(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 October 2023 (19.10.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/201313 A2

(51) International Patent Classification:
C08B 31/00 (2006.01) *A61K 47/36* (2006.01)

(21) International Application Number:
PCT/US2023/065747

(22) International Filing Date:
13 April 2023 (13.04.2023)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
63/330,470 13 April 2022 (13.04.2022) US

(71) Applicants: **CORNELL UNIVERSITY** [US/US]; CTL at Cornell University, 395 Pine Tree Road, Suite 310, Ithaca, New York 14850 (US). **TATE & LYLE SOLUTIONS USA LLC** [US/US]; 5450 Prairie Stone Parkway, Hoffman Estates, Illinois 60192 (US).

(72) Inventors: **ABBASPOURRAD, Alireza**; 700 Warren Road, Apartment 25-3C, Ithaca, New York 14850 (US). **LI, Peilong**; CTL at Cornell University, 395 Pine Treen Road, Suite 310, Ithaca, New York 14850 (US). **WHALEY, Judith K.**; 5450 Prairie Stone Parkway, Hoffman Estates, Illinois 60192 (US). **LIU, Weichang**; 5450 Prairie Stone Parkway, Hoffman Estates, Illinois 60192 (US). **KIERULF, Arkaye Velasquez**; 5450 Prairie Stone Parkway, Hoffman Estates, Illinois 60192 (US).

(74) Agent: **DIMAIO, John** et al.; Hodgson Russ LLP, The Guaranty Building, 140 Pearl Street, Suite 100, BUFFALO, New York 14202-4040 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

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

Published:

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

(54) Title: CHARGED STARCH-BASED PARTICLES

(57) **Abstract:** The present disclosure provides starch-based particles. Also provided are compositions of the starch-based particles, cosmetics containing the starch-based particles, pharmaceutical compositions containing the starch-based particles, food products containing the starch-based particles, and methods of making the starch-based particles.

WO 2023/201313 A2

CHARGED STARCH-BASED PARTICLES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/330,470, filed on April 13, 2022, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE DISCLOSURE

[0002] The research area of patchy particles, surfaces with non-homogenous patterns, has gained considerable interest recently. The patches exhibit different properties than the isotropic particle body and produce materials with different characteristics such as self-assembly behavior. Patchy particles self-assemble through favorable free energy mechanisms such as electrostatic interactions and hydrophobic interactions and have found applications in fabricating photonic crystals, targeted delivery of drugs, as surfactants, and in electronics.

[0003] These smart self-assembly particles have been made using numerous creative approaches to achieve the desired morphological engineering. For example, to prepare patchy particles, polystyrene and silica particles have been used to stabilize emulsions by residing on oil-water interface, and with the internal solvent being evaporated, droplets shrink and eventually form well-defined clusters. Particle lithography was also reported for patterning particle surface by utilizing the contact area between particles to avoid chemical adsorption to the surface. For example, by attaching the positively charged polystyrene particles to a negatively charged glass surface, a mask forms underneath the particles thus avoiding surface absorption to the negatively charged polystyrene sulfate. The approach of glancing-angle deposition, which uses two-step vapor deposition on a monolayer of particles on a tape forming particles with two poles, was also adapted to manipulate surface morphology. This method allows the patches to be accurately positioned with a single patch as small as 3.7% of the total surface area of polystyrene beads. Besides approaches based on surface modification, bottom-up methods were also reported. The particles produced in this manner exhibited anisotropy not only on the surface but also inside the body, which used an electrohydrodynamic co-jetting capillary apparatus to produce a laminar flow of three immiscible streams carrying different polymers. After the solvent evaporated the polymers precipitated as triphasic particles with three compartments formed with immiscible liquid, which provided the proof of concept for using a bottom-up method to prepare self-assembly patchy particles.

[0004] Despite the creativity of the methods for fabricating patchy particles, the majority of them bear the limitation of laboratory production scale. That is, the cost of producing these materials is too high to be practically scaled up for industrial purposes. Future research needs to explore additional approaches that can prepare patchy particles economically. Another gap related to patchy particles is that the materials reported in the literature are made with hazardous organic chemicals, which suggests that future studies could explore alternatives based on ingredients that are biodegradable and food-grade.

[0005] Starch, as a staple source of carbohydrates, is ubiquitous in foods, not only as a calorie source but also as clean-label additives, such as a thickener. The use of starch as a conventional thickener is based on gelatinization by hydrothermal treatment, which cleaves the hydrogen bonds in semi-crystalline region of starch thus providing space in the structure to absorb water. The swollen granules provide a larger volume which results in a stronger resistance to flow thus a higher viscosity and a thicker solution. Meanwhile, amylose molecules are released from gelatinized granules due to the disrupted structure and are able to form a network as a settled gel upon cooling. However, a conventionally cooked starch slurry is susceptible to mechanical stress as the high shear of processing disintegrates the soft, swollen granules and the amylose gel network thus causing issues with food texture. It would be meaningful, therefore, to develop a new shear-reversible approach beyond swelling-based thickeners.

[0006] Instead of trapping water in the swollen granules, a possible alternative to enhance thickening is to retain the water molecules between starch particles. To achieve this, patchy particles would be a potential platform to render the starch granules with self-assembly features. To the best of our knowledge, starch has not been used to fabricate patchy particles though it is a food-grade, affordable, and naturally available ingredient. There are more than 20 different modification methods for starch geared toward improving starch functionality, but none of the conventional approaches has been able to produce starch granules showing a heterogeneous surface with patches providing different properties compared with the native particle body. Previous work from our lab successfully fabricated starch-based Janus particles with two faces using a 2D-masking method. The Janus particles exhibited hydrophobic properties on the hemisphere esterified by octenyl succinic anhydride and allowed the starch granules to assemble into worm-like super micelles.

BRIEF SUMMARY OF THE DISCLOSURE

[0007] The present disclosure provides starch-based particles. Also provided are compositions comprising the starch-based particles, food products comprising the starch-based particles, and methods of making the starch-based particles.

[0008] In an aspect, the present disclosure provides starch-based particles. The starch-based particle may have a longest linear dimension (e.g., diameter) is 10–25 μm, including all 0.1 μm values and ranges therebetween.

[0009] In an embodiment, the starch-based particles have a core and a plurality of domains, wherein the plurality of domains are on an exterior surface of the starch-based particle, wherein the plurality of domains are a positively charged starch and the core is negatively charged or capable of being ionized to a negative charge.

[0010] The starch-based particles may comprise one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) fused to an anionically-modified starch particle (e.g., anionically-modified corn starch particle), wherein at least a portion of a surface of the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) is displayed on an exterior surface of the anionically-modified starch particle (e.g., anionically-modified corn starch particle). The anionically-modified starch particle (e.g., anionically-modified corn starch particle) may have one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, partially deprotonated/protonated species thereof, or similar group. In various embodiments, the anionic groups are carboxylic acid groups or carboxylate groups. The cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) may have one or more alkylated ammonium groups (e.g., trimethylammonium groups or one or more dimethylammonium groups or one or more dimethylammonium groups). In various embodiments, the cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) have one or more trimethylammonium groups.

[0011] In an aspect, the present disclosure provide compositions comprising one or more starch-based particles. The composition may be is a powder, tablet, paste, suspension, slurry, capsule, or gel. In various embodiments, the composition may be added to a medium to thicken or otherwise increase the viscosity of the medium.

[0012] In an aspect, the present disclosure provides methods of making the starch-based particles of the present disclosure.

[0013] In various embodiments, a method for making starch-based particles, comprises: hydrating partially gelatinized starch (e.g., corn starch) and a different starch (e.g., amaranth starch) with water; combining the partially gelatinized starch (e.g., partially gelatinized corn starch) and the different starch (e.g., the amaranth starch) at a ratio of 10:1 to 50:1 by weight (partially gelatinized starch (e.g., partially gelatinized corn starch) to different starch (e.g., amaranth starch)) to form a mixture; incubating the mixture at a temperature in the range of 25–50 °C for 5 to 15 minutes; centrifuging the mixture at 8,000–15,000 g for 5–15 minutes (min); and removing a supernatant from the mixture, where the starch-based particles remains. In various embodiments, the ratio of partially gelatinized starch and different starch (e.g., the partially gelatinized corn starch to amaranth starch) is 50:1 by weight, including all ratio values and ranges therebetween.

BRIEF DESCRIPTION OF THE FIGURES

[0014] For a fuller understanding of the nature and objects of the disclosure, reference should be made to the following detailed description taken in conjunction with the accompanying figures.

[0015] **Figure 1.** XRD curves of native starch, partially gelatinized starch, and fused patchy starch.

[0016] **Figure 2.** SEM images (a & b) of dry patchy particles prepared by incubation at 25 °C followed by centrifugation at 8000 *g* for 5 min, and their water suspension (c); SEM images (d & e) of dry patchy particles prepared by incubation at 50 °C followed by centrifugation at 15,000 *g* for 15 min, and their water suspension (f). The arrows indicate visible patches on surface of corn starch granules. The starches shown in Figure 2 are uncharged to demonstrate that the particle-particle association was not due to electrostatic interaction. The ratio between amaranth starch and corn starch was 1:10.

[0017] **Figure 3.** (a) FTIR spectra of native and anionic corn starch. (b) FTIR spectra of native and cationic amaranth starch. (c). Zeta potentials of native and anionic corn starch. (d) Zeta potentials of native and cationic amaranth starch.

[0018] **Figure 4.** Self-assembly of charged patchy starch in water (a); the water-holding capacity (b), rheological moduli (b), and viscosity (c) of uncharged, mixed charged, and patchy charged starch. The ratio between amaranth starch and corn starch was 1:50.

[0019] **Figure 5.** (a) Processed images of 2% slurry of native corn starch. (b) Distribution of native starch as individual particles, small aggregates, and large clumps. (c) Processed images of 2% slurry of patchy starch. (d) Distribution of patchy starch as individual particles, small aggregates, and large clumps. The ratio between amaranth starch and corn starch was 1:50.

[0020] **Figure 6.** (a) Storage modulus and loss modulus of gelatinized slurry containing 10% uncharged, mixed charged, and patchy starch. (b) Viscosity of gelatinized slurry containing 10% uncharged, mixed charged, and patchy starch. (c) Viscosity of sheared gelatinized slurry containing 10% uncharged, mixed charged, and patchy starch.

[0021] **Figure 7.** Schematic showing the assembly of particles of the present disclosure.

[0022] **Figure 8.** (a) SEM images of patchy starch prepared by incubation at 40 °C and centrifugation at 12,000 g. (b) The zoom-in image of a detached patch after starch fusion.

[0023] **Figure 9.** Suspension of native corn starch (a) and charged patchy starch (b). The scale bar is 50 μm.

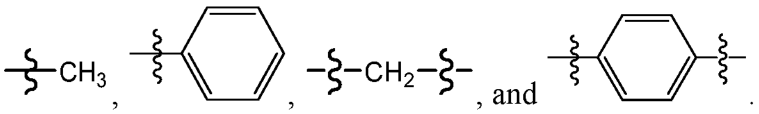
DETAILED DESCRIPTION OF THE DISCLOSURE

[0024] Although claimed subject matter will be described in terms of certain embodiments, other embodiments, including embodiments that do not provide all of the benefits and features set forth herein, are also within the scope of this disclosure. Various structural, logical, and process step changes may be made without departing from the scope of the disclosure.

[0025] Where a range of values is provided in this disclosure, it should be understood that each intervening value, to the tenth of the unit of the lower limit between the upper and lower limit of that range, and any other intervening value in that stated range is encompassed within the disclosure, unless clearly indicated otherwise. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges encompassed within the disclosure.

[0026] As used in this disclosure, the singular forms include the plural forms and vice versa unless the context clearly indicates otherwise.

[0027] As used herein, unless otherwise stated, the term "group" refers to a chemical entity that is monovalent (i.e., has one terminus that can be covalently bonded to other chemical species), divalent, or polyvalent (i.e., has two or more termini that can be covalently bonded to other chemical species). The term "group" also includes radicals (e.g., monovalent and multivalent, such as, for example, divalent, trivalent, and the like, radicals). Illustrative examples of groups include:



[0028] As used herein, unless otherwise indicated, the term “alkyl group” refers to branched or unbranched, linear saturated hydrocarbon groups and/or cyclic hydrocarbon groups. Examples of alkyl groups include, but are not limited to, methyl groups, ethyl groups, propyl groups, butyl groups, isopropyl groups, tert-butyl groups, cyclopropyl groups, cyclopentyl groups, cyclohexyl groups, and the like. Alkyl groups are saturated groups, unless it is a cyclic group. For example, an alkyl group is a C_1 to C_{30} alkyl group, including all integer numbers of carbons and ranges of numbers of carbons therebetween (e.g., C_1, C_2, C_3, C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15}, C_{16}, C_{17}, C_{18}, C_{19}, C_{20}, C_{21}, C_{22}, C_{23}, C_{24}, C_{25}, C_{26}, C_{27}, C_{28}, C_{29}, and C_{30}). The alkyl group may be unsubstituted or substituted with one or more substituents. Examples of substituents include, but are not limited to, halogens (-F, -Cl, -Br, and -I), aliphatic groups (e.g., alkyl groups, alkenyl groups, alkynyl groups, and the like), halogenated aliphatic groups (e.g., trifluoromethyl group), aryl groups, halogenated aryl groups, alkoxide groups, amine groups, nitro groups, carboxylate groups, carboxylic acids, ether groups, alcohol groups, alkyne groups (e.g., acetylenyl groups and the like), and the like, and combinations thereof.

