a liquid at room temperature or readily meltable at moderate temperatures such as below 90°C or less than 50°C and may be a hydrocarbon oil, an alkane, a melted wax, an ester oil, a fatty acid ester, an aliphatic ester, or an alkylene carbonate. Some specific examples include mineral oil, long chain alkanes such as hexadecane

and the like, aliphatic esters such as esters of long chain acids such as caprylates, myristates, oleates, cocoates, palmitates, or stearates including isopropyl myristate as one example, or long chain esters of shorter chain acids or other monohydric or polyhydric esters.

[0132] In another non-limiting embodiment, the present application provides a method for preparing a microcapsule, the method comprising: (a) preparing an oil-in-water emulsion of (i) an oil phase comprising at least one alkenyl functional linker, and at least one lipophilic core; and (ii) a water phase comprising at least one saccharide optionally with added catalyst, initiator, stabilizer, defoamer or emulsifier, (b) optionally adding at least one catalyst, at least one diluent or at least one initiator to the oil phase; (c) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and so forming the polymeric microcapsule shell by an oil-in-water or interfacial reaction of the linker (s) with the saccharide component(s); (d) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell, and (e) a post-reaction modification on the polymeric shell material to introduce additional crosslinking or to add an outer-coating for example in a spray drying process.

[0133] Post modification reactions include for example, reactions with aldehydes or ketones such as glutaraldehyde glyoxal, and other aldehydes or polyphenols such as tannic acid.

[0134] One or more radical initiators are used in the process of encapsulation. Examples of initiators may be a peroxide or an azo based radical initiator or a redox system such as a persulfate based system, or which may be a photo-initiator for UV induced radical reactions and can be added at any stage. They will effect a radical reaction linking of the unsaturated (alkenyl) groups of the linker with the polysaccharide. In one preferred method and embodiment a radical initiator or activating catalyst such as a persulfate is added to the water phase containing the saccharide and the components (saccharide plus initiator) reacted for a defined time, often a short time of several minutes to create active radical sites on the saccharide which can then be used to react with the alkenyl unsaturation of the linkers. In one embodiment the activated saccharide with radical sites serves as a macroinitiator for the free radical linking reactions with alkenyl functional linkers. An additional initiator can be added into the oil phase containing the alkenyl functional linker at any stage of the process. This approach can further facilitate the free radical linking (or crosslinking) of saccharides with the alkenyl functional linkers. Radical linking reactions between the linkers and saccharides lead to coupled or linked materials or components in the capsule shell.

[0135] In all the methods described above, the water phase or oil phase, or where both phases, comprises a radical initiator system selected from peroxide based, an azo based, persulfate or redox based, or comprises a radical chain transfer agent, added at any point of the process.

[These processes incorporate a radical addition or polymerization reaction to introduce linking or crosslinking, wherein such reaction is performed at a temperature $\leq 130\text{ }^{\circ}\text{C}$ or $\leq 100\text{ }^{\circ}\text{C}$ or $\leq 80\text{ }^{\circ}\text{C}$.

[0136] When designing capsule shells for the most demanding of applications, for example encapsulation of fragrances for liquid fabric conditioner products, a higher crosslink density is typically desired and/or some other form of rigidity and ‘solvent/chemical resistance’ or resistance to the more extreme pH’s (as is sometimes experienced in formulated end products), in the shell polymer structure. The capsule shells have to be resistant to lipophilic media such as the cargoes so that they do not leach out or plasticize the shell material from the inside and also be resistant to (stable in) water based media over a range of pHs and in the presence of surfactants or salts or other components. This typically translates to an ability to achieve a noticeable fragrance boost (bloom) or release upon physical crushing or via other triggers, considered highly advantageous for such products. Such capsules are required to remain ‘intact’ as capsules with fragrance inside (note fragrance is an ‘aggressive solvating or plasticising cargo’ compared many others) and retained inside for relatively long time periods, until such a crushing or other triggered release in use (by consumers) occurs. More particularly they are also often required to be stable (‘intact’) when stored before ultimate consumer end-use in formulated products which might be of extreme pH’s such as pH3 and/or long time periods and/or contain solvents or ingredients that might compromise the polymer shell wall. As described above on the prior art examples of capsule technologies reported to meet such demanding needs are melamine-formaldehydes (M-Fs) and crosslinked acrylates.

[0137] These form durable capsule shells with long term storage stability in formulated aqueous media such as pH3 often also containing surfactants, as is the case for some liquid fabric conditioner products, and all in the presence of the ‘aggressive’ cargo (fragrance). However, as also described above in the prior art, these M-F or acrylate or related capsules are not biodegradable in aquatic media such as seawater, river/surface water or activated sludge, nor are they compostable according to recognized international standards (such as EN/ISO, ASTM, OECD etc.). Furthermore, such highly crosslinked capsule shells are not readily made to be biodegradable while retaining performance (fragrance boosts) or storage stability. Our invention has discovered routes to make stable capsules (e.g. stable on storage until use) - so resisting the solvating or plasticising/softening effect from the inside (fragrance cargo) and resisting the effects of the formulation components which may be at an aggressive pH3 and/or contain a surfactant mix (from the ‘outside’ formulation medium), but which will also show biodegradation or evidence of non-persistence in water based media (aquatic systems) and still

perform, for example as a fragrance booster (when fragrance is the cargo) when triggered. Thus, in the case of the more demanding circumstances, where a capsule shell is likely required to retain a cargo, stably, on storage in such situations, the products of the processes described, and compositions described in this invention can achieve that.

[0138] In another non-limiting embodiment, it is disclosed that the microcapsule is stable as a core shell capsule in an aqueous slurry, in a water-based formulation or in a solvent-based formulation. The microcapsule is storage stable as a core shell capsule in solid formulated or printed product.

[0139] Accordingly, the formulation or aging medium has pH in the range of 3-4, 4-5, 5-6, 6-7, 7-8, 8-9, 9-10 or 10-11, or 11-12. The inventive microcapsule is stable as a core-shell capsule in an aqueous slurry or in a water-based formulation having pH in the range 3-5. The inventive microcapsule is stable as a core-shell capsule in an aqueous slurry or in a water-based formulation having pH in the range 9-11.

[0140] In another non-limiting embodiment, the microcapsule is additionally subsequently processed or overcoated and/or further crosslinked, to create a double layered microcapsule, a multi-layered microcapsule, an overcoated microcapsule or a dually crosslinked microcapsule, with the microcapsule inner layer being formed from the linking or crosslinking of saccharide as described. This is the inner or initial layer before the subsequent processing. The double layered, multilayered or an overcoated microcapsule comprises within its outer coating: a polysaccharide, a protein, a hydrogel, a coacervate, a polysaccharide, an oligosaccharide, a monosaccharide, a polyphenol, tannic acid, a sugar derived alcohol or polyol, or a biodegradable polymer or combinations thereof. Preferably, the double layered, multilayered, overcoated or dually crosslinked microcapsule comprises within its outer coating or secondary treatment, a xanthan gum, polysaccharide gum, a polysaccharide, a hydrophobically modified starch or other hydrophobically modified saccharide, an alginate polymer, a cellulose ether including hydroxyethyl cellulose or carboxymethyl cellulose, a guar or modified guar including cationic guar, zein protein or soy protein or other protein, a polypeptide, a hydrogel, a coacervate, a sugar alcohol, a polyphenol or tannin acid. Such overcoated and/or dually crosslinked capsules are particularly stable in more demanding or aggressive formulated end products – and yet can still be described as biodegradable.

[0141] In another non-limiting embodiment, microcapsules are used in in home care (laundry products, cleaning products), personal care (hair, skin, oral products) and industrial sectors (such as coatings, adhesives, agricultural products, energy markets) and others. As such many different formulations or use environments are encountered. *Preferably*, the microcapsule is

used in a consumer care composition selected from the group consisting of laundry care composition, fabric care composition, oral care composition, hair care composition, skin care composition, cosmetic care composition, home care composition and cleaning composition. *Most preferably*, the microcapsule is used in a fabric conditioner composition or a laundry detergent composition.

[0142] In another non-limiting embodiment, the microcapsules of the present invention are formulated into a laundry detergent, fabric softener, fabric conditioner, shampoo, hair conditioner, liquid soap, solid soap, skin deodorant, skin moisturizer, skin conditioner, hair or skin protectant, cleanser, sanitizer, cleaning fluid, dishwashing fluid, dishwashing tablet, washing powder, washing tablet, washing liquid, and cosmetic formulation.

[0143] In a specific embodiment, the microcapsule is used in a fabric conditioner composition or a laundry detergent composition.

[0144] The capsules of this invention are biodegradable or non-persistent in aquatic tests and which show encapsulation can perform and be stable in many formulations, including water-based formulations or solutions at various pH's and with various additives present including surfactants or salts, and in solvent based formulations or products and in dry or waterless or low water content products (tablets, larger capsules, powders or powder blends, gels). In making or formulating such products, the capsules of the invention can be directly incorporated as a slurry as is produced by the process of production or may be added as a dried product (e.g., the capsules may be spray dried or freeze dried or fluid bed dried or dried by any other drying process, to make dried capsules). Examples are given below of spray drying for example to make a free-flowing powder or to make an over-coated capsule.

[0145] For addressing the most demanding of requirements in terms of stability in some formulations, or in solvents, or in water-based formulations away from neutral pH, one possible route, as described above, would be to make higher crosslink density polymers. However, it is well known by those skilled in the art that conventional covalent crosslinking will typically slow down or inhibit biodegradation processes.

[0146] We have found that some particular linked saccharide or crosslinked saccharide structures (as capsule shells), optionally overcoated or dually crosslinked, can show a combination of being robust capsules ('bloom' performance and storage stability in aqueous formulations) can still be hydrolysable or biodegradable or show evidence of non-persistence over time when tested for biodegradability in aquatic media. The use of hydrolysable or cleavable crosslinks or links in the linker components and the choice of saccharides (those which are already known to be biodegradable or which is depolymerized to some degree to

become biodegradable, has enabled, a biodegradable shell to be made and which also surprisingly leads to achieving a combination of robust capsules, stable on storage in water-based formulations, including pH extremes, - and yet which can show biodegradability in aquatic environments or test media.

[0147] Such materials showing evidence of biodegradability in aquatic environments will also be compostable.

[0148] For fragrance encapsulations via *the in-situ or interfacial or related oil-in-water* polymerization routes, it is not convenient to make crosslinked networks via reactions that need high temperatures (e.g., condensation reactions between acids and alcohols) - this is undesirable if encapsulating a volatile or reactive cargo such as a fragrance.

[0149] In another non-limiting embodiment, the present polymeric microcapsule shell is biodegradable in an aquatic medium or solid medium or is compostable. The aquatic or solid medium is selected from group consisting of activated sludge, secondary effluent, river water, surface water, fresh water, sea water, soil, and compost.

[0150] In another non-limiting embodiment, the polymeric microcapsule shell material shows a biodegradation rate of at least 20% in an aquatic medium when measured by an OECD Test method 301, 302 or 306. The polymeric microcapsule shell material shows evidence of biodegradation within 120 days or within 60 days or within 40 days or within 28 days.

[0151] In another non-limiting embodiment, the microcapsule is storage stable as a core-shell capsule in an aqueous slurry, in a water-based formulation or in a solvent-based formulation. The microcapsule is storage stable as a core-shell capsule in a solid, largely waterless formulation or in a printed product.

[0152] In another non-limiting embodiment, the present application provides a microcapsule showing a retained triggered release of cargo or 'a bloom' after storing or aging in a respective medium for at least 4 weeks at ambient temperature (15-25°C), or at least 6 weeks or at least 8 weeks or at least 12 weeks at ambient temperature or at elevated temperatures.

[0153] For the most demanding aqueous media for storage or delivery of the capsules such as pH 2 or 3 or pH 11 or 12 higher crosslink densities are preferred and yet surprisingly the microcapsules made can be biodegradable or non-persistent according to OECD or other standard tests.