[0029] The term “treatment” as used herein refers to reduction or delay in one or more symptoms or features associated with the presence of the particular condition being treated. Treatment does not necessarily mean complete cure and does not preclude relapse. Treatment may be carried out over a short period of time (days, weeks), or over a long period of time (months) or may be on a continuous basis (e.g., in the form of a maintenance therapy). Treatment may be continual or intermittent.

[0030] The term “therapeutically effective” dose or amount as used herein is the amount sufficient to achieve, in a single or multiple doses, the intended purpose of treatment. For example, an effective amount for effect wound healing is the amount sufficient to achieve one or more indicators of wound healing. The exact amount desired or required will vary depending on the mode of administration, patient specifics and the like. Appropriate effective amounts or the length of treatment can be determined by one of ordinary skill in the art (such as a clinician) with the benefit of the present disclosure.

[0031] The terms “anionic groups” and “anionically-modified corn starch particles” as used herein refers to groups that are either negatively charged or have the ability to be ionized such that the group has a negative charge. Examples of anionic groups or groups that would render a particle anionically modified include, but are not limited to, carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof.

[0032] The terms “cationic groups” and “cationically-modified corn starch particles” as used herein refers to groups that are either positively charged or have the ability to be ionized such that the group has a positively charge. Examples of cationic groups or groups that would render a particle cationically modified include, but are not limited to, alkylated ammonium groups or amine groups. Various examples of alkylated ammonium groups include, but are not limited to, trimethylammonium groups or dimethylammonium groups.

[0033] The present disclosure provides starch-based particles. Also provided are compositions comprising the starch-based particles, food products comprising the starch-based particles, and methods of making the starch-based particles.

[0034] In an aspect, the present disclosure provides starch-based particles. The starch-based particle may have a longest linear dimension (e.g., diameter) is 10–25 μm, including all 0.1 μm values and ranges therebetween.

[0035] In an embodiment, the starch-based particles have a core and a plurality of domains, wherein the plurality of domains are on an exterior surface of the starch-based particle, wherein the plurality of domains are a positively charged starch and the core is negatively charged or capable of being ionized to a negative charge.

[0036] The core may be negatively charged or capable of having a negative charge. For example, the core may be functionalized with one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, partially deprotonated/protonated species thereof, or similar group. In various embodiments, the core has one or more carboxylic acid groups or carboxylate groups.

[0037] The cores may comprise various starches. For example, the starch may be a starch with a granular size of greater than or equal to 10 μm. Examples of such starches include, but are not limited to, potato starch, wheat starch, corn starch, barley starch, pea starch, tapioca starch, and the like, and various combinations thereof. In various embodiments, the comprises corn starch. In various examples, when the starch is corn starch, the corn starch may have an amylose content of 0–75%, including all 0.1 values and ranges therebetween (e.g., 0%, 25%, 55%, or 70% (e.g., 55%)).

[0038] The domains are positively charged or capable of having a positive charge. For example, the domains may comprise one or more alkylated ammonium groups (e.g., trimethylammonium groups or one or more dimethylammonium groups). In various embodiments, the domains comprise one or more trimethylammonium groups.

[0039] The domains may comprise various starches. For example, the starch has a granular size of less than 10 μm. Examples of such starches include, but are not limited to, amaranth starch, riche starch, quinoa starch, taro starch, and the like, and various embodiments thereof. In various examples, the domains comprise amaranth starch.

[0040] In various examples, when the core comprises corn starch and the domains comprise amaranth starch, the ratio of amaranth starch to corn starch is 10:1 to 50:1 and the ratio is a weight percent ratio, including all integer ratio values and ranges therebetween.

[0041] The starch-based particles may comprise one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) fused to an anionically-modified starch particle (e.g., anionically-modified corn starch particle), wherein at least a portion of a surface of the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) is displayed on an exterior surface of the anionically-modified starch particle (e.g., anionically-modified corn starch particle). The anionically-modified starch particle (e.g., anionically-modified corn starch particle) may have one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, partially deprotonated/protonated species thereof, or similar group. In various embodiments, the anionic groups are carboxylic acid groups or carboxylate groups. The cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) may have one or more alkylated ammonium groups (e.g., trimethylammonium groups or one or more dimethylammonium groups or one or more dimethylammonium groups). In various embodiments, the cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) have one or more trimethylammonium groups.

[0042] The anionically-modified starch particle (e.g., anionically-modified corn starch particle) may have an amylose content of 0–75%, including all 0.1 values and ranges therebetween (e.g., 0%, 25%, 55%, or 70% (e.g., 55%)) prior to fusion to the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles). The ratio of cationically-modified starch to anionically-modified starch (e.g., cationically-modified amaranth starch particles to anionically-modified corn starch particle) is 10:1 to 50:1 and the ratio is a weight percent ratio, including all integer ratio values and ranges therebetween.

[0043] In an aspect, the present disclosure provide compositions comprising one or more starch-based particles. The composition may be is a powder, tablet, paste, suspension, slurry, capsule, or gel. In various embodiments, the composition may be added to a medium to thicken or otherwise increase the viscosity of the medium.

[0044] Without intending to be bound by any particular theory, the starch-based particles trap water by self-association (e.g., aggregation) due to Coulombic interactions. A composition may comprise 0.01–99% by weight of the starched-based particles, including all 0.01 values and ranges therebetween (e.g., 1–40% by weight). A composition comprising the starch-based particles of the present disclosure has a viscosity higher than that of a composition comprising the same amount of unmodified or commercial cornstarch. In various embodiments, the viscosity of the composition comprising the starch-based particles of the present disclosure at 10 s^{-1} shear rate is ≥1000-fold higher than the viscosity of a composition comprising unmodified or commercial cornstarch at the same 25% by weight concentration.

[0045] In various embodiments, a composition comprises starch-based particles that increase the viscosity or thicken relative to the same composition in the absence of the starch-based particles. In other embodiments, the composition may be added to a medium for the purpose of increasing the viscosity or thicken and/or to texturize the medium.

[0046] In various embodiments, the starch-based particles may aggregate into clusters or aggregates comprising a plurality of starch-based particles. In various embodiments, the aggregates may comprise at least 20 starch-based particles. In various embodiments, at least 80% (e.g., at least 80%, at least 81%, at least 82%, at least 83%, at least 84%, at least 85%, at least 86%, at least 86%, at least 87%, at least 88%, at least 89%, at least 90%, at least 91%, at least 92%, at least 93%, at least 94%, or at least 95%) of the starch-based particles have formed aggregates comprising at least 20 starch-based particles. In various examples, the aggregates may have an average size of 400 μm^2 or larger (e.g., 437 μm^2). Aggregation may be seen in compositions having a concentration of 2 weight percent starch-based particles.

[0047] The composition may have desirable rheological properties. For example, the composition comprising a plurality of the starch-based particles may have a storage modulus of $\geq 10^3$ Pa at a frequency of 1 Hz at a concentration of 25% by weight the starch-based particles. The composition may be a slurry. In various other embodiments, the composition comprising a plurality of the starch-based particles may have a viscosity of ≥ 10 Pa s at a shear rate of 0.1 s^{-1} at a concentration of 25% by weight of the starch-based particles.

[0048] In various embodiments, the composition is a food additive. The food additive may be a thicken or texturizer. For example, the composition (e.g., food additive) may be added to or mixed into a food product for ingestion to thicken, texturize, or increase the viscosity of the food product. For example, the amount of the composition added to the food product may be varied to adjust the desired viscosity of the food product. For example, the composition (e.g., food additive) may be a powder, tablet, paste, suspension, slurry, capsule, or gel prior to addition to the food. Following addition of the composition, the viscosity or the texture of the food product is changed. For example, following addition of the composition, the viscosity of the food product is increased relative to its viscosity prior to the addition of the food additive.

[0049] In various other embodiments, the composition may be suitable for delivery or vehicle for an agent (e.g., a pharmaceutical agent). For example the agent may be one or more small molecules and/or one or more biologically active components.

[0050] Compositions of the disclosure can comprise more than one pharmaceutical agent. For example, a first composition comprising a compound of the disclosure and a first pharmaceutical agent can be separately prepared from a composition which comprises the same compound of the disclosure and a second pharmaceutical agent, and such preparations can be mixed to provide a two-pronged (or more) approach to achieving the desired prophylaxis or therapy in an individual. Further, compositions of the disclosure can be prepared using mixed preparations of any of the compounds disclosed herein.

[0051] The composition may comprise one or more small molecules. Examples of small molecules include, but are not limited to, antibiotics, antifungals, chemotherapy agents, antivirals, analgesics, anesthetics, antiparasitics, anti-septic agents, other wound healing agents, and the like, and combinations thereof.

[0052] The composition may comprise one or more biologically active components. In various examples, the biologically active component is a biologic. The biologically active component may be a protein, peptide, cDNA, siRNA, mRNA, monoclonal antibodies, or the like, or any combination thereof.