[0154] Amines are among the donors often desired to be a portion or component of the designed linker molecules due to their reaction products (β -amino-ester groups) having a good biodegradability profile. They are used in some embodiments to achieve a balance of biodegradability - storage stability and applications performance attributes. However, limited

choice exists in available polyfunctional amines for these processes since for *in-situ oil in water or interfacial* polymerization processes, amines, are often highly water soluble. By pre-reacting (or by reacting in separate or parallel step) the amine(s) neat or in diluent or cargo components (that is in the absence of water) we can avoid the complications that can arise due to the water-solubility of amines where they to be present at the start rather than pre-reacted before water is introduced. When polyfunctional water soluble amines are reacted with excess alkenyl acceptor in Michael Addition reactions the resulting product (the 'linker' molecule) is not very water soluble. This is an effective route to incorporating β -amino-ester groups into the shell material and the subsequent polymerization with saccharide (encapsulation) process proceeds effectively or readily. The linker is also enabled to be dissolved or dispersed in with the cargo or diluent along (oil phase). Amines can be used in combination with other amines and with polyfunctional thiols.

[0155] In the use of the Michael addition reaction to make linker molecules with alkenyl functionality, a mixture of different polyfunctional amine(s) and different polyfunctional thiols as donors can be used advantageously to tailor a balance between biodegradability and encapsulation performance or stability on storage, including in pH's at or away from neutral such as 3 or 11, and including in formulated products such as liquid fabric conditioners/softeners, shampoos, soaps, deodorants, skin creams, insect repellent delivery, cleaning fluids, sanitizers, agricultural active delivery, among others.

[0156] In another non-limiting embodiment, the present application provides a method for preparing microcapsules comprising a polymeric microcapsule shell based on a saccharide and a simple or conventional acrylate or other alkenyl functionalities. Here there is no β -amino ester or β -thio-ester groups - just the ester arising from the original conventional acrylate as linker, the linker may be a readily available multifunctional acrylate. The use of a conventional polyfunctional acrylate with biodegradable unmodified or natural saccharides has also been found to produce good performing capsules which still show biodegradability according to the OECD and other methods mentioned. This embodiment has advantages over prior art in not having to pre-synthesize a designed linker molecule since multifunctional acrylates are widely and cheaply available and, also, not having to use or pre-synthesize a hydrophobic or alkenyl functional polysaccharide. Furthermore, in many comparisons an unmodified saccharide can have greater biodegradability over modified counterparts in such structures.

[0157] We have surprisingly found that for the saccharide to be sufficiently linked with acrylate functional linkers to make capsule shells with good integrity and performance, there is no requirement for a modification of the saccharide such as a hydrophobic modification or

the introduction of radically polymerizable alkenyl groups. The process described can seemingly induce sufficient radical formation on the saccharide which can then react with alkenyl bonds of the linkers. Examples below demonstrate this. In particular good performing capsules were obtained with unmodified corn starch or unmodified potato starch and trehalose as the saccharide, among others. It is known that radical or persulfate or similar treatments of polysaccharides can lead to molecular weight reduction or depolymerization of the starting saccharide - this is also likely to be advantageous in terms of biodegradability performance and other performance parameters if that degradation can be controlled or optimized.

[0158] *However*, conceptually there is a potential risk when using conventional acrylate as the linker or crosslinker for the saccharide that some self-polymerized multifunctional acrylate only capsules may be unintentionally formed - so without linking to saccharide. This may not necessarily be readily detected but remains a potential risk and as such could be a potential complication in seeking a microplastic-free claim or attribute. The use of the β -amino ester / β -thio ester acrylates can overcome this risk since the self-polymerized products of such acrylates can be designed, and shown, to be biodegradable including biodegradable in OECD aquatic test methods. This offers a significant advantage and enhancement over reported prior art in the use of conventional or typical acrylate or other alkenyl crosslinked or linked polysaccharide microcapsules.

[0159] In one embodiment, biodegradable composition of plurality of microcapsules, the composition comprising at least two microcapsules selected from the group consisting of: (i) microcapsules comprising microcapsule shell material comprising saccharide units linked or crosslinked by reaction with β -amino ester having alkenyl functionality and/or β -thio ester having alkenyl functionality, (ii) microcapsules comprising microcapsule shell material comprising crosslinked β -amino ester having alkenyl functionality and/or β -thio ester having alkenyl functionality, (iii) microcapsules comprising microcapsule shell material comprising saccharide or modified saccharide, and (iv) combinations or hybrid or interpenetrating network of (i), (ii) and (iii).

[0160] The composition of a plurality of microcapsules described, or a portion of the microcapsules present, may additionally be overcoated or form part of multi-layer or dually crosslinked system.

[0161] Furthermore, in one preferred embodiment, the product microcapsules composition components as described, where present, comprise a lipophilic core.

[0162] Another significant distinctive enhancement of our invention over reported prior art in the use of acrylate or other alkenyl crosslinked or linked polysaccharide microcapsules is

discovery that the absence of a requirement for the polysaccharide to be pre-modified with a hydrophobic group or to contain a reactive alkenyl group and yet still be able to make robust microcapsules.

[0163] In another non-limiting embodiment, the present application provides a method for preparing a microcapsule comprising (i) a biodegradable polymeric microcapsule shell; and (ii) a lipophilic core; wherein, the polymeric microcapsule shell comprises saccharide units linked or crosslinked with one or more multi-functional linking groups selected from the group consisting of: (a) an ester, a β -amino-ester, or a β -thio-ester alone or combinations thereof, (b) a copolymer comprising two moieties selected from an ester, a β -amino-ester, and a β -thio-ester, or (c) a terpolymer of an ester, a β -amino-ester, and a β -thio-ester; the method comprising: (a) preparing an oil phase, comprising at least one multifunctional linker with alkenyl functionality, at least one lipophilic core, and optionally adding at least one catalyst or initiator, and/or a diluent; (b) preparing a water phase comprising at least one saccharide or polysaccharide and an initiator or catalyst, and optionally a stabilizer, defoamer, and/or emulsifier; (c) mixing the two phases together and emulsifying to make an oil in water emulsion; (d) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by an oil-in-water reaction of the linker components with the saccharide component(s); and (e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0164] In another non-limiting embodiment, the present application provides a method for preparing microcapsules or biodegradable composition of plurality of microcapsules, the method comprising: (a) preparing an oil phase, optionally with heating, comprising at least one multifunctional linker with alkenyl functionality, optionally with a diluent, and adding, after completion of any heating applied and allowing to cool, a catalyst or initiator and a lipophilic core; (b) preparing a water phase comprising at least one saccharide or polysaccharide, an initiator or catalyst, optionally a stabilizer, a defoamer, and/or an emulsifier and heating for a predetermined time until the point at which the oil phase and water phase are mixed; (c) mixing the two phases together and emulsifying to make an oil-in-water emulsion; (d) heating the oil-in-water emulsion of step (c) with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by an oil-in-water reaction of the linker components with the saccharide component(s); and (e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0165] In another non-limiting embodiment, the present application provides a method for preparing microcapsules or biodegradable composition of plurality of microcapsules, the

method comprising: (a) preparing a multifunctional alkenyl functional linker containing β -amino-ester and/or β -thio-ester groups by reacting, for a predetermined time prior to the mixing of phases in step (c), in a Michael Addition reaction and optionally in the presence of a diluent, a multifunctional conjugated alkenyl functional ester acceptor with a multifunctional amine and/or thiol donor, wherein the alkenyl functionality of the acceptor is in stoichiometric excess compared to the total donor functionality of amine (primary and secondary) and/or thiol groups; (b) preparing a water phase comprising at least one saccharide or polysaccharide and an initiator or catalyst, and optionally a stabilizer, defoamer, or emulsifier and heating for a pre-determined time before the mixing of the phases in step (c); (c) after the predetermined time, mixing the two phases together and emulsifying to make an oil in water emulsion; (d) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by an oil-in-water reaction of the linker components with the saccharide component(s); and (e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

[0166] Optionally the microcapsule shell may also contain an added polymer. As such the polymeric microcapsule shell may further comprise added zein, other protein, a polypeptide, or other biodegradable polymer. The polymer may be added at any stage of the process as a powder, dispersion or can be solubilized in one of the phases or in one of the components of the phases. For example, zein or other polymer can be added as a pre-dissolved solution in the linker and or diluent or cargo.

[0167] It will also be understood that the capsules of the invention, and through any of the embodiments or variations, can be dried or made into coated or double layered capsules via that route. This can enhance storage stability further and/or performance further. The double layered, multilayered, or over coated microcapsule comprises, in one embodiment, a hydrogel or a crosslinked alginate. Microcapsules, prior to overcoating, of the present application have an average diameter of about 100 nm to 100 μ m though distributions can span outside of this range and capsules can be made larger if desired. More typically average particle size ranges from about 1 μ m to 100 μ m. By varying reaction conditions and relative concentrations, particle sizes can be varied. All examples below fall within these ranges.

[0168] A cationic polymer for example a cationic polysaccharide such as cationic guar is dissolved in the aqueous phase. A stabilizer such as polyvinyl alcohol may be present as well as other additives for example a defoamer if required. The aqueous phase is mixed with the oil phase (which contains the cargo and all reactants) and the mixture stirred and homogenized. The encapsulation reaction is then progressed, and at any point during this or after completion

of shell formation an anionic polymer, for example an anionic polysaccharide such as xanthan gum is then added. The orders of addition can be reversed for the anionic and cationic components. Furthermore, either of the components could be introduced at other points of the process whether at the start or during the encapsulation reaction or process or after the shell wall completion. Other cationic and anion polymer combinations can be used (to facilitate coacervate formation). Anionic polysaccharides (carboxymethylcellulose, xanthan gum, gum arabic, carrageenan, alginic acid/alginate, pectin), or cationic polysaccharides such as cationic -guars, or -gums or -dextran, or cationic surfactants are preferred. These coacervates, present as outer or secondary coatings can also be crosslinked for example by aldehydes such as glutaraldehyde or glyoxal. Such crosslinking may also encompass crosslinking of the poly β -amino esters if there are suitable reactive moieties available, which include amine or hydroxyl group among others.

[0169] Routes to applying outer coatings, for example polysaccharide or protein based coatings, to capsules made by linking or crosslinking saccharides as described may include applying a coacervate overlayer, spray drying, fluid bed drying and applying crosslinked sodium alginate. In such an approach one way of demonstrating that is to filter the microcapsules as made and disperse into a buffered solution of sodium alginate in water. That mixture can then be added slowly with stirring (via an addition funnel or syringe) into a stirred solution of calcium chloride, which crosslinks the alginate around the capsules, so forming an outer or secondary coating. Larger capsules than the original ('visible beads') were formed which were composed of the microcapsules of the invention surrounded or embedded in a crosslinked alginate coating or overlayer. Other crosslinked outer coatings can be similarly applied with acid functional polysaccharides and calcium or other di- or multi-valent chlorides or bases. Other crosslinking reactions and approaches as may be required. This includes hydrogels from polysaccharides for example.

[0170] Another route to applying an outer coating is via complexation or coacervate formation optionally followed by crosslinking. The saccharide based shell materials generally can in some circumstances form complexes or coacervates under certain conditions, which may involve pH adjustment for optimizations for example, with added anionic or cationic molecules or polymers. For example, where β -amino esters have been used there will be tertiary amine environments. Such moieties can form complexes or coacervates with added anionic polymers or molecules and may form the basis of an outer coating with or without crosslinking. *Similarly*, acid functional saccharides may be present or added and form complexes with added cationic polymers or proteins. In all such coated microcapsules the coatings may be formed *in-situ* as

slurries and may be spray dried to produce solid coated microcapsules which may then be used as is, or via redispersion into an aqueous slurry. When additional functional groups such as described are also present in the polymeric shell the complexation or coacervation may in some cases be enhanced. β -amino ester shell materials of the invention which bear tertiary amine or quaternary ammonium or charged or acidic or pH responsive moieties can also participate in coacervate formation (overcoating) and subsequent (dual) crosslinking, this aiding the formation of an outer coating. They may also be designed to be crosslinkable for example via the use of aldehydes or polyphenols for example.

[0171] In some examples of the invention a microcapsule with a lipophilic core and a biodegradable polymeric shell is demonstrated by: (a) making an oil-in-water emulsion of an oil phase which comprises linker or crosslinker reagents and a cargo, optionally with added diluent or solvent mixed together where necessary aided by application of heat, and optionally adding an initiator or catalyst after any heating has subsided, and a water phase containing a saccharide and an initiator or catalyst, optionally with a stabilizer or emulsifier, optionally with other additives, (b) optionally adding another catalyst or initiator to one phase (c) forming the polymeric capsule shell wall by an oil-in-water or interfacial polymerization reaction; and (d) obtaining the cargo encapsulated in a polymeric microcapsule shell.

[0172] The diluent will preferably be a water immiscible liquid at room temperature or readily meltable at moderate temperatures such as below 90°C or less than 50°C and may be a hydrocarbon oil, an alkane, a melted wax, an ester oil, a fatty acid ester, an aliphatic ester, or an alkylene carbonate. Some specific examples include mineral oil, long chain alkanes such as hexadecane and the like, aliphatic esters such as esters of long chain acids such as caprylates, myristates, oleates, cocoates, palmitates, or stearates including isopropyl myristate as one example, or long chain esters of shorter chain acids or other monohydric or polyhydric esters.

[0173] The initiator in oil phase is preferably an azo- or a peroxide based initiator for radical polymerization, and the initiator for the water phase is preferably a persulfate or redox couple or a peroxide or an azo-based initiator. Non-limiting examples include ammonium persulfate, ferrous persulfate, sodium persulfate or potassium persulfate, ceric ammonium nitrate, potassium peroxy sulphate/ascorbic acid, potassium peroxydiphosphate/thiourea, potassium peroxydiphosphate/silver nitrate, potassium peroxydiphosphate/glycolic, ferrous ammonium-hydrogen peroxide (Fenton's reagent), ferrous sulfate/potassium bromate, benzoyl peroxide, hydrogen peroxide any peroxide or hydroperoxide, azoisobutyronitrile and other azo compounds. An inert atmosphere such as nitrogen is optionally used for the reactions and may be preferred in some embodiments.

[0174] Further, certain aspects of the present application are illustrated in detail by way of the following examples. The examples are given herein for illustration of the application and are not intended to be limiting thereof. Figures 1-10 show optical microscopy images of examples of microcapsules made using various polymers and via various processes described. Figure 11 show sensory test results for fragrance release from microcapsules prepared via the various processes described. Table 3 shows biodegradation data of microcapsule shell materials prepared by various processes described.

[0175] *Thus*, in the range of process variants and/or compositional variations, embodiments, descriptions and examples of the microcapsules of the invention it will be understood that they are able to be used for many types of lipophilic cargoes and in many media or applications (formulated end products, including waterless or solid format products or solvent based products or formulations or in neutral or near neutral pH aqueous formulation media) and do perform in delivering some fragrances and/or other cargoes more readily encapsulated or retained and/or stored, while also showing biodegradability or non-persistence.

[0176] In another non-limiting embodiment, the present application provides a polymeric microcapsule shell biodegradable in an aquatic medium or solid medium or is compostable. The aquatic or solid medium is selected from group consisting of activated sludge, secondary effluent, river water, surface water, fresh water, sea water, soil, and compost.

[0177] In another non-limiting embodiment, the polymeric microcapsule shell material shows a biodegradation rate of at least 20% in an aquatic medium when measured by an OECD Test method 301, 302 or 306. The polymeric microcapsule shell material shows evidence of biodegradation within 120 days or within 60 days or within 40 days or within 28 days.

[0178] In another non-limiting embodiment, the microcapsule is storage stable as a core-shell capsule in an aqueous slurry, in a water-based formulation or in a solvent-based formulation. The microcapsule is storage stable as a core-shell capsule in a solid, largely waterless formulation or in a printed product.

[0179] In another non-limiting embodiment, the present application provides a microcapsule showing a retained triggered release of cargo or ‘a bloom’ after storing or aging in respective medium for at least 4 weeks at ambient temperature (15-25°C), or at least 6 weeks or at least 8 weeks or at least 12 weeks at ambient temperature.

[0180] In another non-limiting embodiment, the present application provides a microcapsule showing a retained triggered release of cargo or ‘a bloom’ after storing or accelerated aging in respective medium for at least 2 weeks, for at least 3 weeks, for at least 4 weeks, for at least 6 weeks, for at least 8 weeks, for at least 10 weeks or for at least 12 weeks at an elevated temperature

of 40°C. Accordingly, the microcapsule shows a retained triggered release of cargo or ‘a bloom’ after storing or aging in a liquid laundry detergent formulation of acidic pH for at least 4 weeks at ambient temperature or 40°C, or for at least 6 weeks or for at least 8 weeks or for at least 12 weeks at ambient temperature or 40°C.

[0181] In another non-limiting embodiment, the present application provides a double layered microcapsule, a multi-layered microcapsule or an overcoated microcapsule. Accordingly, the double layered, multilayered or an overcoated microcapsule comprises within its outer coating a polysaccharide, a protein, a hydrogel, a coacervate or is a biodegradable polymer or formulations of polymers comprising one or more such polymers. Accordingly, the double layered, multilayered or an overcoated microcapsule comprises within its outer coating a xanthan gum, a polysaccharide gum, an alginate polymer, a cellulose ether including hydroxyethyl cellulose or carboxymethyl cellulose, a guar or modified guar including cationic guar, zein protein, soy protein, any other protein, a hydrogel, a coacervate or a biodegradable polymer.

[0182] In another non-limiting embodiment, the present application provides inventive microcapsule having an average diameter of about 100 nm to 150 µm or about 1 µm to 100 µm.

[0183] The following examples illustrate the present disclosure, parts and percentages being by weight, unless otherwise indicated. Each example is provided by way of explanation of the present disclosure, not limitation of the present disclosure. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present disclosure without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment, can be used on another non-limiting embodiment to yield a still further embodiment. Thus, it is intended that the present disclosure covers such modifications and variations as come within the scope of the appended claims and their equivalents.

[0184] EXAMPLES

[0185] In examples below the weight ratios of the principal reactants (saccharide and linker) are designed to be at 70 *wt. %* saccharide and 30 *wt. %* linker. Reactions with other ratios were also undertaken as described further below. In addition, it is to be noted that in these reactions, for some saccharides, the initial aqueous phase reaction between saccharide and persulfate (or similar initiators) may lead to depolymerized or oxidized components of the saccharide being formed prior to, or during, the subsequent shell formation reaction involving linker molecules.

[0186] In some embodiments this is a deliberate intention. Figures 1-7 show optical micrograph images of microcapsules prepared according to some of the examples below.

[0187] **Example 1:** Preparation of acrylate crosslinked polysaccharide microcapsules. This example illustrates the preparation of microcapsules having a polymer shell comprising Potato Starch and/or its components, linked with ester groups and prepared from Pentaerythritol tetraacrylate (PETA) and Potato starch, radically reacted for the encapsulation of home care fragrance Sunburst fresh R14-3913. Capsules Ref: 226-83-1.

[0188] An oil phase was prepared by dissolving 1.84g of PETA in 25.50g of Fragrance Sunburst fresh and 5.10g of Propylene glycol dicaprylate/caprate under mechanical stirring. 0.13g of 2,2'-Azodi(2-methylbutyronitrile) was then added as an oil phase radical initiator.

[0189] An aqueous phase was prepared by mixing 4.28g of potato starch to 90.83g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C. An aqueous initiator solution was prepared by dissolving 0.09g of sodium persulphate in 10g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24g of 10% aqueous solution of polyvinyl alcohol was added.

[0190] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for 1 hour. The temperature was then further increased to 80°C and left to react for 2 hours.

[0191] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 1 Optical Micrograph Images of Microcapsules; capsule reference: 226-83-1).

[0192] **Example 2:** Preparation of Poly-β-amino ester (PBAE) crosslinked polysaccharide microcapsules. This example illustrates the preparation of microcapsules having a polymer shell comprising a PBAE (made via reaction of Pentaerythritol tetraacrylate (PETA) and 4,4'-Trimethylenedipiperidine (TMPP) with a 2:1 (acrylate : amine) *molar ratio*, so having residual or excess acrylate functionality), with potato starch, radically reacted with the PBAE, for the encapsulation of home care fragrance Sunburst fresh R14-3913. Capsules Ref: 226-90-1

[0193] An oil phase containing a PBAE with excess acrylate functionality was prepared by dissolving 1.41g of PETA and 0.42 g of TMPP in 25.50 g of 2-propanol and 5.10 g of Propylene

glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 75°C then left to react for a further 2 hours to form an oligomeric PBAE (with acrylate functionality on the PBAE). The oil phase was then cooled to 30°C and the 2-propanol removed via evaporation under mechanical stirring. 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) dissolved in 25.50 g of Fragrance Sunburst fresh was then added as an oil phase radical initiator.

[0194] An aqueous phase was prepared by mixing 4.28 g of potato starch to 90.83 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C. An aqueous initiator solution was prepared by dissolving 0.09 g of sodium persulphate in 10 g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of polyvinyl alcohol was added.

[0195] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for 1 hour. The temperature was then further increased to 80°C and left to react for 2 hours.

[0196] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (*see Figure 2, Optical Micrograph Images of Microcapsules; capsule reference: 226-90-1*).

[0197] Example 3: Preparation of Poly- β - amino ester (PBAE) crosslinked polysaccharide microcapsules with secondary crosslinking with Tannic acid. This example illustrates the preparation of microcapsules having a polymer shell comprising a PBAE (made via reaction of Pentaerythritol tetraacrylate (PETA) and 4,4'-Trimethylenedipiperidine (TMPP) with a 2:1 molar ratio (acrylate: amine), so having residual or excess acrylate functionality on the PBAE), with Potato starch, radically reacted with the acrylate functional-PBAE, for the encapsulation of home care fragrance Sunburst fresh R14-3913. A secondary crosslinking step then carried out with Tannic acid. Capsules Ref: 226-90-2.

[0198] The process described in Example 2 was used with the addition of a secondary crosslinking step after microcapsule formation. 2.14g of a 10% solution of tannic acid was added to the microencapsulation slurry under mechanical stirring. The slurry was then heated to 50°C and left to react for 4 hours.

[0199] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 3, Optical Micrograph Images of Microcapsules; capsule reference: 226-90-2).

[0200] **Example 4:** Preparation of poly- β -amino ester-co- β -thio-ester (P β ATE) crosslinked polysaccharide microcapsules. Microcapsules having a polymer shell comprising a P β ATE copolymer (made via reaction of pentaerythritol tetraacrylate (PETA), pentaerythritol hexakis (3-mercaptopropionate) (PHKMP), and 4,4'-trimethylenedipiperidine (TMPP) in the ratio of 5.6 : 0.9 : 0.1 *mol eq.* (acrylate: thiol: amine) so having residual or excess acrylate functionality on the P β ATE), with Potato Starch radically reacted with the P β ATE copolymer for the encapsulation of home care fragrance Sunburst fresh R14-3913. Capsule Ref: 226-91-1.

[0201] An oil phase containing a P β ATE with excess acrylate functionality was prepared by dissolving 1.46 g of PETA, 0.35 g of PHKMP and 0.03 g of TMPP in 25.50 g of Fragrance Sunburst fresh and 5.10 g of Propylene glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 30°C then left to react for a further 24 hours to form an oligomeric P β ATE (with acrylate functionality). 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) was then added as an oil phase radical initiator.

[0202] An aqueous phase was prepared by mixing 4.28 g of potato starch to 90.86 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C. An aqueous initiator solution was prepared by dissolving 0.09 g of Sodium persulphate in 10 g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of polyvinyl alcohol was added.

[0203] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for 1 hour. The temperature was then further increased to 80°C and left to react for 2 hours.

[0204] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 4, Optical Micrograph Images of Microcapsules; capsule reference: 226-91-1).