[0053] Examples of agents include, but are not limited to, anti-androgens (e.g., Casodex, Flutamide, MDV3100, or ARN-509, Enzaluatide, apalutamide, darolutamid and abiraterone), MEK (e.g. MEK1, MEK2, or MEK1 and MEK2) inhibitors (e.g. XL518, CI-1040, PD035901, selumetinib/AZD6244, GSK1120212/trametinib, GDC-0973, ARRY-162, ARRY-300, AZD8330, PD0325901, U0126, PD98059, TAK-733, PD318088, AS703026, BAY 869766), BRAF inhibitor (e.g. Vemurafenib), CDK4/6 inhibitors, SHP1 inhibitors, SHP2 inhibitors (e.g. TNO155; RMC-4630), PTPN22 inhibitors, PTPN1 inhibitors, PTPN2 inhibitors, CCR2 inhibitors, CXCR2 inhibitors, TORC1/TORC 2 inhibitors, PI-3K-AKT inhibitors, PARP inhibitors (e.g. Olaparib, Niraparib, Rucaparib), CDK4/6 inhibitors, CDK2 inhibitors, CDK7 inhibitors, TEAD inhibitors, alkylating agents (e.g., cyclophosphamide, ifosfamide, chlorambucil, busulfan, melphalan, mechlorethamine, uramustine, thiotepa, nitrosoureas, nitrogen mustards (e.g., mechloroethamine, cyclophosphamide, chlorambucil, meiphalan), ethylenimine and methylmelamines (e.g., hexamethlymelamine, thiotepa), alkyl sulfonates (e.g., busulfan), nitrosoureas (e.g., carmustine, lomusitne, semustine, streptozocin), triazenes (decarbazine)), anti-metabolites (e.g., 5-azathioprine, leucovorin, capecitabine, fludarabine, gemcitabine, pemetrexed, raltitrexed, folic acid analog (e.g., methotrexate), pyrimidine analogs (e.g., fluorouracil, floxouridine, Cytarabine), purine analogs (e.g., mercaptopurine, thioguanine, pentostatin), etc.), plant alkaloids (e.g., vincristine, vinblastine, vinorelbine, vindesine, podophyllotoxin, paclitaxel, docetaxel, etc.), topoisomerase inhibitors (e.g., irinotecan, topotecan, amsacrine, etoposide (VP16), etoposide phosphate, teniposide, etc.), antitumor antibiotics (e.g., doxorubicin, adriamycin, daunorubicin, epirubicin, actinomycin, bleomycin, mitomycin, mitoxantrone, plicamycin, etc.), platinum-based compounds (e.g. cisplatin, oxaloplatin, carboplatin), anthracenedione (e.g., mitoxantrone), substituted urea (e.g., hydroxyurea), methyl hydrazine derivative (e.g., procarbazine), adrenocortical suppressant (e.g., mitotane, aminoglutethimide), epipodophyllotoxins (e.g., etoposide), enzymes (e.g., L-asparaginase), inhibitors of mitogen-activated protein kinase signaling (e.g. U0126, PD98059, PD184352, PD0325901, ARRY-142886, SB239063, SP600125, or BAY 43-9006), inhibitors of phosphatidylinositol 3-kinase signaling (e.g. wortmannin or LY294002), mTOR inhibitors, antibodies (e.g., rituxan), MAP4K1 inhibitor (e.g ZYF0033), 5-aza-2′-deoxycytidine, doxorubicin, vincristine, etoposide, gemcitabine, imatinib (Gleevec®), geldanamycin, dasatinib, 17-N-Allylamino-17-Demethoxygeldanamycin (17-AAG), bortezomib, carfilzomide, trastuzumab, anastrozole; angiogenesis inhibitors; antiandrogen, antiestrogen; antisense oligonucleotides; apoptosis gene modulators; apoptosis regulators; arginine deaminase; BCR/ABL antagonists; beta lactam derivatives; bFGF inhibitor; bicalutamide; camptothecin derivatives; casein kinase inhibitors (e.g., ICOS, Silmitasertib); clomifene analogues; cytarabine dacliximab; dexamethasone; estrogen agonists; estrogen antagonists; etanidazole; etoposide phosphate; exemestane; fadrozole; finasteride; fludarabine; fluorodaunorunicin hydrochloride; gadolinium texaphyrin; gallium nitrate; gelatinase inhibitors; gemcitabine; glutathione inhibitors; hepsulfam; immunostimulant peptides; insulin-like growth factor-1 receptor inhibitor; interferon agonists; interferons; interleukins; letrozole; leukemia inhibiting factor; leukocyte alpha interferon; leuprolide+estrogen+progesterone; leuprorelin; matrilysin inhibitors; matrix metalloproteinase inhibitors; MIF inhibitor; mifepristone; mismatched double stranded RNA; monoclonal antibody; mycobacterial cell wall extract; nitric oxide modulators; oxaliplatin; panomifene; pentrozole; phosphatase inhibitors; plasminogen activator inhibitor; platinum complex; platinum compounds; prednisone; proteasome inhibitors; protein A-based immune modulator; protein kinase C inhibitor; protein tyrosine phosphatase inhibitors; purine nucleoside phosphorylase inhibitors; RAS farnesyl protein transferase inhibitors; RAS inhibitors; RAS-GAP inhibitor; ribozymes; signal transduction inhibitors; signal transduction modulators; single chain antigen-binding protein; stem cell inhibitor; stem-cell division inhibitors; stromelysin inhibitors; synthetic glycosaminoglycans; tamoxifen methiodide; telomerase inhibitors; thyroid stimulating hormone; translation inhibitors; tyrosine kinase inhibitors; urokinase receptor antagonists; steroids (e.g., dexamethasone), finasteride, aromatase inhibitors, gonadotropin-releasing hormone agonists (GnRH) such as goserelin or leuprolide, adrenocorticosteroids (e.g., prednisone), progestins (e.g., hydroxyprogesterone caproate, megestrol acetate, medroxyprogesterone acetate), estrogens (e.g., diethlystilbestrol, ethinyl estradiol), antiestrogen (e.g., tamoxifen), androgens (e.g., testosterone propionate, fluoxymesterone), antiandrogen (e.g., flutamide), immunostimulants (e.g., Bacillus Calmette-Guérin (BCG), levamisole, interleukin-2, alpha-interferon, etc.), monoclonal antibodies (e.g., anti-CD20, anti-CD22, anti CD25,anti-CD37, anti-CD38, anti-HER2, anti-CD52, anti-HLA-DR, anti Nectin-4, anti Trop2, anti-Muc1, anti-mesothelin, anti-alpha-folate, anti DLL3, anti-GPRNMB, anti-Glypican3, anti-VEGF, anti-EGFR monoclonal antibodies), immunotoxins (e.g., anti-CD33 monoclonal antibody-calicheamicin conjugate, anti-CD22 monoclonal antibody-pseudomonas exotoxin conjugate, anti-CD30 etc.), radioimmunotherapy (e.g., anti-CD20 monoclonal antibody conjugated to 111In, 90Y, or 131I, etc.), triptolide, homoharringtonine, dactinomycin, doxorubicin, epirubicin, topotecan, itraconazole, vindesine, cerivastatin, vincristine, deoxyadenosine, sertraline, pitavastatin, irinotecan, clofazimine, 5-nonyloxytryptamine, vemurafenib, dabrafenib, erlotinib, gefitinib, EGFR inhibitors, epidermal growth factor receptor (EGFR)-targeted therapy or therapeutic (e.g. gefitinib (Iressa™), erlotinib (Tarceva™), cetuximab (Erbitux™), lapatinib (Tykerb™), panitumumab (Vectibix™), vandetanib (Caprelsa™), afatinib/BIBW2992, CI-1033/canertinib, neratinib/HKI-272, CP-724714, TAK-285, AST-1306, ARRY334543, ARRY-380, AG-1478, dacomitinib/PF299804, OSI-420/desmethyl erlotinib, AZD8931, AEE788, pelitinib/EKB-569, CUDC-101, WZ8040, WZ4002, WZ3146, AG-490, XL647, PD153035, BMS-599626), sorafenib, imatinib, sunitinib, dasatinib, pyrrolo benzodiazepines (e.g. tomaymycin), carboplatin, CC-1065 and CC-1065 analogs including amino-CBIs, nitrogen mustards (such as chlorambucil and melphalan), dolastatin and dolastatin analogs (including auristatins: e.g., monomethyl auristatin E), anthracycline antibiotics (such as doxorubicin, daunorubicin, etc.), duocarmycins and duocarmycin analogs, enediynes (such as neocarzinostatin and calicheamicins), leptomycin derivaties, maytansinoids and maytansinoid analogs (e.g. mertansine), methotrexate, mitomycin C, taxoids, vinca alkaloids (such as vinblastine and vincristine), epothilones (e.g. epothilone B), camptothecin and its clinical analogs topotecan and irinotecan, or the like, vaccines (e.g., Bacillus Calmette–Guérin (BCG), CSF1R inhibitors (e.g., pexidartinib); class 3 receptor tyrosine kinases (RTKs), such as KIT, FLT3, and platelet-derived growth factor receptors PDGFRα and PDGFRβ.

[0054] The compositions may be suitable for topical or transdermal application or oral administration. The compositions can be produced in any solid, liquid or semi-solid formulation, including creams, emulsions, anhydrous compositions, aqueous dispersions, oils, foams, lotions, gels, ointments, sprays or aerosols or any other form suitable via the skin or mucosal surface. The formulations can be incorporated into support materials that can be applied to a wound surface, such as, for example, bandages, gauzes, clothing, diapers, dressings, adhesive or non-adhesive patches, and the like. The formulations can also be incorporated into cosmetic materials, such as foundations, lipsticks, moisturizers, creams, masks, and the like.

[0055] The composition may comprise one or more cosmetic components. Examples of cosmetic components include, but are not limited to, scented ingredients (e.g., essential oils and the like), exfoliating agents (e.g., salicylic acid and the like), lubricants (e.g., hyaluronic acid and the like), anti-cellulite agents (e.g., caffeine and the like), and the like, and various combinations thereof. Other examples of any of the foregoing components are known in the art and may be suitable for use in the composition of the present disclosure.

[0056] Addition ingredients may also optionally be included in the cosmetic compositions. Non-limiting examples include water, non-volatile fatty substances, inorganic pigments, soft focus particles/powders, fragrances, preservatives, coalescents, wetting agents, water-soluble solvents, emollients, suspending agents, surfactants, actives, and the like. One unique feature of the cosmetic compositions is that they may include water (aqueous compositions) or may be free of water (anhydrous compositions).

[0057] The compositions may include pharmaceutically or cosmetically acceptable excipients, such as, buffering agents, antioxidants, preservatives, colorants, carriers, diluents, adjuvants, salts, and the like. Suitable water soluble buffering agents include carbonates, phosphates, bicarbonates, citrates, borates, acetates, succinates and the like, such as sodium phosphate, citrate, borate, acetate, bicarbonate, carbonate and the like. These agents are advantageously present in amounts sufficient to maintain a pH of the system about 6, such as between about 7 to about 10 and more preferably about 7 to about 9. Suitable water soluble preservatives include sodium bisulfite, sodium bisulfate, sodium thiosulfate, ascorbate, benzalkonium chloride, chlorobutanol, thimerosal, phenylmercuric acetate, phenylmercuric borate, phenylmercuric nitrate, parabens, methylparaben, polyvinyl alcohol, benzyl alcohol, phenylethanol and the like and mixtures thereof. The excipients may be present in amounts of from 0.001 to about 5% by weight, such as, for example, 0.01 to about 2% by weight. Pharmaceutical composition ingredients and preparation can be carried out by standard pharmaceutical formulation techniques such as those disclosed in *Remington: The Science and Practice of Pharmacy* (2012) 22nd Edition, Philadelphia, PA. Lippincott Williams & Wilkins.

[0058] In an aspect, the present disclosure provides food products. The food product may comprise the starch-based particles of the present disclosure or a composition comprising the starch-based particles of the present disclosures.

[0059] Various food products may comprise the starch-based particles of the present disclosure or a composition comprising the starch-based particles of the present disclosures. Non-limiting examples of food products include sauces, soups, fillings, custards, puddings, desserts, dressings, and the like. Other food products are known in the art and are within the scope of the present disclosure. The food products are suitable for ingestion may humans and/or animals.

[0060] In an aspect, the present disclosure provides methods of making the starch-based particles of the present disclosure.

[0061] In various embodiments, a method for making starch-based particles, comprises: hydrating partially gelatinized starch (e.g., corn starch) and a different starch (e.g., amaranth starch) with water; combining the partially gelatinized starch (e.g., partially gelatinized corn starch) and the different starch (e.g., the amaranth starch) at a ratio of 10:1 to 50:1 by weight (partially gelatinized starch (e.g., partially gelatinized corn starch) to different starch (e.g., amaranth starch)) to form a mixture; incubating the mixture at a temperature in the range of 25–50 °C for 5 to 15 minutes; centrifuging the mixture at 8,000–15,000 g for 5–15 minutes (min); and removing a supernatant from the mixture, where the starch-based particles remains. In various embodiments, the ratio of partially gelatinized starch and different starch (e.g., the partially gelatinized corn starch to amaranth starch) is 50:1 by weight, including all ratio values and ranges therebetween.

[0062] In various embodiments, the partially gelatinized starch (e.g., the partially gelatinized corn starch) is modified such that it comprises one or more anionic groups (e.g., one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof). In various examples, the one or more anionic groups are carboxylate groups. The partially gelatinized starch may be corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or the like, or various combinations thereof. In various embodiments, the partially gelatinized starch is corn starch.

[0063] The different starch (e.g., starch other than corn starch) (e.g., amaranth starch) may be modified such that is comprises one or more cationic groups (e.g., quaternary amines, such as, for example, alkylated amines). In various embodiments, one or more cationic groups are one or more trimethylammonium groups or one or more dimethylammonium groups. In various embodiments, the one or more cationic groups are one or more trimethylammonium groups. In various embodiments, the starch is amaranth starch, rice starch, quinoa starch, taro starch, or the like, or various combinations thereof. In various embodiments, the starch is amaranth starch.

[0064] In various embodiments, the partially gelatinized starch (e.g., partially gelatinized corn starch) and the different starch (e.g., amaranth starch) are hydrated with water at a ratio of 1:5 (starch to water) by weight.

[0065] The steps of the method described in the various embodiments and examples disclosed herein are sufficient to carry out the methods of the present disclosure. Thus, in an embodiment, the method consists essentially of a combination of the steps of the methods disclosed herein. In another embodiment, the method consists of such steps.

[0066] The following Statements provide various embodiments of the present disclosure.

Statement 1. A starch-based particle having a core and a plurality of domains, wherein the plurality of domains are on an exterior surface of the starch-based particle, wherein the plurality of domains are a positively charged starch (e.g., a positively charged amaranth starch) and the core is negatively charged or capable of being ionized to a negative charge.

Statement 2. A starch-based particle according to Statement 1, wherein the core has one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof.

Statement 3. A starch-based particle according to Statement 1 or Statement 2, wherein the core has one or more carboxylic acid groups or carboxylate groups.

Statement 4. A starch-based particle according to any one of the preceding Statements, wherein the domains have one or more trimethylammonium groups or one or more dimethylammonium groups.

Statement 5. A starch-based particle according to any one of the preceding Statements, wherein the domains have one or more trimethylammonium groups.

Statement 6. A starch-based particle according to any one of the preceding Statements, wherein at least one of the plurality of domains comprises amaranth starch, rice starch, quinoa starch, taro starch, or the like, or various combinations thereof.

Statement 7. A starch-based particle according to any one of the preceding Statements, wherein at least one of the plurality of domains comprises amaranth starch.

Statement 8. A starch-based particle according to any one of the preceding Statements, wherein the core comprises corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or the like, or various combinations thereof.

Statement 9. A starch-based particle according to any one of the preceding Statements, wherein the core comprises corn starch.

Statement 10. A starch-based particle according to any one of the preceding Statements, wherein the core (e.g., corn starch) has an amylose content of 0–70%, including all 0.1% values and ranges therebetween.

Statement 11. A starch-based particle according to any one of the preceding Statements, wherein the core has an amylose content of 0%, 25%, 55%, or 70%.

Statement 12. A starch-based particle according to any one of Statements 9–11, wherein the corn starch has an amylose content of 55%.

Statement 13. A starch-based particle according to any one of Statements 7 or 9–12, wherein the ratio of amaranth starch to corn starch is 10:1 to 50:1 and the ratio is a weight percent ratio.

Statement 14. A starch-based particle comprising one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) fused to an anionically-modified starch particle (e.g., anionically-modified corn starch particle), wherein at least a portion of a surface of the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) is displayed on an exterior surface of the anionically-modified starch particle (e.g., anionically-modified corn starch particle).

Statement 15. A starch-based particle according to Statement 14, wherein at least a portion of the cationically-modified starch particles comprise amaranth starch, rice starch, quinoa starch, taro starch, or the like, or various combinations thereof.

Statement 16. A starch-based particle according to Statement 14 or Statement 15, wherein at least a portion of the cationically-modified starch particles comprise amaranth starch.

Statement 17. A starch-based particle according to any one of Statements 14–16, wherein the anionically-modified starch particle comprises corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or the like, or various combinations thereof.