[0205] Example 5: Preparation of Poly- β - amino ester (P β AE) crosslinked hydrophobically modified polysaccharide microcapsules. This example illustrates the preparation of microcapsules having a polymer shell comprising a P β AE (made via reaction of Pentaerythritol tetraacrylate (PETA) and 4,4'-Trimethylenedipiperidine (TMPP), in a *mol eq* ratio of 2:1 (acrylate : amine) so having residual or excess acrylate functionality on the P β AE), with octenyl succinic anhydride modified starch (OSA starch), radically reacted with the acrylate functional P β AE, for the encapsulation of home care fragrance Sunburst fresh R14-3913. Capsules Ref: 230-11-1.

[0206] An oil phase containing a P β AE with excess acrylate functionality was prepared by dissolving 1.41 g of PETA and 0.42 g of TMPP in 25.50 g of Fragrance Sunburst fresh and 5.10 g of Propylene glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 30°C then left to react for a further 24 hours to form an oligomeric P β AE (with acrylate functionality). 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) as an oil phase radical initiator.

[0207] An aqueous phase was prepared by mixing 4.28 g of OSA starch to 90.83 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C. An aqueous initiator solution was prepared by dissolving 0.09 g of Sodium persulphate in 10g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of polyvinyl alcohol was added.

[0208] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for 1 hour. The temperature was then further increased to 80°C and left to react for 2 hours.

[0209] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 5, Optical Micrograph Images of Microcapsules; capsule reference: 230-11-1).

[0210] Example 6: Preparation of poly- β -thio-ester (P β TE) crosslinked hydrophobically modified polysaccharide microcapsules. Microcapsules having a polymer shell comprising a P β TE (made via reaction of pentaerythritol tetraacrylate (PETA) and pentaerythritol hexakis (3-mercaptopropionate) (PHKMP), with a *molar ratio* of 6:1 acrylate : thiol) so having residual or excess acrylate functionality on the P β TE), with octenyl succinic modified starch

(OSA starch), radically reacted with the acrylate functional P β TE for the encapsulation of home care fragrance Sunburst fresh R14-3913. Capsule Ref: 230-12-1.

[0211] An oil phase containing a P β TE with excess acrylate functionality was prepared by dissolving 1.46 g of PETA and 0.50 g of PHKMP in 25.50 g of Fragrance Sunburst fresh and 5.10 g of Propylene glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 30°C then left to react for a further 24 hours to form an oligomeric P β TE (with acrylate functionality). 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) was then added as an oil phase radical initiator.

[0212] An aqueous phase was prepared by mixing 4.28 g of OSA starch to 90.86 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C. An aqueous initiator solution was prepared by dissolving 0.09 g of Sodium persulphate in 10 g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of polyvinyl alcohol was added.

[0213] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for 1 hour. The temperature was then further increased to 80°C and left to react for 2 hours.

[0214] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 6, Optical Micrograph Images of Microcapsules; capsule reference: 230-12-1).

[0215] Example 7: Preparation of poly- β -amino ester-co- β -thio-ester (P β ATE) crosslinked hydrophobically modified polysaccharide microcapsules. Microcapsules having a polymer shell comprising a P β ATE copolymer (made via reaction of pentaerythritol tetraacrylate (PETA), pentaerythritol hexakis (3-mercaptopropionate) (PHKMP), 4,4'-trimethylene dipiperidine (TMPP), in a *mol eq ratio* of 5.6:0.9:0.1 (acrylate : thiol : amine) so having residual or excess acrylate functionality on the P β ATE) with octenyl succinic anhydride modified starch (OSA starch), where the OSA starch is radically reacted with the acrylate functional P β ATE copolymer for the encapsulation of home care fragrance Sunburst fresh R14-3913. Capsule Ref: 230-13-1.

[0216] An oil phase containing a P β AE with excess acrylate functionality was prepared by dissolving 1.46 g of PETA, 0.35 g of PHKMP and 0.03 g of TMPP in 25.50 g of Fragrance Sunburst fresh and 5.10 g of Propylene glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 30°C then left to react for a further 24 hours to form an oligomeric P β AE (with acrylate functionality). 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) was then added as an oil phase radical initiator.

[0217] An aqueous phase was prepared by mixing 4.28 g of OSA starch to 90.86 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C. An aqueous initiator solution was prepared by dissolving 0.09 g of Sodium persulphate in 10g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of polyvinyl alcohol was added.

[0218] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for 1 hour. The temperature was then further increased to 80°C and left to react for 2 hours.

[0219] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 7, Optical Micrograph Images of Microcapsules; capsule reference: 230-13-1).

[0220] Example 8: Preparation of Poly- β - amino ester (P β AE) copolymer (poly- β -amino ester-co- β -thio-ester) capsules with a modified corn starch polysaccharide Capsule Ref : 230-20-1.

[0221] Microcapsules having a polymer shell comprising a P β AE copolymer, containing β -amino-ester and β -thio-ester groups, were made via reaction of 4.3 mol.eq pentaerythritol tetraacrylate (PETA), 1 mol.eq pentaerythritol tetrakis (3-mercaptopropionate) (PTKMP), 0.2 mol.eq 4,4'-trimethylenedipiperidine (TMPP) and 0.005 mol.eq octenyl succinic anhydride modified waxy corn starch (OSA waxy starch) radically reacted with the P β AE copolymer, for the encapsulation and encapsulation of home care fragrance Sunburst fresh R14-3913.

[0222] An oil phase was prepared by dissolving 1.35 g of pentaerythritol tetraacrylate (PETA), 0.44 g of pentaerythritol tetrakis (3-mercaptopropionate)(PTKMP) and 0.04 g of 4,4'-trimethylenedipiperidine (TMPP) in 25.50 g of Fragrance Sunburst fresh and 5.10 g of

propylene glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 30°C then left to react for 24 hours. 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) was added.

[0223] An aqueous phase was prepared by mixing 4.28 g of octenyl succinic anhydride modified waxy corn starch to 90.87 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C.

[0224] An aqueous phase initiator solution was prepared by dissolving 0.09 g of sodium persulphate in 10 g of deionized water. The initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of Polyvinyl alcohol was added. The oil phase was added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm.

[0225] The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The temperature was then increased to 60°C and left to react for a further 1 hour. The temperature was then increased to 80°C and left to react for a further 2 hours. The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the capsules.

[0226] The resulting microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope. Fragrance release from within the microcapsules was strongly evident upon crushing (applying pressure) to the microscope slide (see Figure 8, Optical Micrograph Images of Microcapsules; capsule reference: 230-20-1).

[0227] Examples 9-27

[0228] Using process conditions, recipe guidelines and ratios and weights, replicated from Example 1 further microcapsules were also able to be formed with the following saccharides, including polysaccharides, where the saccharide directly replaces potato starch (weight for weight bases on saccharide, so maintaining a ratio of 70 wt. % saccharide and 30 wt. % functional linker, which is the PETA tetra acrylate):

Table 1: Microcapsules prepared following method of Example 1 (using PETA (tetraacrylate) as linker).

Capsule reference	Polysaccharide
226-84-1	Waxy corn starch
230-28-1	Guar Gum

230-28-2	Maltodextrin
230-28-3	Blanose CMC (carboxymethyl cellulose)
230-28-5	Trehalose
230-28-6	Lactose
230-28-7	Maltose
230-28-8	K-Carrageenan
230-28-9	Pectin
230-28-10	Gum Acacia
230-28-13	Xanthan Gum
230-28-14	Cassia Gum
230-28-15	Aqualon EC-N7 (ethyl cellulose)
230-28-16	Benecel K4M (hydroxypropyl methylcellulose)
30-42-1	Chitosan
230-43-1	Sucrose
230-44-1	Fructose

[0229] The saccharides above encompass examples of mono- and di-saccharides as well as polysaccharides, some of which will be depolymerized in the process. Most are unmodified and where they are modified (readily available derivatives) the examples are of hydrophilic modified (CMC) saccharide, and other modified saccharides which are not specifically modified with a hydrophobe having an alkenyl C=C double bond or long carbon chain.

[0230] In addition, examples of capsules containing fragrance cargo were made with Hydroxy ethyl cellulose (HEC; Natrosol 250L). These examples were :

[0231] Capsule Ref 230-03-1, with a *wt. %* ratio of 70:30 HEC: linker, and with the linker based on poly- β -thio-ester (P β TE) prepared as described in Example 6 and following the general procedure of Example 6 above, using a P β TE made via reaction of pentaerythritol tetraacrylate (PETA) and pentaerythritol hexakis (3-mercaptopropionate) (PHKMP), with a *molar ratio* of 6:1 acrylate : thiol, so having residual or excess acrylate functionality on the P β TE), and encapsulating the fragrance Sunburst fresh R14-3913.

[0232] Capsule Ref 230-04-1 70:30 HEC (Natrosol 250L), with a *wt. %* ratio of 70:30 HEC: linker, and with the linker based on a poly- β -amino ester - β -thio-ester (P β ATE) prepared as described in Example 7 such P β ATE being made via reaction of pentaerythritol tetraacrylate (PETA), pentaerythritol hexakis (3-mercaptopropionate) (PHKMP), 4,4'-trimethylene dipiperidine (TMPP), in a *mol eq ratio* of 5.6:0.9:0.1 (acrylate:thiol: amine) so having residual

or excess acrylate functionality on the P β ATE and encapsulating the fragrance Sunburst fresh R14-3913.

[0233] Examples 28-33

[0234] Further Examples with different Weight Ratios

[0235] In addition, other examples were prepared at different weight ratios of unmodified saccharide: linker (PETA tetraacrylate) such as 80 wt.% saccharide : 20 wt.% and others. All formed capsules. Examples are listed below.

Table 2 : Microcapsules at various Weight % Ratios

Capsule reference	Weight ratio	Potato Starch (g)	Sodium Persulphate (g)	PETA (g)	2,2'-Azodi(2-methylbutyronitrile) (g)
226-83-1	70:30	4.28	0.09	1.84	0.13
230-05-1	80:20	4.90	0.10	1.22	0.09

Table 3 : Microcapsules at various Weight % Ratios

Capsule reference	Weight ratio	Pectin (g)	Sodium Persulphate (g)	PETA (g)	2,2'-Azodi(2-methylbutyronitrile) (g)
230-28-9	70:30	4.28	0.09	1.84	0.13
230-40-1	80:20	4.90	0.10	1.22	0.09
230-41-1	90:10	5.51	0.11	0.61	0.04

[0236] Examples of Coated /Multilayered Capsules

[0237] The microcapsules made by reactions such as above wherein saccharide or polysaccharide is linked or crosslinked via ester or β -amino or β -thio-ester links can be overcoated or further (additional) crosslinked via application of an overcoating (which may or may not involve reactions) and/or by simple additional crosslinking. Examples illustrating such concepts are described below.

[0238] Example 34: Capsules made from a saccharide with β - amino ester (P β AE) links and additional coating and/or crosslinking with tannic acid. Capsule Ref : 226-24-3

[0239] An oil phase was prepared by dissolving 1.41g of pentaerythritol tetraacrylate (PETA) and 0.42 g of 4,4'-trimethylenedipiperidine (TMPP) in 25.50 g of 2-Propanol and 5.10g of propylene glycol dicaprylate/caprate under mechanical stirring. The oil phase was heated to 80°C and left to react for 2 hours. The oil phase was cooled to 30°C and the solvent or majority of solvent, was removed by evaporation from an open reactor under fume hood extraction for 24 hours.

[0240] An oil phase initiator was prepared by dissolving 0.13 g of 2,2'-Azodi(2-methylbutyronitrile) in 25.50 g of Fragrance Sunburst fresh. The oil phase initiator was added to the oil phase.

[0241] An aqueous phase was prepared by mixing 4.28 g of octenyl succinic anhydride modified waxy corn starch to 90.83 g of deionized water under mechanical stirring. Once fully homogeneous the aqueous phase was heated to 80°C.

[0242] An aqueous phase initiator solution was prepared by dissolving 0.09 g of Sodium persulphate in 10 g of deionized water. This initiator solution was added to the aqueous phase and left to react for 5 minutes. The aqueous phase was cooled to 40°C. 12.24 g of 10% aqueous solution of polyvinyl alcohol was added.

[0243] The oil phase was then added to the aqueous phase under mechanical stirring to form a coarse emulsion. The coarse emulsion was homogenized using an IKA magic lab homogenizer, 1 pass at 4000 rpm. The formed emulsion was transferred to a reactor pot and the emulsion was heated to 40°C. The oil-in-water emulsion was then left to react for 1 hour. The reaction temperature was then increased to 60°C and left to react for a further 1 hour. The reaction temperature was then increased to 80°C and left to react for a further 2 hours. Microcapsules containing fragrance inside were formed (within a slurry).

[0244] Additional Post-Encapsulation Process/Layer: A solution was prepared by dissolving 0.21g of Tannic acid in 10g of deionized water. The reaction mixture (slurry) above containing the fragrance microcapsules was cooled, or allowed to cool, to 50°C after the 80°C reaction stage. The tannic acid solution was added to the microcapsule slurry and left to react for 4 hours. The resulting modified microcapsule slurry was an aqueous slurry of microcapsules which were visible under a light microscope, and which clearly released fragrance upon crushing (see Figure 9, Optical Micrograph Images of Microcapsules; capsule reference: 226-24-3).

[0245] Example 35: Spray dried overcoating of an initial microcapsule made from a polysaccharide linked with poly-β-amino ester-co-β-thio-ester (PβATE) links - such microcapsules overcoated with a protein. This example illustrates the use of Soy Protein to overcoat via spray drying. Capsules ref: 229-74-1.

[0246] 3 g of Soy Protein Isolate was added to 175.8 g of de-ionized water and the pH was adjusted to 10. Then the solution was mixed at 50°C for 1hr and cooled to room temperature.

[0247] 25 g of poly- β-amino ester-co-β-thio-ester (PβATE) crosslinked polysaccharide microcapsules (sample reference: 226-91-1 – Example 4 above) was added to the Soy Protein Isolate solution.

[0248] The mixture was homogenized using IKA Ultraturrax for 1min at 3000 rpm.

[0249] 1.25 g of Sipernat 50S (hydrophobically modified silica) was added to the slurry and left to mix for 30 mins. The slurry was spray dried using the Lab Plant SD-06 Spray dryer at 180°C. Figure 10 shows optical micrographs of these dried capsules redispersed into water before and after crushing (229-74-1).

[0250] In all cases described in the various examples above and their variants, microcapsules were formed and clearly released fragrance upon crushing under a microscope slide. Images of examples of examples of microcapsules are shown further below.

[0251] **Examples 36-38:** β -amino-ester linked or crosslinked saccharide, overcoated with soy protein (by spray drying)

[0252] Following the same procedures as described in Examples 35, and Examples 2 and 4, additional examples of β -amino-ester-saccharide capsules, made using three different amines, as in the process of Example 2, were then overcoated with soy protein (as described in Example 35 where microcapsules from Example 4 were used) to make overcoated or multilayered β -amino-ester linked (or crosslinked) potato starch polysaccharide microcapsules. In these examples the initial microcapsules were each spray dried according to the same procedure as described in Example 35. However, in these three cases the spray drying was planned or pre-determined to occur to begin within 1 hour of the completion of the process for making the initial (β -amino-ester linked or crosslinked saccharide) microcapsules. Excellent capsules were formed after spray drying-coating showing release of fragrance upon crushing. The Table below shows the details of three examples of β -amino-ester-saccharide capsules that were prepared and then promptly overcoated with soy protein by spray drying within an hour of completing the process for the initial microcapsules. Such capsules will have enhanced stability attributes while still being biodegradable.

Table 4 : β -amino-ester linked or crosslinked saccharide, overcoated with soy protein (by spray drying)

Initial β -amino-ester-saccharide Capsule reference	Amine used in β -amino-ester linker for the initial microcapsules	Amine Weight (g)	PETA Weight (g) (used in stoichiometric excess)	Spray dried capsules reference (with soy protein)
233-10-1	4,4'-Trimethylenedipiperidine	0.42	1.41	229-76-1
233-11-1	Pentaethylenhexamine	0.14	1.70	229-75-1
233-12-2	Isophorone diamine	0.2	1.64	229-77-1

[0253] Details of test methods and example results are given below for a selection of the examples:

[0254] BIODEGRADATION TESTING:

[0255] This was carried usually out according to OECD methods. For example, methods such as OECD 301D, 301F, 302B, 306, were variously used, some over extended timelines. Samples that are insoluble in aqueous media often require development for a suitable dispersion or form for the test. In some cases, the EN 14852:2018 or EN ISO 14851:2004 test can be used, which runs for period of 6 months in aquatic media (and is also cited, along with others such as those above, in ECHA draft protocols for avoidance of microplastics concerns). Inocula and suitable water (secondary effluent surface water, seawater or activated sludge) were used as supplied from a local sources such as a wastewater treatment plant. A mineral medium specified by the OECD 301D method, and the inoculum were added to deionized water which was subsequently aerated for 20 minutes prior to addition of the sample polymer sample at a concentration of 4-10 mg/ml depending on predicted biodegradability.

[0256] In some examples, biodegradation was monitored from measurements of dissolved oxygen content. In some examples this test is done in fresh water using inoculum supplied by a local water treatment plant. This test is used to mimic the environment these polymers will be in after going through a freshwater waste treatment plant. This test uses a readily biodegradable sodium benzoate reference as a positive control. All samples are run in duplicate. Measurements were taken approximately at 7 day intervals to at least 28 days and in many cases beyond. Example data is given in the table below.

[0257] Biodegradability measurements of Example capsule shells (301F Activated Sludge)

[0258] There is a balance for some applications where a low, but perceptibly ongoing, biodegradation rate can be accepted, and where, combined with for example a higher fragrance or other lipophilic cargo compatibility and/or higher water resistance, can still make a desirable end product which will be non-persistent.

[0259] Examples Samples for Biodegradation Testing

[0001] Equivalent compositions (analogous shell materials) of the microcapsules described above could also be made, without fragrance, using dichloromethane or ethyl acetate ('solvent') as another lipophilic cargo, which was, for the purposes of testing, then subsequently evaporated to leave polymeric shell material only, for use in biodegradation testing.

[0260] Encapsulated solvent (subsequently removed by evaporation) for biodegradation testing of polymeric shell material, The same procedures for the capsule formation were used

but dichloromethane or ethyl acetate solvent was used in place of fragrance. Following completion of the shell formation (formed around the solvent cargo) the mixture was transferred to a beaker with a magnetic stirred bar and allowed to stir in a fume hood for a minimum of 72 hours to allow evaporation of the solvent. No solvent was detected via GC following this - samples were checked to ensure no residual solvent. This dispersion was assessed for biodegradability via 301F, using an activated sludge inoculum.

[0261] Representative samples prepared with solvent based cargo subsequently evaporated were similar to (equivalent shell prepared with fragrance, described above, which showed a fragrance release/bloom after formulation into a representative fabric conditioner system), showed biodegradation after 28, 30, 40 days or 60 days in the OECD 301F test using activated sludge sourced from a local water treatment plant (Yorkshire Water) and showed ongoing biodegradation thereafter.

[0262] Examples of biodegradation test data are given in the Table below :

Table 5 : Biodegradation Test Data on Example Capsules (ethyl acetate cargo removed)

Sample Reference (Biodegradability sample process)	Sample Description	Biodegradability (%) (OECD 301F)				Sample Reference of analogous capsule with fragrance cargo
		14 days	21 days	30 days	60 days	
230-02-1	70:30 Potato Starch - PETetA	40	59	63	75	226-83-1
230-03-1	70:30 HEC-6:1 PETetA/PTHKMP	2	13	17	31	226-67-1
230-04-1	70:30 HEC-5.6: 0.9:0.1 PETetA/PTHKMP/TMPP	1	9	12	27	226-68-1

[0263] SENSORY AND FRAGRANCE RELEASE TESTING

[0264] Test procedures for samples for fragrance bloom testing (fabric conditioner base):

[0265] Capsule slurries were tested in blind sensory evaluations (fragrance bloom tests) with a collection of people (minimum 2, typically 3-5). Note: Microcapsules produced typically contained ~15-30 *wt. %* fragrance encapsulated in the slurry - most used in the data reported were ~15-17 *wt. %*.

[0266] Typical pre-screening sensory test ('Fragrance Bloom')

[0267] A test mixture of the slurry is prepared using 18g of a fabric conditioner/softener formulation and an amount of slurry such that the fragrance loading in the test mixture is 0.1g

fragrance (based on the fragrance amount encapsulated in a slurry) and water added to make 20g of test mixture.

[0268] In parallel a fabric wash mixture was prepared using each test mixture, each in a 2-litre beaker using an overhead stirrer at 250 rpm. This comprised 2g of each test mixture above and 998 g of water (tap). Small squares (approx. 75mm x 75mm; number is according to the number of people testing the samples of that slurry) of towel material were added to the beaker and stirred for 5 minutes after which they were removed and hung to dry in the air overnight, for 16 hours.

[0269] The next day another person or people (who did not make up the samples) smelt (sniffed) an untreated towel and then sniffed a sample of pure fragrance and marked each in terms of an intensity number for these reference points, between 1 to 9 (9 = highest fragrance intensity - as in neat fragrance typically). Randomly, samples prepared on towels as described were selected and sniffed and an intensity number recorded. Then the towel material is rubbed together for 5 seconds and sniffed again. The intensity after rubbing (post rub) was also recorded. This was repeated at random until all samples are tested as such by each panel member.

[0270] An average intensity is calculated for a before (pre-rub) and after (post rub) the rubbing for each sample. Example data are shown further below.

[0271] Where there is significant difference between a pre-rub and post-rub assessment (Δ) such potential is indicated. For example, a Δ of 2 or more is a particularly good indicator of some such potential in some applications though a higher Δ is better. In parallel though stability aging (see later) is indicative of longevity of performance and storage stability. For some applications this is more readily achieved though for laundry applications such as fabric conditioners, this is often more challenging due to the relative aggressiveness of such formulations.

[0002] **Fragrance Bloom data from Sensory Tests:** Pre-screening fragrance bloom tests in fabric conditioner formulation - pre- and post- rubbing of treated fabrics. Higher more intensity of fragrance.

[0272] **Figure 11** shows examples of fragrance bloom test screening results.

[0273] While the compositions and methods of the disclosed and/or claimed inventive concept(s) have been described in terms of particular aspects, it will be apparent to those of ordinary skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the disclosed and/or claimed inventive concept(s). All such

similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the disclosed and/or claimed inventive concept(s).

What is claimed is:

1. A microcapsule comprising:
 - (i) a biodegradable polymeric microcapsule shell; and
 - (ii) a lipophilic core;

wherein, the polymeric microcapsule shell comprises saccharide units linked or crosslinked with one or more multi-functional linking groups selected from the group consisting of: (a) an ester, a β -amino-ester, or a β -thio-ester alone or combinations thereof, (b) a copolymer comprising two moieties selected from an ester, a β -amino-ester, and a β -thio-ester, or (c) a terpolymer of an ester, a β -amino-ester, and a β -thio-ester.

2. The microcapsule according to claim 1, wherein the polymeric microcapsule shell is formed by a reaction between (a) the saccharides units and (b) one or more multi-functional alkenyl linking group selected from the group consisting of an ester having alkenyl functionality, a β -amino-ester having alkenyl functionality and a β -thio-ester having alkenyl functionality.

3. The microcapsules according to claim 1, wherein the polymeric microcapsule shell is formed by a reaction between (a) the saccharide units and (b) an β -amino-ester and/or a β -thio-ester linking group having alkenyl multifunctionality.

4. The microcapsule according to claims 2 and 3, wherein the reaction is a free radical reaction, a conjugate addition reaction, or a Michael addition reaction.

5. The microcapsule according to claim 2 (b) and 3, wherein the alkenyl functionality of the ester, β -amino-ester or β -thio-ester is selected from the group consisting of an acrylate, a methacrylate, a maleate, a fumarate, an itaconate, , a crotonate, a citraconate, a maleimide, an acrylamide, a methacrylamide and combinations thereof.