Statement 18. A starch-based particle according to any one of Statements 14–17, wherein the anionically-modified starch particle comprises corn starch.

Statement 19. A starch-based particle according to Statement 18, wherein the anionically-modified starch particle (e.g., anionically-modified corn starch particle) has one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof. In various embodiments, the anionically-modified starch particle (e.g., anionically-modified corn starch particle) has one or more carboxylic acid groups or carboxylate groups.

Statement 20. A starch-based particle according to any one of Statements 14–19, wherein the cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) have one or more trimethylammonium groups or one or more dimethylammonium groups. In various embodiments, the cationically-modified starch particles (e.g., cationically-modified amaranth starch particles) have one or more trimethylammonium groups.

Statement 21. A starch-based particle according to any one of Statements 14–20, wherein the anionically-modified starch particle (e.g., anionically-modified corn starch particle) has an amylose content of 0–70% prior to fusion to the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles). In various embodiments, the corn starch has an amylose content of 0%, 25%, 55%, or 70% prior to fusion to the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles). In various embodiments, the anionically-modified starch particle (e.g., anionically-modified corn starch particle) has an amylose content of 55% prior to fusion to the one or more cationically-modified starch particles (e.g., cationically-modified amaranth starch particles).

Statement 22. A starch-based particle according to any one of Statements 14–21, wherein the ratio of cationically-modified starch to anionically-modified starch (e.g., cationically-modified amaranth starch to anionically-modified corn starch) is 10:1 to 50:1 and the ratio is a weight percent ratio.

Statement 23. A starch-based particle according to any one of the preceding Statements, wherein the starch-based particle is 10–25 μm, including all 0.1 μm values and ranges therebetween.

Statement 24. A composition comprising one or more starch-based particles according to any one of the preceding Statements.

Statement 25. A composition according to Statement 24, wherein the composition is a powder, tablet, paste, suspension, slurry, capsule, or gel.

Statement 26. A composition according to Statement 24 or Statement 25, comprising one or more aggregates comprising the one or more starch-based particles according to any one of Statements 1–23.

Statement 27. A composition according to Statement 26, wherein a portion of the aggregates individually comprise at least 20 starch-based particles.

Statement 28. A composition according to Statement 26 or Statement 27, wherein at least 80% of the starch-based particles have formed aggregates comprising at least 20 starch-based particles.

Statement 29. A composition according to any one of Statements 24–28, wherein the aggregates have an average size of 400 μm^2 or larger. This size is an area of aggregation from image processing during microscopy.

Statement 30. A composition according to any one of Statements 24–29, wherein the composition has a storage modulus of $>10^3$ Pa at a frequency of 1 Hz.

Statement 31. A composition according to any one of Statements 24–30, wherein the composition is 25% by weight the starch-based particles.

Statement 32. A composition according to any one of Statements 24–31, wherein the composition is a food additive.

Statement 33. A composition according to any one of Statements 24–32, wherein the composition is a thickener or a texturizer.

Statement 34. A composition according to any one of Statements 24–33, wherein the one or more starch-based particles are present at a concentration of 1–40% by weight.

Statement 35. A composition according to any one of Statements 24–31, 33, or 34, further comprising one or more small molecules and/or biologically active component.

Statement 36. A composition according to Statement 35, wherein the one or more small molecules are chosen from antibiotics, antifungals, chemotherapy agents, antivirals, analgesics, anesthetics, and the like, and combinations thereof.

Statement 37. A composition according to Statement 35, wherein the biologically active component is a biologic.

Statement 38. A composition according to Statement 35 or Statement 37, wherein the biologically active component is a protein, peptide, cDNA, siRNA, mRNA, monoclonal antibodies, or the like, or any combination thereof.

Statement 39. A composition according to any one of Statements 24–31 or 33–38, further comprises one or more cosmetic components.

Statement 40. A composition according to Statement 39, wherein the one or more cosmetic components are chosen from scented ingredients (e.g., essential oils and the like), exfoliating agents (e.g., salicylic acid and the like), lubricants (e.g., hyaluronic acid and the like), anti-cellulite agents (e.g., caffeine and the like), and the like, and various combinations thereof.

Statement 41. A food product comprising the one or more starch-based particles according to any one of Statements 1–23 or the composition according to any one of Statements 24–33.

Statement 42. A food product according to Statement 41, wherein the food product is a sauce, a soup, a filling, a custard, a pudding, a dessert, a dressing, or the like.

Statement 43. A method for making starch-based particles according to any one of Statements 1–23, comprising: hydrating partially gelatinized starch (e.g., partially gelatinized corn starch) and a different starch (e.g., amaranth starch) with water; combining the partially gelatinized corn starch and amaranth starch at a ratio of 10:1 to 50:1 by weight (partially gelatinized corn starch to amaranth starch) to form a mixture; incubating the mixture at a temperature in the range of 25–50 °C for 5 to 15 minutes; centrifuging the mixture at 8,000-15,000 g for 5 to 15 min; and removing a supernatant from the mixture, wherein the starch-based particles remains.

Statement 44. A method according to Statement 43, wherein at least a portion of the different starch comprises amaranth starch, rice starch, quinoa starch, taro starch, or the like, or various combinations thereof.

Statement 45. A method according to Statement 43 or Statement 44, wherein at least a portion of the cationically-modified starch particles comprise amaranth starch.

Statement 46. A method according to any one of Statements 43–45, wherein the partially gelatinized starch comprises corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or the like, or various combinations thereof.

Statement 47. A method according to any one of Statements 43–46, wherein the partially gelatinized starch comprises corn starch.

Statement 48. A method according to any one of Statements 43–47, wherein the ratio of partially gelatinized starch (e.g., partially gelatinized corn starch) and different starch (e.g., amaranth starch) is 50:1 by weight.

Statement 49. A method according to any one of Statements 43–48, wherein the partially gelatinized starch (e.g., partially gelatinized corn starch) is modified such that it comprises one or more anionic groups.

Statement 50. A method according to Statement 49, wherein the one or more anionic groups are carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof.

Statement 51. A method according to Statement 49 or Statement 50, wherein the one or more anionic groups are carboxylate groups.

Statement 52. A method according to any one of Statements 43–51, wherein the different starch (e.g., amaranth starch) is modified such that is comprises one or more cationic groups.

Statement 53. A method according to Statement 52, wherein the one or more cationic groups are quaternary amines.

Statement 54. A method according to Statement 53, wherein the quaternary amines are alkylated ammonium groups.

Statement 55. A method according to Statement 54, wherein the alkylated ammonium groups are trimethylammonium groups or dimethylammonium groups.

Statement 56. A method according to any one of Statement 54 or Statement 55, wherein the alkylated ammonium group is a trimethylammonium group.

Statement 57. A method according to any one of Statements 43–56, wherein the partially gelatinized starch (e.g., partially gelatinized starch) and different starch (e.g., amaranth starch) are hydrated with water at a ratio of 1:5 (starch to water) by weight.

[0067] The following example is presented to illustrate the present disclosure. It is not intended to be limiting in any matter.

EXAMPLE

[0068] This example provides a description of particles of the present disclosure.

[0069] The work presented here describes a new approach to develop a scalable modification method to yield a heterogeneous surface on corn starch granules.

[0070] The granular size of starch depends on the botanical sources and can vary from 1 μm (amaranth starch) to over 50 μm (potato starch). A possible approach to prepare a fused starch particle is partial gelatinization. Alcohols precipitate starch from aqueous solutions and have been used to limit the degree of gelatinization. With the hydrothermal treatment in aqueous alcohols, the granules would still maintain the intact shape, even though the double helices of starch dissociate. Alcohols have also been shown to enter the single helix of amylose forming metastable inclusion complexes. When the partially gelatinized starch was redispersed in water, the granules swell, and exhibit lower particle stiffness and higher deformability due to the decreased crystallinity. It was hypothesized that the swollen starch would fuse particles together as the conformational entropy of the polymer chains increases with partial gelatinization, and the tangled chains would fuse after dehydration re-forming crystallized particles. In addition to surface modifications, this project investigated methods for creating charged starches to fabricate starch-based patchy particles with a negatively charged core and positively charged patches. Our design aims to allow starch granules to interact and associate into superstructures that could be able to trap water and improve viscoelasticity. The starch with the enhanced rheological properties would act as stronger thickener and as such the food industry could use less starch to achieve the same textures, and consumers can reduce the calorie intake from the energy dense carbohydrates.

[0071] Materials and methods.

[0072] Materials. Corn starch (Hylon V, amylose content = 55%) was purchased from Ingredion (IL, USA). Ethyl alcohol (> 99% purity) was purchased from bioPLUS (NY, USA). Chloroacetic acid, sodium hydroxide, epoxy-propyltrimethylammonium chloride (ETMAC), sodium chloride, and calcium chloride were obtained from Sigma-Aldrich (MO, USA).

[0073] Extraction of amaranth starch. The amaranth starch was extracted from amaranth flour by a previously published method. Specifically, amaranth flour (100 g) was blended with 500 mL of a 0.15 % w/v NaOH solution at ambient temperature for 60 min. The mixture then was sieved (53 μm mesh opening, VWR, IL, USA) with a laboratory shaker (Derrick Mfg. Co., Buffalo, NY, USA). The fine starch granules dispersed in liquid passed through the sieve and the remaining solid was redispersed in fresh NaOH solution (100 mL) followed by another 10 min of mixing. The extract was filtered using the sieve with 53 μm mesh opening and combined with the first batch, which was then centrifuged at 3,000 *g* for 20 min. The supernatant was discarded, and the top brown protein layer was removed using spatula. The sediments were redispersed in deionized water with pH adjusted to 6.0 ± 0.1 using 1 M HCl. The yellow protein layer that formed after pH adjustment was removed again to purify the starch. The remaining lower white layer was freeze-dried and ground into powders. The isolated starch contained 2.4% protein and 2.2% fat.

[0074] Preparation of partially gelatinized starch. The starch was partially gelatinized by hydrothermal processing in alcohol as previously published. Specifically, 100 g of native starch was mixed with 500 mL of aqueous ethanol (50% v/v for amaranth starch and 30% v/v for corn starch). The starch-in-solvent suspensions were heated at 80 °C for 30 min. After thermal incubation, 100 mL ethanol was added to the slurry, and the starch was then filtered (Grade 1, Waterman). The filtered starch was washed three times with ethyl alcohol, and the solvent was removed in an oven at 80 °C for 8 h to remove residuals. The dry starch was ground with a homogenizer (Oster 2095357, FL, USA) for 2 min, and the powder was sieved (#50 mesh) then stored for future use.

[0075] Preparation of negatively charged corn starch. The corn starch was modified to carry a negative charge by the large based on the carboxylation by chloroacetic acid. Specifically, 50 g of NaOH was dissolved in 266 mL DI water, and 1,066 mL ethanol was added to the alkaline solution. Chloroacetic acid (81.3 g) was then added, and the mixture was stirred for 1 h, after which, 100 g of partially gelatinized corn starch was mixed with the reaction solution. The mixture was stirred for 2 hours at room temperature, and the resulting slurry was filtered using a Whatman Grade 1 filter paper and the solid collected was washed with 80% ethanol. The washed starch was subsequently centrifuged at 3,000 *g* for 3 min and then washed with additional 80% ethanol and centrifuged twice more. The starch was then dispersed in 200 mL DI water and 0.1 M HCl was used to adjust the pH to 7 to neutralize residual NaOH. The neutralized starch was centrifuged (3000 *g* for 3 min) and washed twice to remove residual salts. The starch pellet was freeze-dried for further use.

[0076] Preparation of cationic amaranth starch. The amaranth starch was positively charged by a modification method previously established. Specifically, we dispersed 1 g amaranth starch in 2 mL of water containing 1.91 g of ETMAC. The pH of the slurry was adjusted to 10.5 using 0.1 M NaOH. The mixture was then stirred at room temperature for 24 hours after which, the slurry was centrifuged (5000 *g* for 3 min) and the sediment was further washed with DI water twice, and the collected starch was further washed using ethanol. The starch was dried in a ventilated oven at room temperature.

[0077] Preparation of patchy starch via particle fusion. Separately, partially gelatinized corn starch and amaranth starch were hydrated with excess water (starch:water ratio = 1:5). Then these solutions were mixed (with amaranth-starch-to-corn-starch ratio at 10:1 or 50:1), and incubated at different temperature (25, 40, or 50 °C) for 5 or 20 min. After incubation the solutions were centrifuged (8000 *g*, 12000 *g*, or 15000 *g*) for different durations (5 or 15 min). When the granules are swollen with water, the starch granules were less rigid, and the conformational freedom of polymer chains increases owing to less hydrogen bonding. Therefore, the swollen granules interpenetrated the other granules while being centrifuged, and the polymer chains tangled together. After centrifuging, the clear supernatant was decanted, and the starch was dried in a ventilated oven at room temperature for 96 h and then stored at 4 °C for further characterization.

[0078] Attenuated total reflectance-Fourier transform infrared spectroscopy (FTIR). The FTIR spectra of starches were measured with an ATR-FTIR (Affinity-1S, Shimadzu) to identify the chemical composition of the charge modification of starch. Samples were measured from 400 to 4000 cm^{-1} in transmittance mode with 2 cm^{-1} resolution and 128 scans.