6. The microcapsule according to claim 1, wherein the saccharide is a mono-saccharide, a di-saccharide, or a poly-saccharide.

7. The microcapsule according to claim 1, wherein the saccharide is not modified with an alkenyl, a hydrophobic or an amine group.

8. The microcapsule according to claim 3, wherein the saccharide is either modified with hydrophobic or alkenyl or amine or is unmodified.

9. The microcapsule according to claim 1, wherein the saccharide is selected from the group consisting of (i) unmodified starch, potato starch, corn starch, wheat starch, pea starch, guar gum, cassia gum, lactose, maltose, sucrose, fructose, trehalose, or oligomers thereof, or

(ii) a degraded or depolymerized cellulose, cellulose ether, starch, guar or saccharide gum; or

(iii) combinations of (i) and (ii).

10. The microcapsule according to claim 3, wherein the multifunctional alkenyl β -amino-ester or β -thio-ester linking units are formed from a Michael or conjugate Addition reaction of at least one amine or thiol donor and at least one acceptor containing conjugated alkenyl groups, wherein at least one acceptor component has a reactive alkenyl functionality of at least two.

11. The microcapsule according to claim 3, wherein the wherein the multifunctional alkenyl β -amino-ester or β -thio-ester linking units are formed from a Michael or conjugate Addition reaction of at least one amine or thiol donor and at least one conjugated multifunctional alkenyl functional acceptor, and wherein the resulting β -amino-ester or β -thio-ester linkers display an average overall alkenyl functionality of at least two.

12. The microcapsule according to claims 10 and 11, wherein one or more of the amine or thiol donors is difunctional or multifunctional with respect to primary or secondary amine or to thiol, or any combinations thereof.

13. The microcapsule according to claim 10 and 11, wherein one or more of the amine or thiol donor components has C2-C20 aliphatic chain functionality, a C4-C7 cyclic ring functionality or a C4-C7 heterocyclic ring functionality.

14. The microcapsule according to claims 10 and 11, wherein the acceptor is selected from the group consisting of:

- (a) an itaconate containing polyester,
- (b) an acrylate, diacrylate, or multifunctional acrylate of a polyester;
- (c) an acrylate, diacrylate, or multifunctional acrylate of an epoxide;
- (d) an acrylate, diacrylate, or multifunctional acrylate of a urethane;
- (e) an acrylate, diacrylate, or multifunctional acrylate of a polyether or a diol or a polyol;

(f) an acrylate, diacrylate, or multifunctional acrylate of an amine;

(g) methacrylate analogue of (b) to (f) components, and combinations thereof.

15. The microcapsule according to claim 14, wherein the acceptor is selected from the group consisting of butanediol diacrylate, trimethylol propane triacrylate, pentaerythritol triacrylate, pentaerythritol tetra-acrylate, dipentaerythritol penta-acrylate, dipentaerythritol hexa-acrylate and methacrylate analogues thereof.

16. The microcapsule according to claim 2, wherein the total saccharide units and linking units having alkenyl multifunctionality, on a weight ('solids') in the reactant feed, are present in a ratio, wherein the total saccharide loading is greater than the total linking unit weight loading.

17. The microcapsule according to claim 16, wherein the ratio of total saccharide to total linking units having alkenyl functionality in the reactant feed, on a weight ('solids') % basis is 51:49, 60:40, 65:35, 70:30, 75:25, 80:20, or 90:10 (saccharide:linker).

18. The microcapsule according to claim 1, wherein the microcapsule further comprises an added biodegradable polymer.

19. The microcapsule according to claim 1, wherein the lipophilic core is selected from the group comprising agrochemicals, aliphatic esters, anti-microbial agents, anti-fungal, anti-fouling agents, anti-perspirant, antioxidants, anti-viral agents, biocides, catalysts, cosmetic actives, colorants, dyes, detergents, edible oils, emollient oils, essential oils, fats, fatty acids, fatty acid esters, food additives, flavors, fragrances, hair care actives, halogenated compounds, hydrocarbons, insecticides, insect repellants, lipids, lipophilic scale inhibitors, mineral oil, oral care actives, organic solvents, organic esters, chlorinated solvents, pesticides, perfumes, preservatives, skin care actives, UV absorbers, vegetable oils and combinations thereof.

20. The microcapsule according to claim 19, wherein the lipophilic core is a fragrance, a perfume, or an essential oil.

21. The microcapsule according to claim 1, wherein the polymeric microcapsule shell is biodegradable in an aquatic medium, or in solid medium or is compostable.

22. The microcapsule according to claim 21, wherein the aquatic or solid medium is selected from group consisting of activated sludge, secondary effluent, river water, surface water, fresh water, sea water, soil, and compost.

23. The microcapsule according to claim 22, wherein the polymeric microcapsule shell material shows evidence of biodegradation within 120 days or within 60 days or within 40 days or within 30 or 28 days.

24. The microcapsule according to claims 22 or 23, wherein the polymeric microcapsule shell material shows a biodegradation rate of at least 20% in an aquatic medium when measured by an OECD Test method 301, 302 or 306.

25. The microcapsule according to claim 24, wherein the polymeric microcapsule shell material shows a biodegradation rate of at least 20% in an aquatic medium when measured by an OECD Test method 301, 302 or 306.

26. The microcapsule according to claim 1, wherein the microcapsule is used in a consumer care composition selected from the group consisting of laundry care composition, fabric care composition, oral care composition, hair care composition, skin care composition, cosmetic care composition, home care composition and cleaning composition.

27. The microcapsule according to claim 26, wherein the microcapsule is used in a fabric conditioner composition or a laundry detergent composition.

28. The microcapsule according to claim 26, wherein the microcapsule is used in a formulated product wherein the formulation is selected from the group consisting of laundry detergent, fabric softener, fabric conditioner, shampoo, hair conditioner, liquid soap, solid soap, skin deodorant, skin moisturizer, skin conditioner, hair or skin protectant, cleanser, sanitizer, cleaning fluid, dishwashing fluid, dishwashing tablet, washing powder, washing tablet, washing liquid, and cosmetic formulation.

29. The microcapsule according to claim 1, wherein the microcapsule is additionally subsequently processed or overcoated and/or further crosslinked, to create a double layered microcapsule, a multi-layered microcapsule, an overcoated microcapsule or a dually crosslinked microcapsule, with the microcapsule described in claim 1 as the inner layer or initial particle or capsule before the subsequent processing.

30. The microcapsule according to claim 29, wherein the double layered, multilayered or an overcoated microcapsule comprises within its outer coating: a polysaccharide, a protein, a hydrogel, a coacervate, a polysaccharide, an oligosaccharide, a monosaccharide, a polyphenol, a sugar derived alcohol or polyol, or a biodegradable polymer or combinations thereof.

31. The microcapsule according to claim 29, wherein the double layered, multilayered, overcoated or dually crosslinked microcapsule comprises within its outer coating or secondary treatment, a xanthan gum, other polysaccharide gum, a polysaccharide, a hydrophobically modified starch or other hydrophobically modified saccharide, an alginate polymer, a cellulose ether including hydroxyethyl cellulose or carboxymethyl cellulose or their degraded products, a guar or modified guar including cationic guar, zein protein or soy protein or other protein, a polypeptide, a hydrogel, a coacervate, sorbitol, xylitol, isosorbide or tannin acid.

32. The microcapsule according to claim 1, wherein the microcapsule has an average diameter of about 100 nm to 150 μm or about 1 μm to 100 μm .

33. A biodegradable composition of a plurality of microcapsules, the composition comprising at least two microcapsules selected from the group consisting of:

(i) microcapsules comprising microcapsule shell material comprising saccharide units linked or crosslinked by reaction with β -amino ester having alkenyl functionality and/or β -thio ester having alkenyl functionality,

(ii) microcapsules comprising microcapsule shell material comprising crosslinked β -amino ester having alkenyl functionality and/or β -thio ester having alkenyl functionality,

(iii) microcapsules comprising microcapsule shell material comprising saccharide or modified saccharide, and

(iv) combinations or hybrids or interpenetrating networks of (i), (ii) or (iii).

34. The composition according to claim 33, wherein the microcapsules, or a portion of the microcapsules are overcoated or form part of multi-layer or dually crosslinked system.

35. The composition of claim 33, wherein the microcapsule composition comprises a lipophilic core.

36. A method for preparing a microcapsule of claim 1, or a biodegradable composition of plurality of microcapsules claim 33, the method comprising:

(a) preparing an oil phase, comprising at least one multifunctional alkenyl linker, at least one lipophilic core, and optionally adding at least one catalyst or initiator, and/or a diluent;

(b) preparing a water phase comprising at least one saccharide or polysaccharide and an initiator or catalyst, and optionally a stabilizer, defoamer, and/or emulsifier;

(c) mixing the two phases together and emulsifying to make an oil-in-water emulsion;

(d) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by a reaction of the linker components with the saccharide component(s); and

(e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

37. A method for preparing a microcapsule of claim 1, or a biodegradable composition of plurality of microcapsules of claim 33, the method comprising:

(a) preparing an oil phase, optionally with heating, comprising at least one multifunctional alkenyl linker, optionally with a diluent, and adding, after completion of any optional heating applied and allowing to cool, a catalyst or initiator and a lipophilic core;

(b) preparing a water phase comprising at least one saccharide or polysaccharide, an initiator or catalyst, optionally a stabilizer, a defoamer, and/or an emulsifier and heating for a predetermined time until the point at which the oil phase and water phase are mixed;

(c) mixing the two phases together and emulsifying to make an oil-in-water emulsion;

(d) heating the oil-in-water emulsion of step (c) with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by a reaction of the linker components with the saccharide component(s); and

(e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

38. A method for preparing a microcapsule of claim 1, or a biodegradable composition of plurality of microcapsules of claim 33, the method comprising:

(a) preparing a multifunctional alkenyl linker containing β -amino-ester and/or β -thio-ester groups by reacting, for a predetermined time to prior to the mixing of phases in step (c), in a Michael Addition reaction and optionally in the presence of a diluent, a multifunctional conjugated alkenyl functional ester acceptor with a multifunctional amine and/or thiol donor, wherein the alkenyl functionality of the acceptor is in stoichiometric excess compared to the total donor functionality of amine (primary and secondary) and/or thiol groups;

(b) preparing a water phase comprising at least one saccharide or polysaccharide and an initiator or catalyst, and optionally a stabilizer, defoamer, or emulsifier and heating and/or stirring for a pre-determined time before the mixing of the phases in step (c);

(c) after the predetermined times, mixing the two phases together and emulsifying to make an oil in water emulsion;

(d) heating the oil-in-water emulsion with stirring to a temperature between 25°C and 100°C and forming the polymeric microcapsule shell by a reaction of the linker components with the saccharide component(s); and

(e) obtaining the lipophilic core encapsulated in a polymeric microcapsule shell.

39. The methods according to claims 36-38, wherein the initial slurry product, with optional pH adjustment, is subsequently dried, overcoated, and/or additionally crosslinked.

40. The method according to claim 39, wherein the drying, overcoating, or additional crosslinking is effected via spray drying, fluid-bed drying, or direct heating, optionally using introduced additives.

41. The method according to claims 39 and 40, wherein the drying, overcoating, or secondary crosslinking step is started within a predetermined time after completion of the final step of forming the polymeric microcapsule shell around the lipophilic core by an oil-in-water reaction to obtain (i) an overcoated or dried microcapsule, (ii) a dried and overcoated microcapsule, or (iii) a multilayered capsule.

42. The method according to claim 41, wherein the predetermined time between completion of microcapsule formation and the subsequent drying, overcoating or secondary crosslinking step is less than 12 hours, less than 8 hours, less than 6 hours, preferably less than 4 hours, more preferably less than 2 hours, less than 1 hour.

43. The method according to claims 36-38, wherein the weight of saccharide is greater than the weight of the linking group present, such that the ratio of total saccharide to total functional linking molecules having alkenyl functionality in the reactant feed for the shell formation step is, on a weight ('solids') % basis, 51:49, 60:40, 65:35, 70:30, 75:25, 80:20, or 90:10.