[0079] Zeta-potential. The zeta-potential of starches was measured with a NanoZS90 zeta-sizer (Malvern Instrument Ltd., UK) with a He/Ne laser ($\lambda = 633$ nm) at 25 °C. Starch was homogenized in water (0.1%); the zeta-potential was calculated from electrophoretic mobility based on the Smouluchowski model and was reported as an average value from triplicates.

[0080] X-ray diffractometry (XRD). The XRD patterns of the starch samples were collected using a Bruker D8 Advance ECO powder diffractometer (MA, USA) operating at 40 kV and 25 mA with Cu Kα radiation. The samples were examined for the angles 2θ between 5° and 40°.

[0081] Scanning electron microscopy (SEM). Samples were coated with Au-Pd using a sputter coater (Denton Desk V, NJ, USA). The coated samples were examined with an SEM (Zeiss Gemini 500, Jena, Germany). Objects were scanned with 1 keV and imaged by a high efficiency secondary electron detector with a 20.0 μm aperture.

[0082] Water-holding capacity. To study the water-holding capacity, 0.5 g dry starch was weighed in a 15 mL tube and 5 mL water was added. The slurry was mixed vigorously for 1 min. The self-assembly sedimentation occurred overnight, and the volume of the sediment was recorded. The water held in the slurry was calculated by deducting out supernatant volume. Experiments were carried out in triplicate.

[0083] Quantification of flocculation. To visualize the flocculation of the patchy particles, a diluted starch slurry (2%) was prepared. The slurry was vortexed and homogenized with a high-shear mixer at 5,000 rpm for 1 min, and 20 μL of each sample was transferred to a glass slide and covered with slip. The suspension was examined by a Leica Model DMIL LED Inverted Phase Contrast Microscope (100x). For each sample, 10 images were taken which contained > 10,000 particles in total, and the particle size was quantified using ImageJ (v1.51, National Institute of Health, USA) with pixel calculation. The mean size (μm^2) for each sample was recorded.

[0084] Rheological measurements. The dynamic oscillation study was conducted using a rheometer (Anton Paar MCR301, Graz, Austria) with a 25 mm parallel plate and the gap set at 0.5 mm. The slurry containing 25 wt% starch was prepared. The storage modulus (G') and loss modulus (G'') were recorded using the amplitude sweep (1 Hz, 0.1-100% strain) to scan the linear region. The 0.3% strain was chosen, and the frequency sweep was conducted from 0.5-100 Hz. The rotational shear study was also carried out from 0.01-100 s^{-1} and viscosity was plotted against shear rate.

[0085] Statistical analysis. Analyses were carried out in triplicates and the results were presented as means ± standard deviations, which were tested by one-way analysis of variance (ANOVA) using JMP Pro (Version 14, SAS Institute, USA) to identify significant difference ($p < 0.05$).

[0086] Results and Discussion.

[0087] Fabrication of starch-based patchy particles.

[0088] The hydrogen bonding in starch can be disrupted by thermal processing at temperatures higher than its gelatinization temperature in aqueous alcohol. Ethanol as the precipitant of starch is able to inhibit amylose leaching and the original granular shape of the starch is maintained. This partial gelatinization allows the starch to absorb the water and the swollen starch becomes softer, less crystalline. The XRD curves (Figure 1) indicate that native starch exhibits typical B-type crystals with peaks at 5.5°, 15°, 17°, 20°, and 22.5°, which were in agreement with the data reported previously. After partially gelatinized starch were produced by hydrothermal processing in aqueous alcohol, however, those peaks diminished suggesting the dissociation of the hydrogen bonding between polymer chains and thus lower crystallinity.

[0089] The partially gelatinized starch undergoes retrogradation, which refers to the spontaneous process by which disordered polymer chains recrystallize. The patchy starch after dehydration showed recovered crystallization compared with the partially gelatinized starch (Figure 1). During storage, water evaporates allowing the hydroxyl groups on the polymer chains to get close enough to reform the hydrogen bonds. Although retrogradation is usually considered an undesirable process for food products causing bread staling, it can also be utilized as an approach to construct patchy particles.

[0090] Patchy starch formed after centrifuging the partially gelatinized starch under the mild processing conditions of incubation at room temperature, followed by centrifugation at 8,000 *g* for 5 min (Figures 2a and 2b). The starch granules interpenetrated each other as the partially gelatinized swollen starch turned less rigid, then, after centrifugation and dehydration, the starch particles were fused together, though the connection was only less than one quarter of amaranth starch granule (Figure 2b). When the patchy starch was re-dispersed in water (Figure 2c), a considerable amount of amaranth starch granules dethatched as free particles in water, and only a small number remained attached to the main corn starch particles. The weak connection, less than 0.25 μm, could be the reason for the free particles observed (Figure 2c).

[0091] When starch was incubated at 50 °C for 20 min followed by high-speed centrifugation (15,000 *g*)for 20 min, the morphology changed significantly, and there was almost no observable amaranth starch (Figure 2d) although the mixing ratios used were the same. The image captured at higher magnification (Figure 2e) shows the connection is much stronger such that almost the entire body of the small particle has been fused into the large particle suggesting that the higher incubation temperature and stronger centrifugation strengthened the connection. It would be reasonable to hypothesize that the amaranth particles could be completely engulfed as many of the small particles were missing (Figure 2d). When the patchy starch was re-dispersed in water (Figure 2f), only few free amaranth starch granules were observed. It should be noticed the starch presented in Figure 2 were all uncharged, suggesting that the majority of the small particles were physically grafted onto the corn starch rather than attracted by the electrostatic interaction, which is also attributed to the stronger fusion of particles.

[0092] The principle behind fabricating starch-based patchy particles is attributed to the partially gelatinized and hydrated starch granules. The softening of the starch granule is an indication of the increased degree of freedom of polymer chains and then the strong centrifugation helps them penetrate into the other granules. The polymer chains tangle together, and during the processing of dehydration and refrigeration, can recrystallize through hydrogen bonding. This retrogradation allows multiple particles to fuse as a single particle.

[0093] Although the intense treatment enhanced the connection between the patches and the primary granule, it was found that after treatment there was a small amount of amaranth starch granules extremely gelatinized, which was not entirely unexpected due to the elevated incubation temperature. During centrifugation these extremely swollen granules rise to the top of starch sediments due to their lighter density. This thin layer of gelatinized starch on the top retained moisture well and slowed down recrystallization. Therefore, an intermediate processing condition was used: incubation at 40 °C for 15 min followed by centrifugation at 12,000 *g* for 15 min. The patchy starch prepared under these conditions showed that about half of the particle body of the amaranth starch had fused (Figure 8a). A patch where a small particle had indicated that two particles were physically stitched together via molecular entanglement (Figure 8b). Because the intermediated conditions (incubation at 40 °C for 15 min, centrifugation at 12,000 *g* for 15 min) was able to produce fused particles with a shorter dehydration process, these samples were the focus of the studies herein.

[0094] Effect of charge and patchy modification on starch functionality

[0095] The infrared (FTIR) spectra of native corn starch and carboxylated corn starch has a band at 1750 cm^{-1} which is attributed to the C=O stretching from carboxyl groups (Figure 3a). The carboxyl modification gives the starch a negative charge which we observe at -19.1 mV at neutral pH (Figure 3c). The FTIR spectra shows that the native amaranth starch exhibits a band at 1750 cm^{-1} (Figure 3b) suggesting the presence of carbonyl groups, which can be attributed to the minor protein content (~2.5%) after extraction from flour. The negative zeta-potential (–19.4 mV) of the native amaranth starch was also rendered by the minor protein content (Figure 3d). After cationic modification using ETMAC, the amaranth starch had a zeta-potential of +19.6 mV (Figure 3d) and the carbonyl band on FTIR spectra was diminished, confirming that the ETMAC reacted with the carboxyl group of the proteins. Additionally, the new band at 1300 cm^{-1} can be attributed to the C-N stretch indicating the presence of the trimethyl ammonium group.

[0096] The charged starches were physically fused together and exhibited a negatively charged core and positively charged patches on the surface. When the charged patchy starch was re-dispersed in water, the particles were able to assemble via electrostatic interactions (Figure 4a) resulting a heterogeneous opacity, and the flocculated starch sedimented to the bottom after 10-min settling. The amount of water held in the sediments was quantified. The rheological moduli, and viscosity of uncharged, mixed charged, and patchy charged starches were also examined (Figure 4). The control group of uncharged starch held 2.1 g water per unit of starch in the slurry sediment, but when starch particles are oppositely charged (corn starch negatively charged and amaranth positively charged) the mixture was able to hold 3.3 g water per unit of starch (Figure 4b). When the charged particles are physically fused into patchy starch, the water-holding capacity increased further to 5.7 g per unit starch. The rheological study shows that the slurry of uncharged mixed starch exhibits a weak storage modulus which was below detection limits when the angular frequency was higher than 10 s^{-1}, suggesting that the control group behaves fluid-like (Figure 4c). However, the charged groups showed an increase in rheological moduli, and the G' was higher than G'' indicating that the behavior was dominated by storage modulus and the slurries showed gel-like behavior (Figure 4c). Improvement was also observed on the viscosity of the physically fused patchy starch with heterogeneously charged surface which was two-orders of magnitude higher compared with the uncharged starch (Figure 4d). The viscosity-enhancing effect was more pronounced when particles were physically stitched together when compared with the mixed charge particles. The higher flexibility of mixed particles is most likely why they were not as effective at trapping water. The slurry of native starch was a Newtonian fluid with a constant viscosity under shear, but the charged groups exhibited shear-thinning with low viscosity at higher shear rates, which can be attributed to the dissociation of short-distance electrostatic interactions when shear rate increased.

[0097] The charge-induced flocculation formed pockets which trapped water molecules and inhibited the movement of liquid which led to enhanced functionalities. Starch granules were dispersed individually in the slurry of native corn starch (Figure 9a), while the charged patchy starch in water showed significant flocculation (Figure 9b). The images examined by microscope were processed to quantitatively characterize the interaction between particles. The suspension of native corn starch in water showed particle sizes calculated by pixels was 127.9 μm^2 based on image processing of over 10,000 particles (Figure 5a). The particle distribution indicated that 51.4% of starch in native corn starch samples are present as individual particles (Figure 5b). However, when starch was charged and physically fused (Figure 3c), particles flocculated to a large extent, 86.2% of starch particles formed the large clumps (> 20 particles) and only 1.3% particles were in the individual state, with the average size of all particles in the sample as high as 437.3 μm^2 (Figure 5d).

[0098] Effect of charge and patchy modification after gelatinization and mechanical processing on starch functionality

[0099] Starch present in foods is usually gelatinized. The viscoelasticity of a starch slurry after gelatinization at 90 °C for 10 min, showed that the charge modification and patchy fusion enhanced both storage and loss modulus, which is similar to the observation of the non-gelatinized starch (Figures 6a and 6b). This means that the heating process did not impair the charged-induced interaction. As mechanical stress is usually involved in food processing, the viscosity of gelatinized starch was tested after blending with a homogenizer for 5,000 rpm for 1 min. The shearing process after gelatinization was found to not be an issue for the charged-induced interaction meaning that this platform could be used as a shear-reversible thickener in the food industry. The difference between a mixed group and fused group was less obvious after homogenization (Figure 6c), which is likely due to the dissociation of the patchy construction at high shear.

[0100] Conclusions

[0101] The present disclosure provides a facile method for preparing patchy particles using two different sized starches as food-grade ingredients, and it is the first time a study of heterogeneous surface model has been extended to biodegradable natural materials. After partial gelatinization, the swollen starch granules were centrifuged and dehydrated, which yielded a corona-shaped patchy structure where the smaller amaranth starch grafted onto the larger corn starch particles. Further the patchy starch exhibited an anionic core and cationic patches after charge modification. The patchy particles also showed higher water-holding capacity as the interparticle interactions allowed water to be trapped in pockets of the superstructure formed by granules. This impacted the rheological properties with the enhanced storage modulus, loss modulus, and viscosity as compared to the native starch and the mixed charged starch with the same blending ratio between amaranth and corn starch. The enhanced functionality of the patchy starch particles was stable to cooking and mechanical stress as the enhanced viscoelasticity was not impaired by the processing, showing potential as a shear-reversible texturizer in food products. It could be used to reduce the amount of calorie-dense starch from diets. Future work is needed to investigate the impact of fabrications, including patchiness and charge density, on the self-assembly properties, and overall functionality. The effects of different environmental factors such as pH and ionic strength also need to be evaluated in order to incorporate the charged patchy particles into the complicated food matrix.

[0102] Although the present disclosure has been described with respect to one or more particular embodiments and/or examples, it will be understood that other embodiments and/or examples of the present disclosure may be made without departing from the scope of the present disclosure.

Claims:

1. A starch-based particle having a core and a plurality of domains, wherein the plurality of domains are on an exterior surface of the starch-based particle, wherein the plurality of domains are a positively charged starch and the core is negatively charged or capable of being ionized to a negative charge.

2. The starch-based particle according to claim 1, wherein the core has one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof.

3. The starch-based particle according to claim 2, wherein the core has one or more carboxylic acid groups or carboxylate groups.

4. The starch-based particle according to claim 1, wherein the domains have one or more trimethylammonium groups or one or more dimethylammonium groups.

5. The starch-based particle according to claim 4, wherein the domains have one or more trimethylammonium groups.

6. The starch-based particle according to claim 1, wherein at least one of the plurality of domains comprises amaranth starch, rice starch, quinoa starch, taro starch, or combinations thereof.

7. The starch-based particle according to claim 6, wherein at least one of the plurality of domains comprises amaranth starch.

8. The starch-based particle according to claim 1, wherein the core comprises corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or combinations thereof.

9. The starch-based particle according to claim 8, wherein the core comprises corn starch.

10. The starch-based particle according to claim 1, wherein the core has an amylose content of 0–70%.

11. The starch-based particle according to claim 10, wherein the core has an amylose content of 0%, 25%, 55%, or 70%.

12. The starch-based particle according to claim 11, wherein the core has an amylose content of or about 55%.

13. The starch-based particle according to claim 1, wherein the core comprises corn starch and the plurality of domains comprise amaranth and the ratio of amaranth starch to corn starch is 10:1 to 50:1 and the ratio is a weight percent ratio.

14. A starch-based particle comprising one or more cationically-modified starch particles fused to an anionically-modified starch particle, wherein at least a portion of a surface of the one or more cationically-modified starch particles is displayed on an exterior surface of the anionically-modified starch particle.

15. The starch-based particle according to claim 14, wherein at least a portion of the cationically-modified starch particles comprise amaranth starch, rice starch, quinoa starch, taro starch, or combinations thereof.

16. The starch-based particle according to claim 15, wherein at least a portion of the cationically-modified starch particles comprise amaranth starch.

17. The starch-based particle according to claim 14, wherein the anionically-modified starch particle comprises corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or combinations thereof.

18. The starch-based particle according to claim 17, wherein the anionically-modified starch particle comprises corn starch.

19. The starch-based particle according to claim 17, wherein the anionically-modified corn starch particle has one or more carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof.

20. The starch-based particle according to claim 17, wherein the anionically-modified corn starch particle has one or more carboxylic acid groups or carboxylate groups.

21. The starch-based particle according to claim 15, wherein the cationically-modified amaranth starch particles have one or more trimethylammonium groups or one or more dimethylammonium groups.

22. The starch-based particle according to claim 21, wherein the cationically-modified amaranth starch particles have one or more trimethylammonium groups.

23. The starch-based particle according to claim 14, wherein the anionically-modified starch particle has an amylose content of 0–70% prior to fusion to the one or more cationically-modified starch particles.

24. The starch-based particle according to claim 16, wherein the ratio of cationically-modified starch to anionically-modified starch is 10:1 to 50:1 and the ratio is a weight percent ratio.

25. The starch-based particle according to claim 14, wherein the starch-based particle is 10–25 μm.

26. A composition comprising one or more starch-based particles according to claim 1 or claim 14.

27. The composition according to claim 26, wherein the composition is a powder, tablet, paste, suspension, slurry, capsule, or gel.

28. The composition according to claim 26, comprising one or more aggregates comprising the one or more starch-based particles.

29. The composition according to claim 28, wherein a portion of the aggregates individually comprise at least 20 starch-based particles.

30. The composition according to claim 28, wherein at least 80% of the starch-based particles have formed aggregates comprising at least 20 starch-based particles.

31. The composition according to claim 21, wherein a portion of the individual aggregates have an average size of 400 μm^2 or larger.

32. The composition according to claim 26, wherein the composition has a storage modulus of $>10^3$ Pa at a frequency of 1 Hz.

33. The composition according to claim 26, wherein the one or more starch-based particles are present at a concentration of 1–40% by weight relative to the total weight of the composition.

34. The composition according to claim 26, wherein the composition is 25% by weight the starch-based particles.

35. The composition according to claim 26, wherein the composition is a thickener or a texturizer.

36. The composition according to claim 26, wherein the composition is a food additive.

37. The composition according to claim 26, further comprising one or more small molecules and/or one or more biologically active components.

38. The composition according to claim 37, wherein the one or more small molecules are chosen from antibiotics, antifungals, chemotherapy agents, antivirals, analgesics, anesthetics, antiparasitics, and combinations thereof.

39. The composition according to claim 37, wherein the biologically active component is a biologic.

40. The composition according to claim 37, wherein the biologically active component is a protein, peptide, cDNA, siRNA, mRNA, monoclonal antibodies, or any combination thereof.

41. The composition according to claim 26, further comprises one or more cosmetic components.

42. The composition according to claim 41, wherein the one or more cosmetic components are chosen from scented ingredients, exfoliating agents, lubricants, anti-cellulite agents, and combinations thereof

43. A food product comprising the one or more starch-based particles according to claim 1 or claim 14.

44. The food product according to claim 43, wherein the food product is a sauce, a soup, a filling, a custard, a pudding, a dessert, or a dressing.

45. A method for making starch-based particles according to claim 1 or claim 14, comprising:

hydrating partially gelatinized starch and a different starch with water;

combining the partially gelatinized starch and the different starch at a ratio of 10:1 to 50:1 by weight (partially gelatinized corn starch to amaranth starch) to form a mixture;

incubating the mixture at a temperature in the range of 25–50 °C for 5 to 15 minutes;

centrifuging the mixture at 8,000-15,000 g for 5-15 min; and

removing a supernatant from the mixture,

wherein the starch-based particles remains.

46. The method according to claim 45, wherein at least a portion of the different starch comprises amaranth starch, rice starch, quinoa starch, taro starch, or combinations thereof.

47. The method according to claim 46, wherein at least a portion of the cationically-modified starch particles comprise amaranth starch.

48. The method according to claim 45, wherein the partially gelatinized starch comprises corn starch, potato starch, wheat starch, barley starch, pea starch, tapioca starch, or combinations thereof.

49. The method according to claim 48, wherein the partially gelatinized starch comprises corn starch.

50. The method according claim 45, wherein the ratio of partially gelatinized starch and different starch is 50:1 by weight.

51. The method according to claim 45, wherein the partially gelatinized starch is modified such that it comprises one or more anionic groups.

52. The method according to claim 51, wherein the one or more anionic groups are carboxylic acid groups or carboxylate groups, sulfonic groups, phosphate groups, or partially deprotonated/protonated species thereof

53. The method according to claim 51, wherein the one or more anionic groups are carboxylate groups.

54. The method according to claim 45, wherein the different starch is modified such that is comprises one or more cationic groups.

55. The method according to claim 54, wherein the one or more cationic groups are quaternary amines.

56. The method according to claim 55, wherein the quaternary amines are alkylated ammonium groups.

57. The method according to claim 56, wherein the alkylated ammonium groups are trimethylammonium groups or dimethylammonium groups.

58. The method according to claim 56, wherein the alkylated ammonium group is a trimethylammonium group.

59. The method according to claim 56, wherein the partially gelatinized starch and different starch are hydrated with water at a ratio of 1:5 (starch to water) by weight.

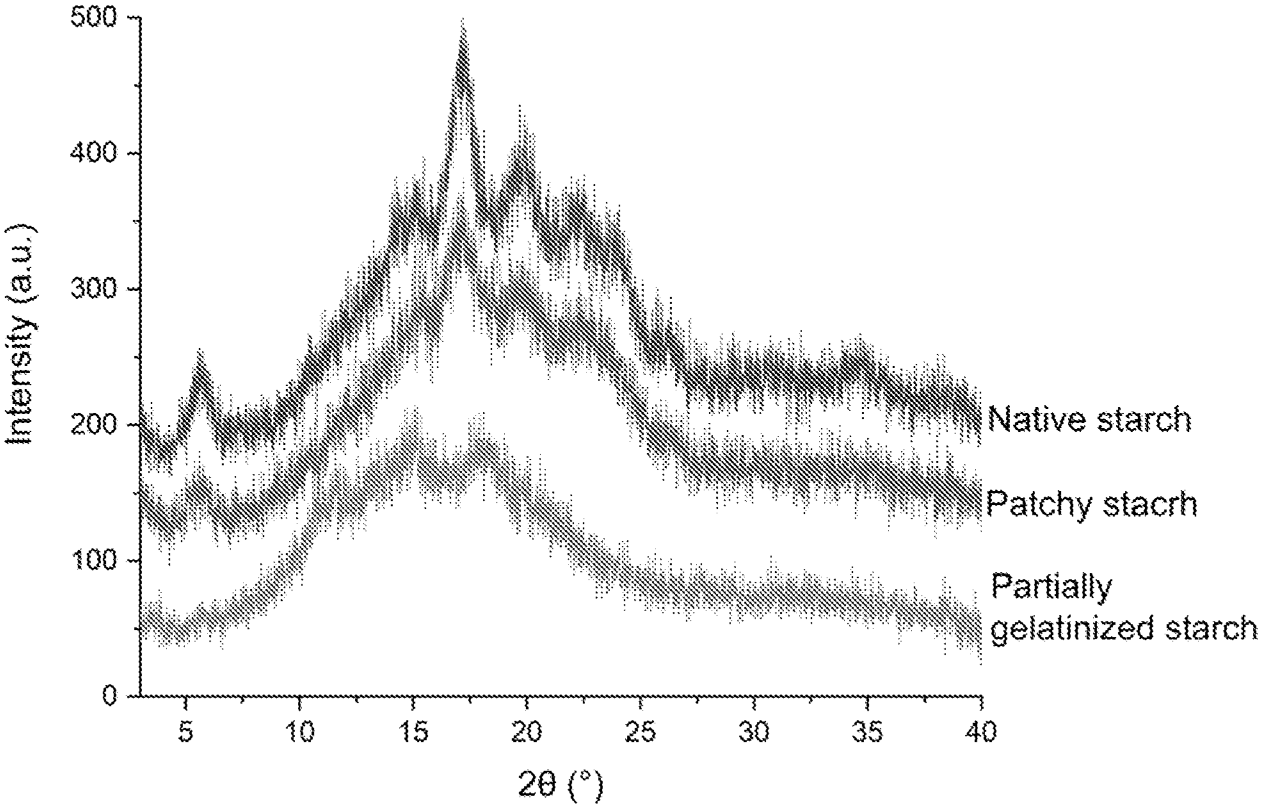


Figure 1

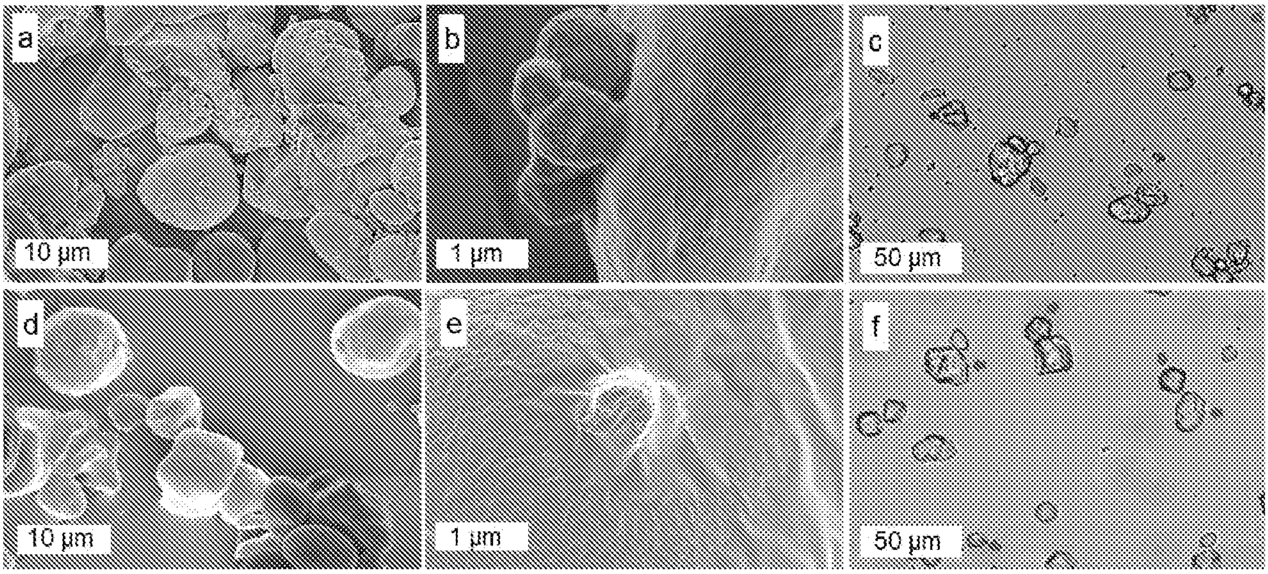
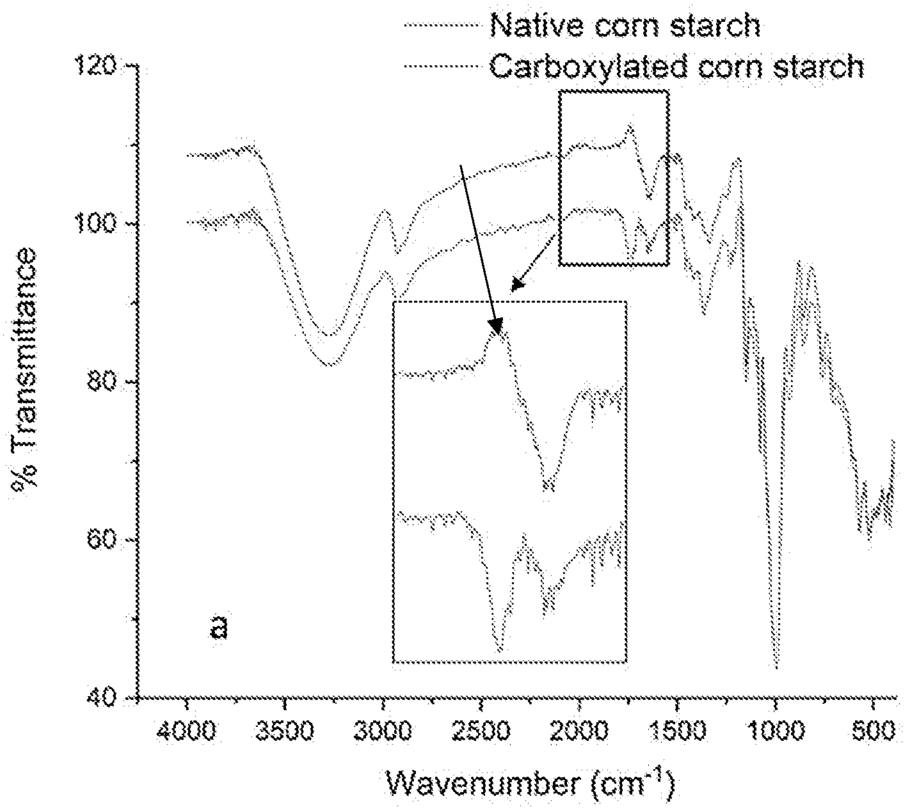