44. The method according to claims 36-38, wherein the saccharide is an unmodified mono-saccharide, unmodified di-saccharide, unmodified oligo-saccharide, or an unmodified polysaccharide.

45. The method according to claims 36 and 37, wherein the linking group is an alkenyl functional β -amino-ester or β -thio-ester, and wherein the saccharide is a modified mono-saccharide, a modified di-saccharide, a modified oligo-saccharide, or a modified polysaccharide.

46. A method according to claims 36-38, wherein the alkenyl functional group is selected from the group consisting of an acrylate, a methacrylate, a maleate, a fumarate, an itaconate, , a crotonate, a citraconate, a maleimide, an acrylamide, a methacrylamide and combinations thereof.

47. The method according to claims 36-38, wherein the average alkenyl functionality of the linker(s) is at least two.

48. The method according to claims 36 and 37, wherein the alkenyl functional linker is selected from, the group consisting of butanediol diacrylate, trimethylol propane triacrylate, pentaerythritol triacrylate, pentaerythritol tetra-acrylate, dipentaerythritol penta-acrylate, dipentaerythritol hexa-acrylate, or their methacrylate analogues.

49. The method according to claim 38, wherein one or more of the amine or thiol components has C2-C20 aliphatic chain functionality, a C4-C7 cyclic ring functionality or a C4-C7 heterocyclic ring functionality.

50. The method according to claims 36-38, wherein the initiator in the oil phase is an azo- or a peroxide based initiator for radical polymerization.

51. The method according to claims 36-38, where the initiator for the water phase is a persulfate, redox couple, a peroxide, or an azo-based initiator.

52. The method according to claims 51, wherein the initiator for the water phase is selected from the group consisting of ammonium persulfate, ferrous persulfate, sodium persulfate, potassium persulfate, ceric ammonium nitrate, potassium peroxy sulphate/ascorbic acid, potassium peroxydiphosphate/thiourea, potassium peroxydiphosphate/ silver nitrate, potassium peroxy monosulphate/glycolic, ferrous ammonium-hydrogen peroxide (Fenton's reagent), ferrous sulfate/potassium bromate, benzoyl peroxide, and hydrogen peroxide.

53. The method according to claims 39-41, wherein an additive is introduced to form the overcoated, or secondary crosslinked capsule and where such additive is selected from the group consisting of a saccharide, polysaccharide, a hydrogel, alginate, a polymer forming a coacervate, a modified saccharide, a modified polysaccharide, zein, soy protein, other protein,

a polyphenol, an aldehyde, a sugar derived alcohol, a sugar derived polyol, and combinations thereof.

54. The method according to claims 39-41, wherein the overcoated or crosslinked microcapsule comprises within its outer coating or secondary treatment, a xanthan gum, a polysaccharide gum, a polysaccharide, a hydrophobically modified starch, an alginate polymer, a cellulose ether including hydroxyethyl cellulose or carboxymethyl cellulose, a guar or modified guar including cationic guar, zein protein or soy protein, a polypeptide, a hydrogel, a coacervate, a sugar alcohol, a polyphenol, tannin acid, glyoxal, or glutaraldehyde.

55. The method according to claims 36-38, wherein the stabilizer or emulsifier is selected from the group consisting of polyvinyl alcohol, hydroxyethyl cellulose, guar, cationic guar, xanthan gum, polysaccharides, polyvinylpyrrolidone and combinations thereof.

56. The method according to claims 36-38, wherein the defoamer is selected from the group consisting of liquid hydrocarbons, oils, hydrophobic silicas, fatty acids, alkoxylated compounds, polyethers, polyalkylene glycols, and nonionic emulsifiers.

57. An article made by the methods of claims 36-38.

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Microcapsules of Example 1 (226-83-1)

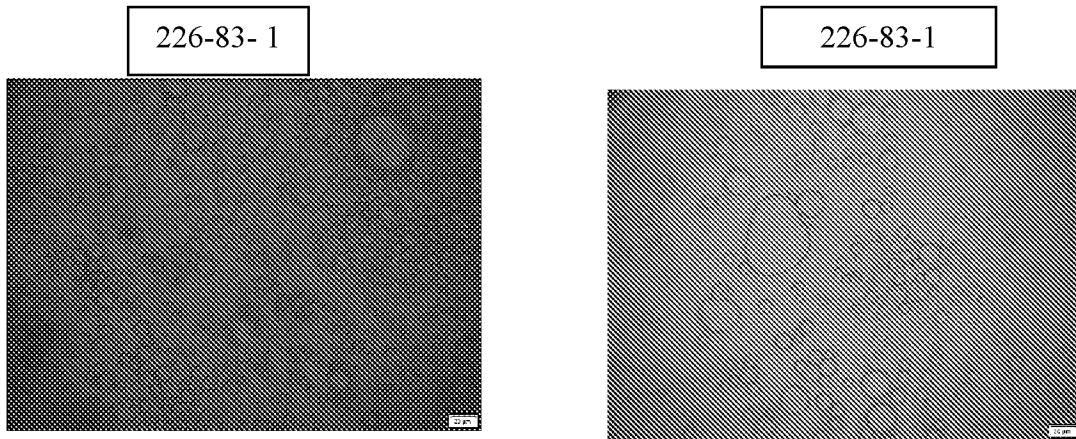


Fig. 1

Microcapsules of Example 2 (226-90-1)

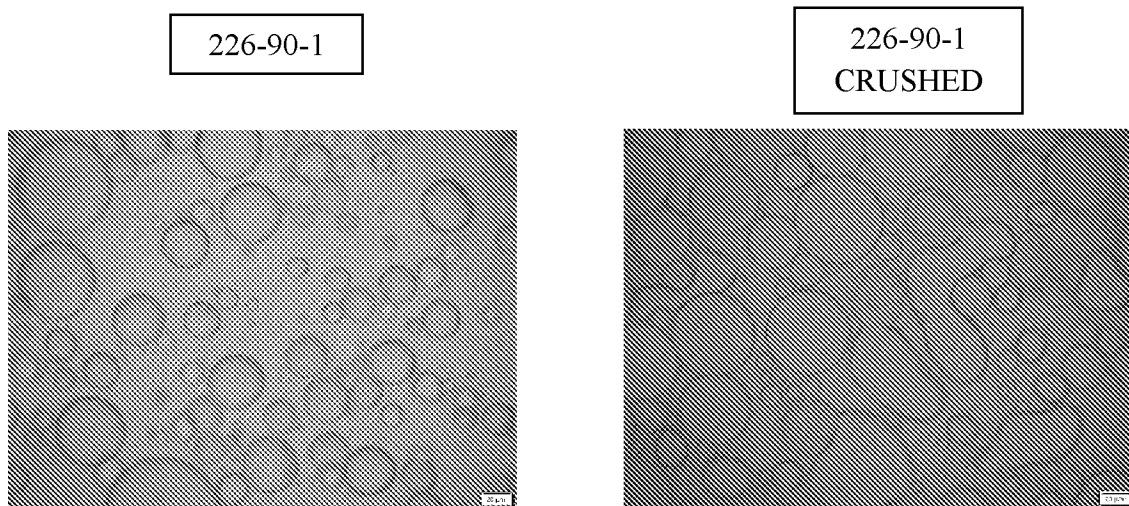
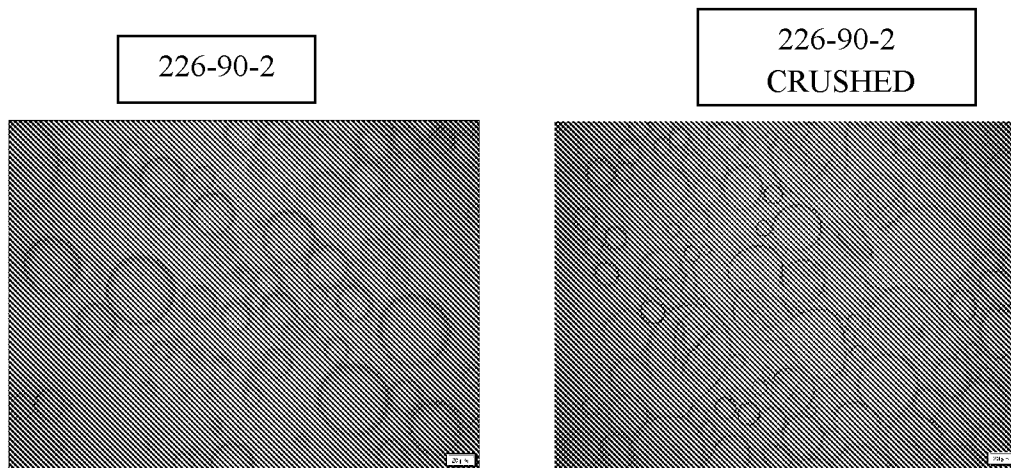
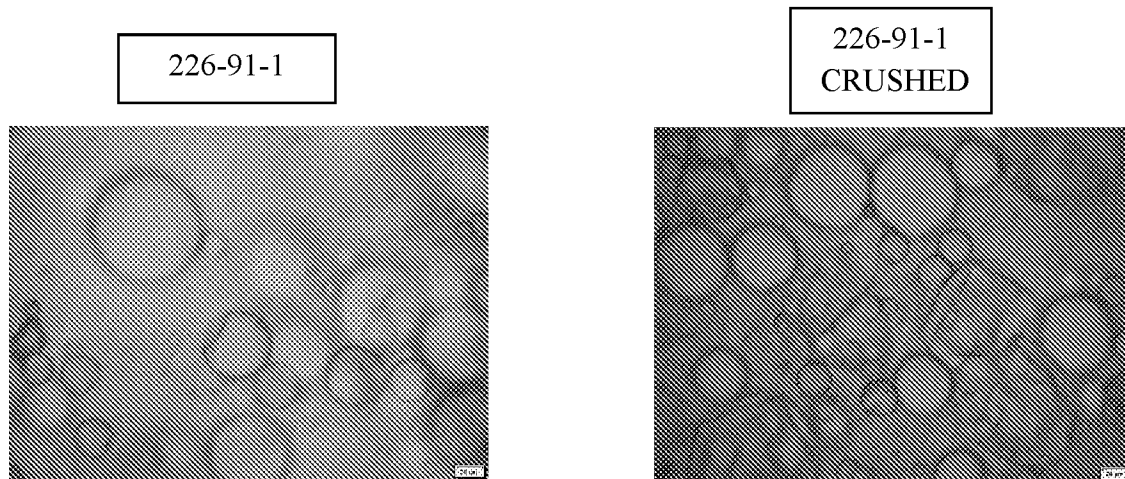


Fig. 2

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Microcapsules of Example 3 (226-90-2)**Fig. 3****Microcapsules of Example 4 (226-91-1)****Fig. 4**

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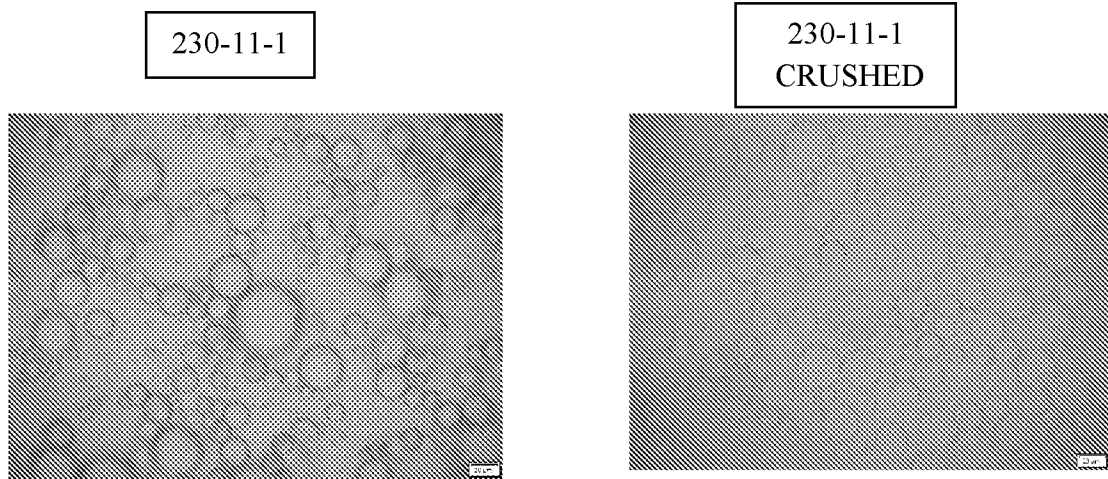
Microcapsules of Example 5 (230-11-1)