Figure 2


Native corn starch
Carboxylated corn starch
120
100
80
60
40
% Transmittance
a
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

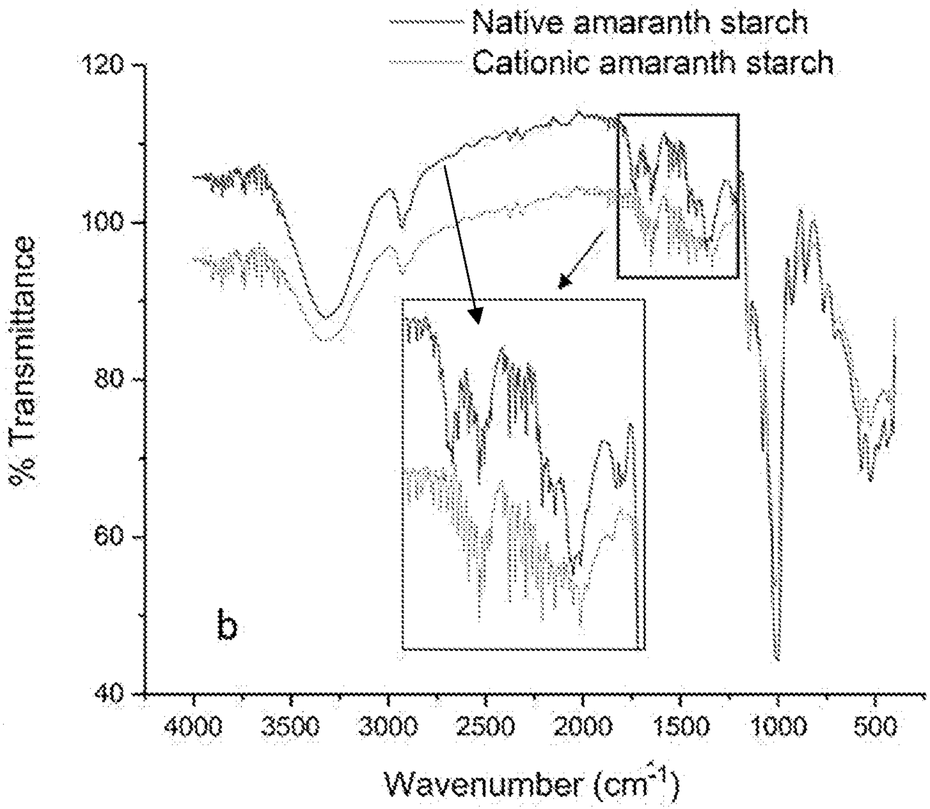
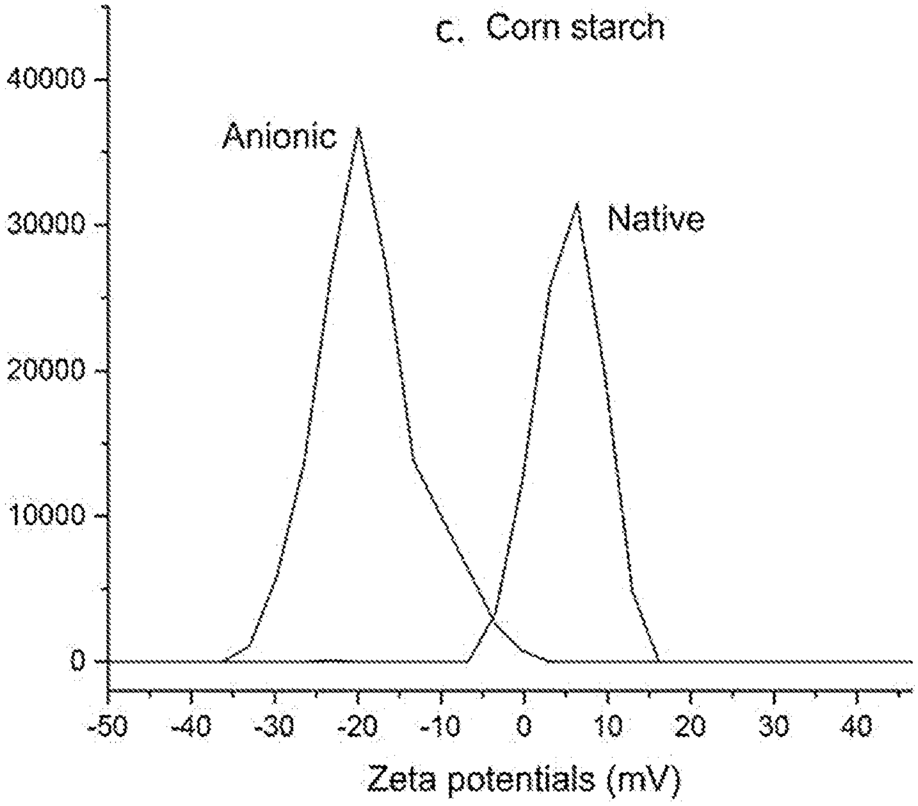

Native amaranth starch
Cationic amaranth starch
120
100
80
60
40
% Transmittance
b
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Figure 3



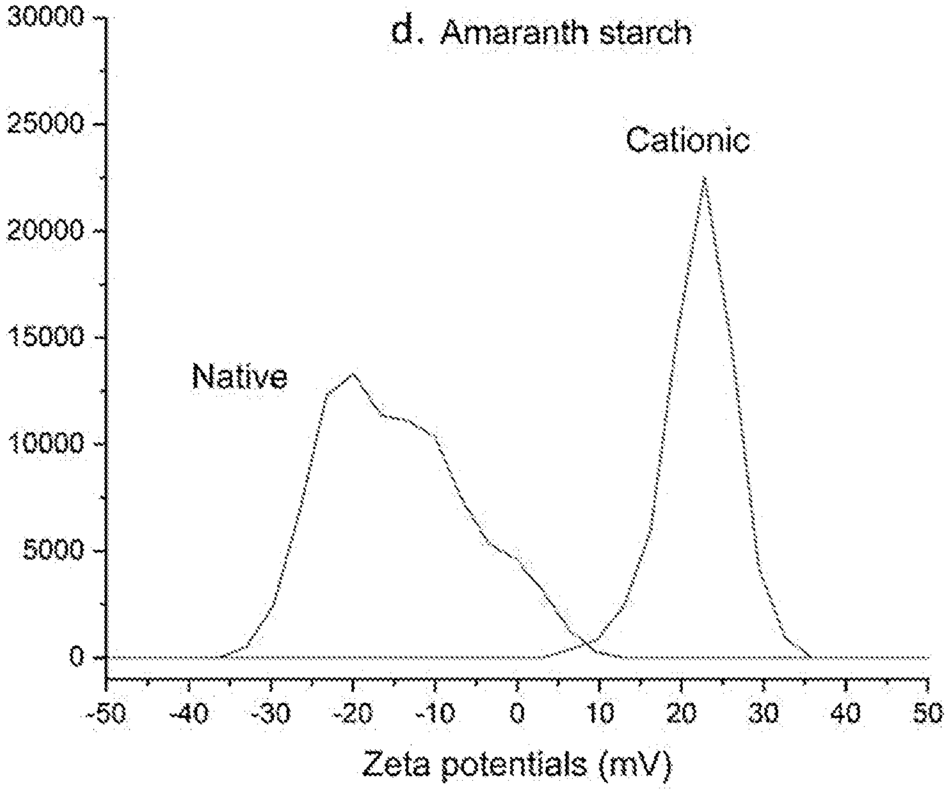


Figure 3 (continued)

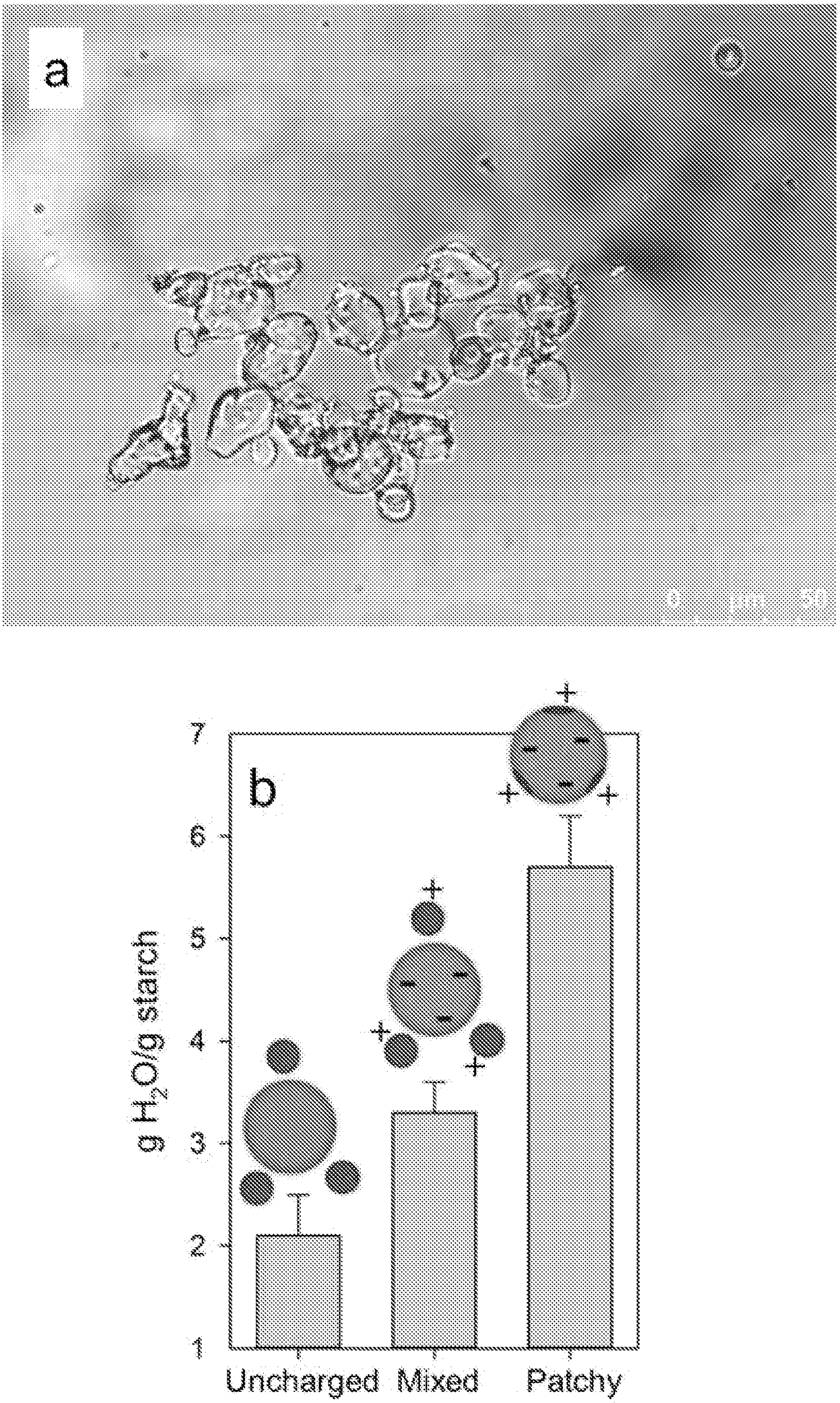
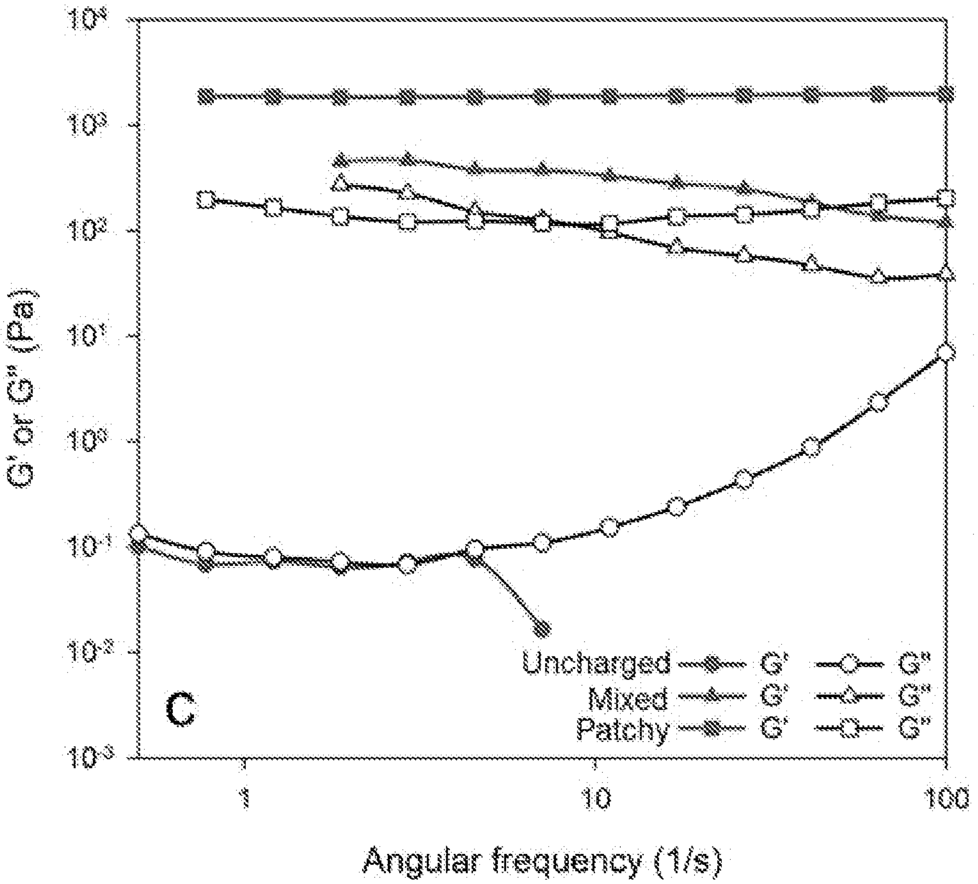