Fig. 5

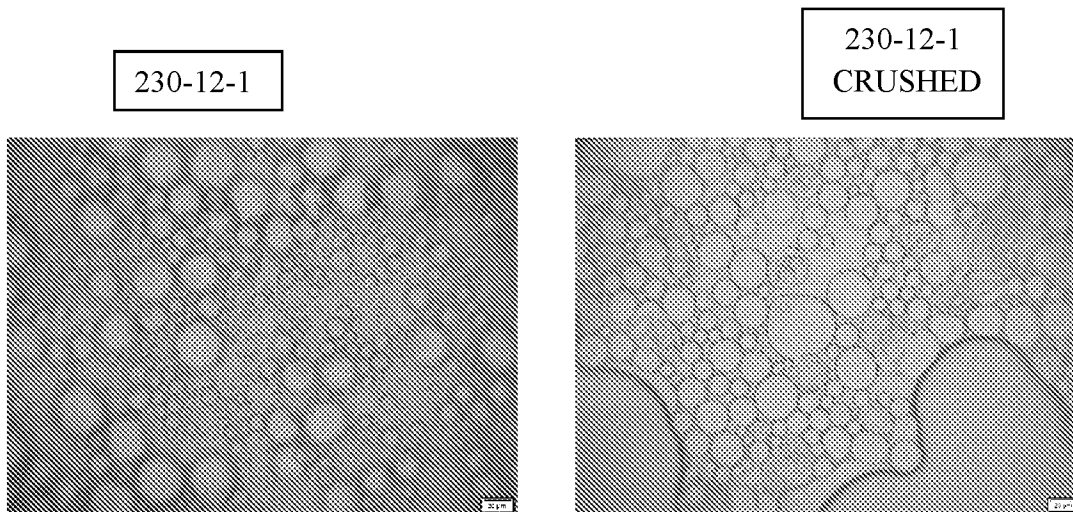
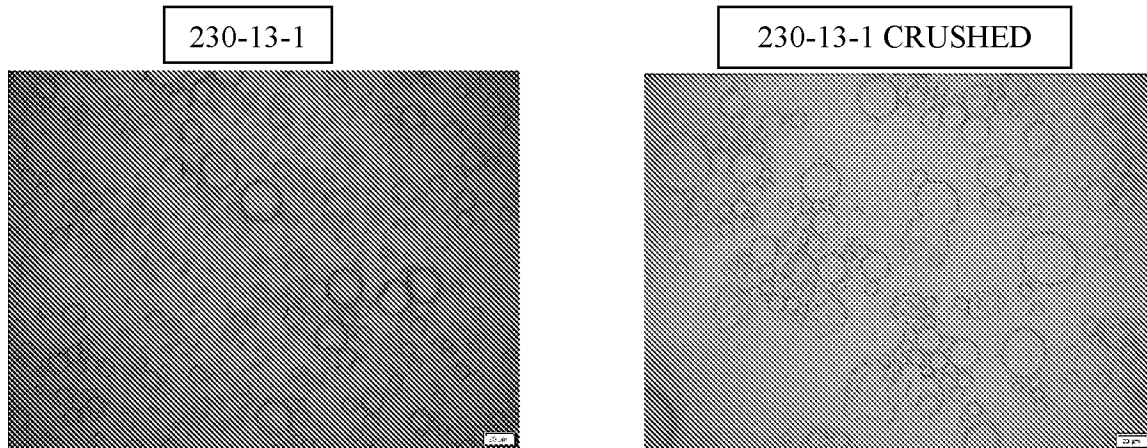
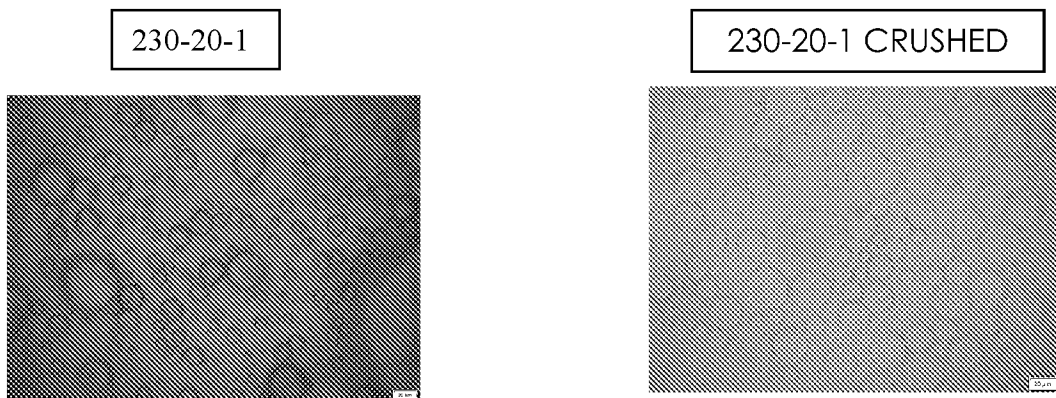
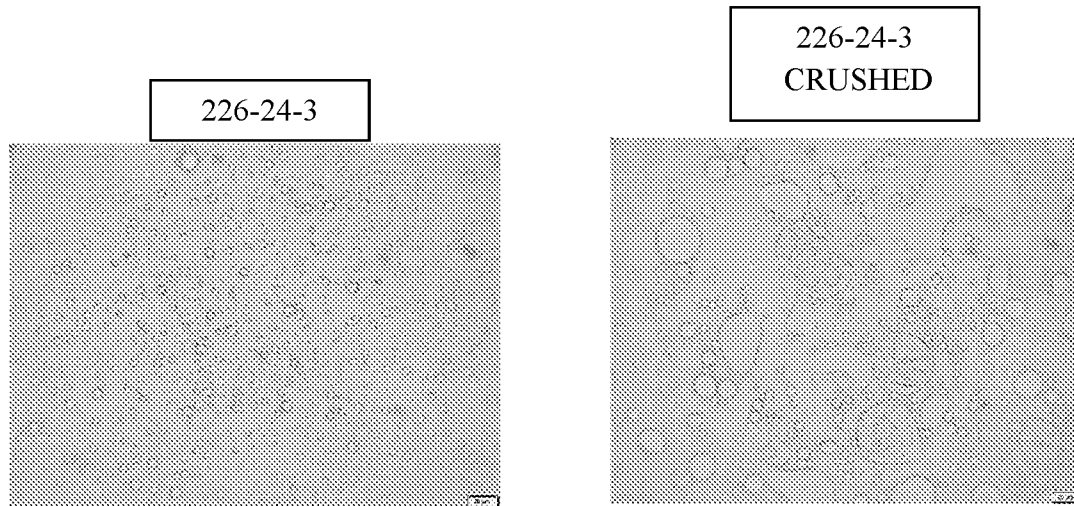
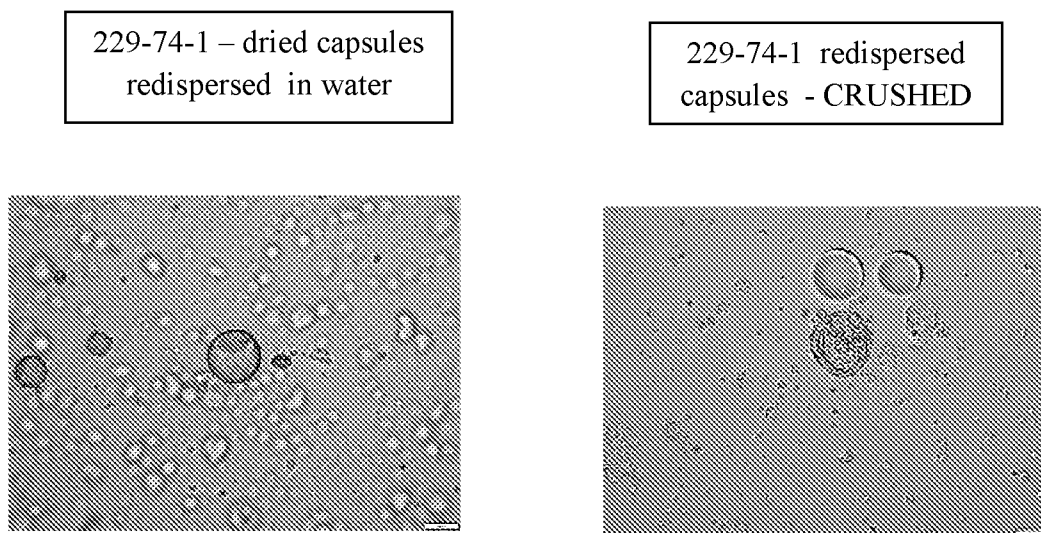
Microcapsules of Example 6 (230-12-1)

Fig. 6

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Microcapsules of Example 7 (230-13-1)**Fig. 7****Microcapsules of Example 8 (230-20-1)****Fig. 8**

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Microcapsules of Example 9 (226-24-3)**Fig. 9****Microcapsules of Example (229-74-1)****Fig. 10**

Sensory (Fragrance Bloom) results of some of the microcapsules from the Examples

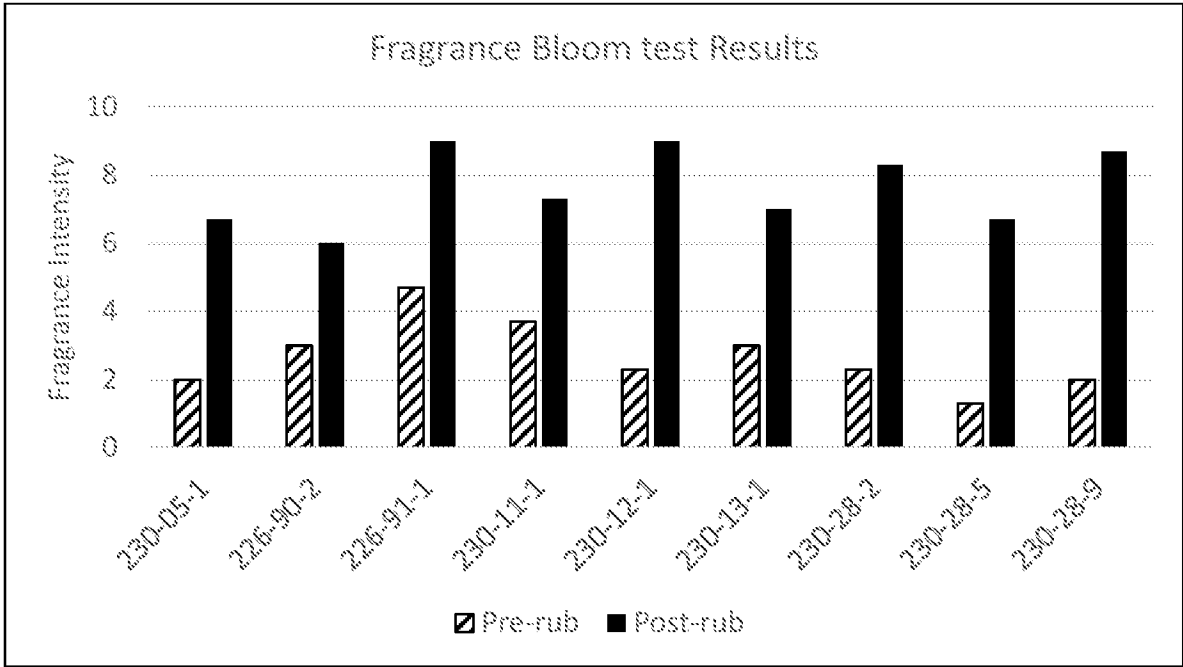


Fig. 11