Figure 4



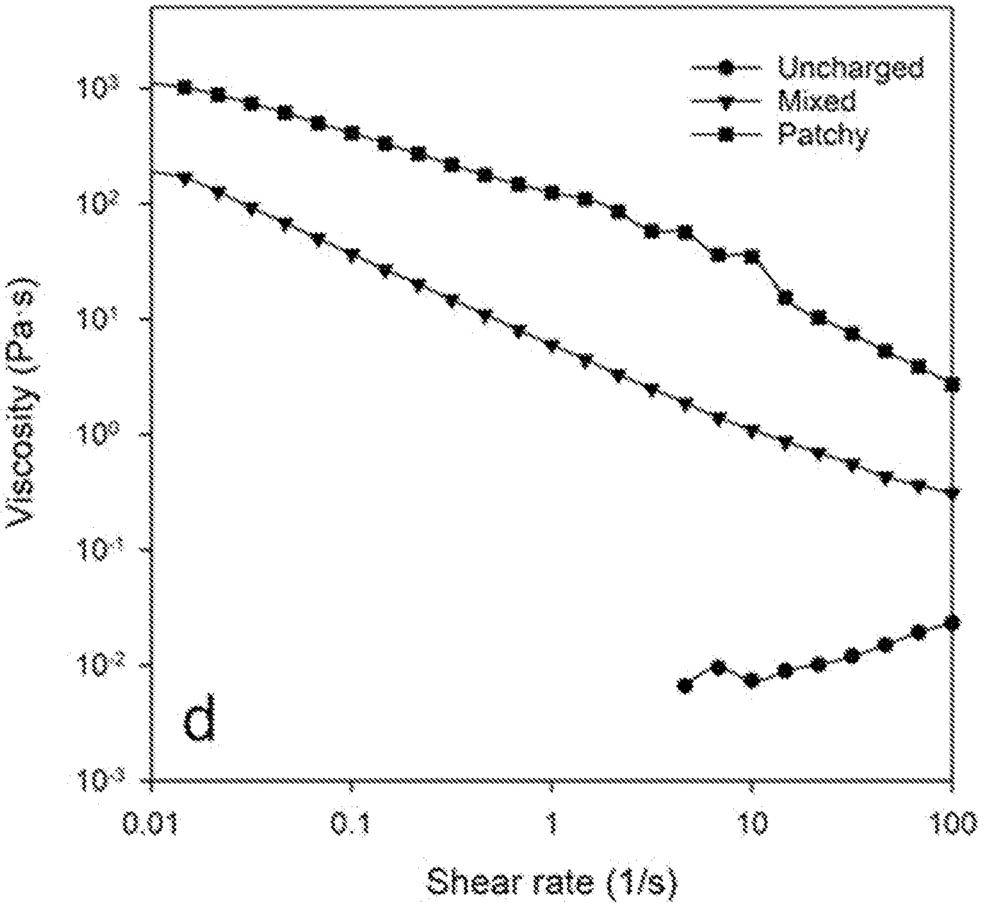


Figure 4 (continued)

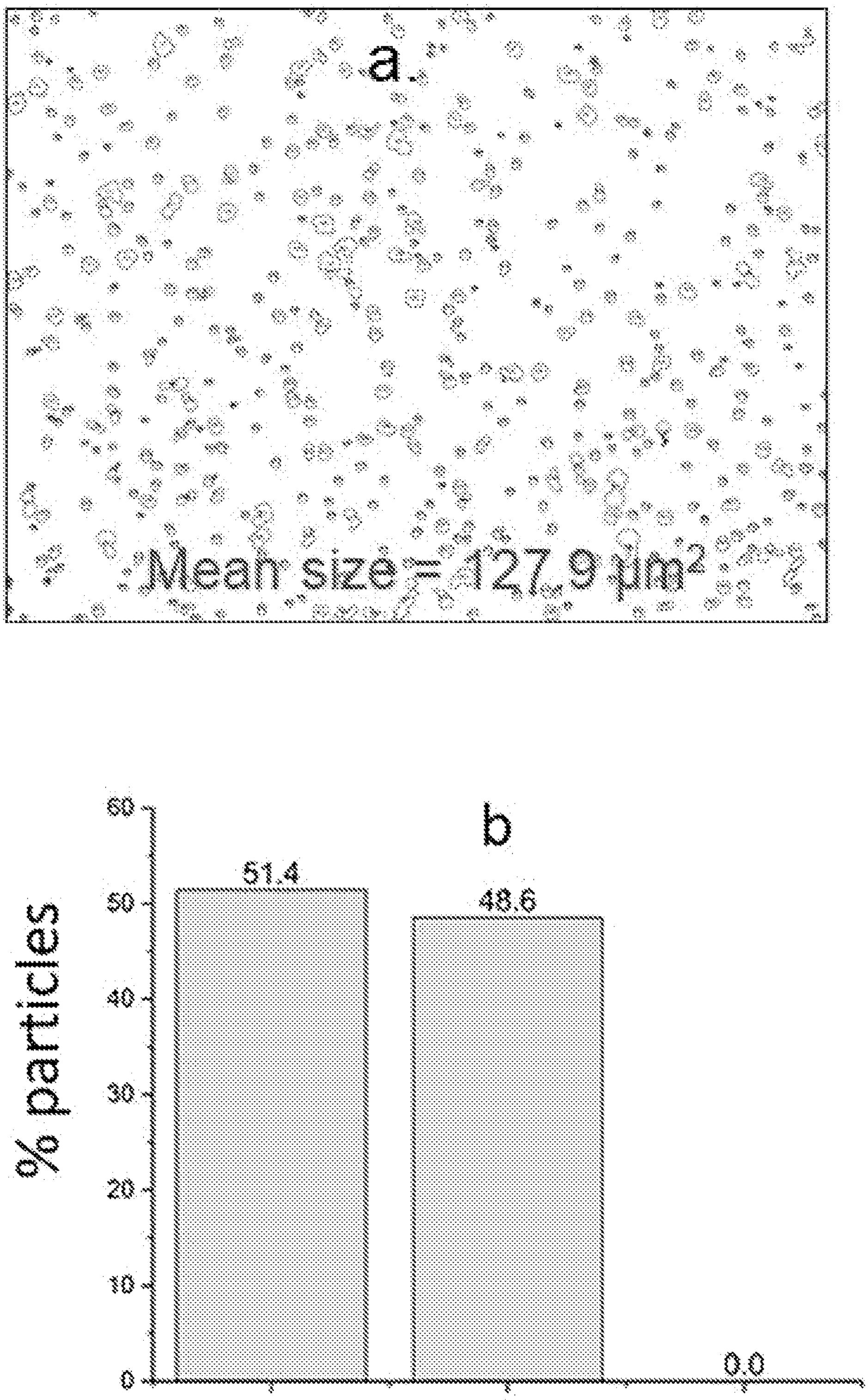
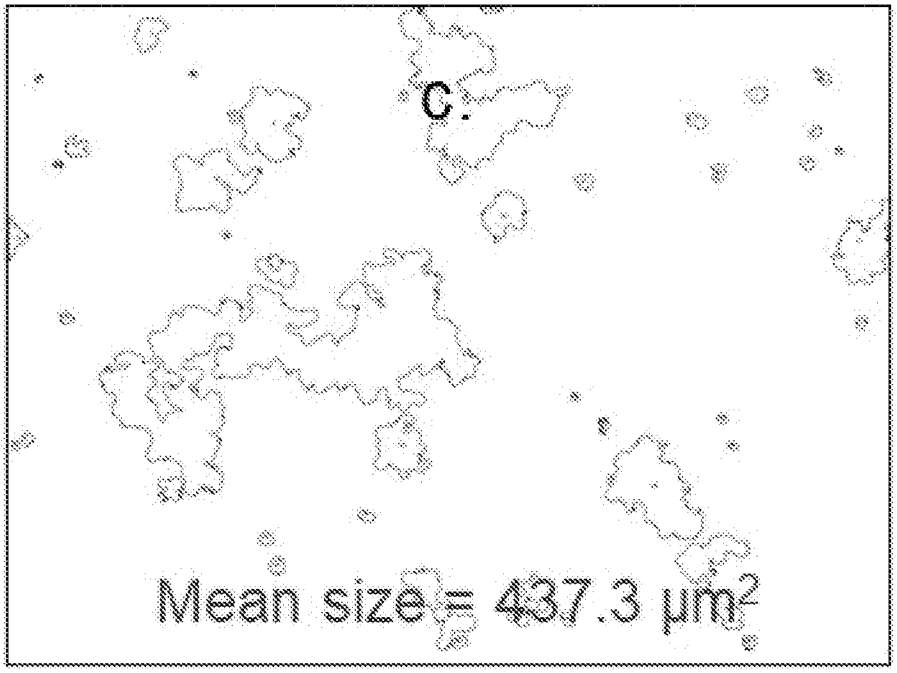


Figure 5



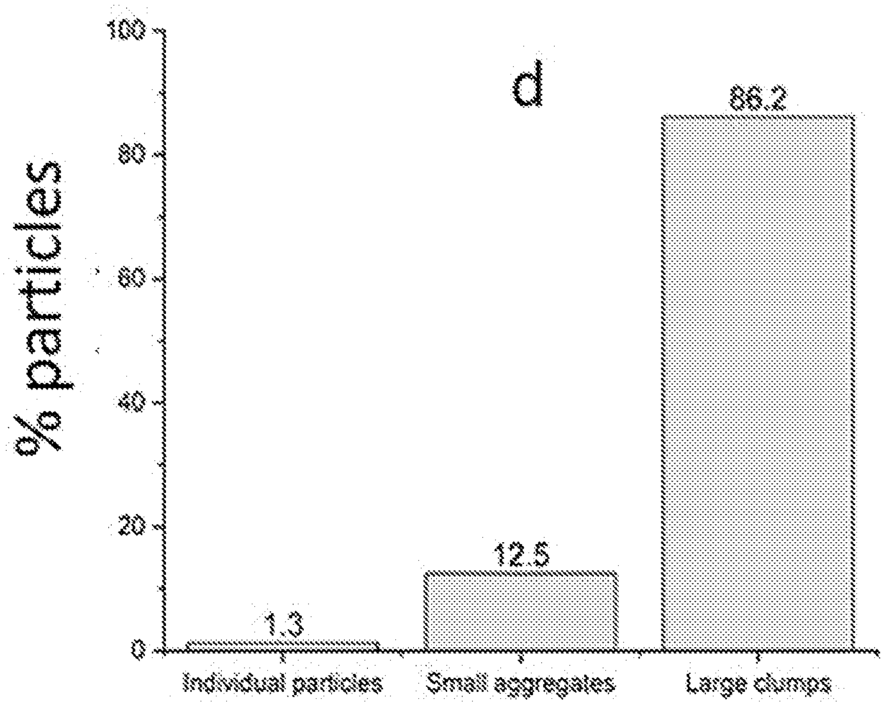


Figure 5 (continued)

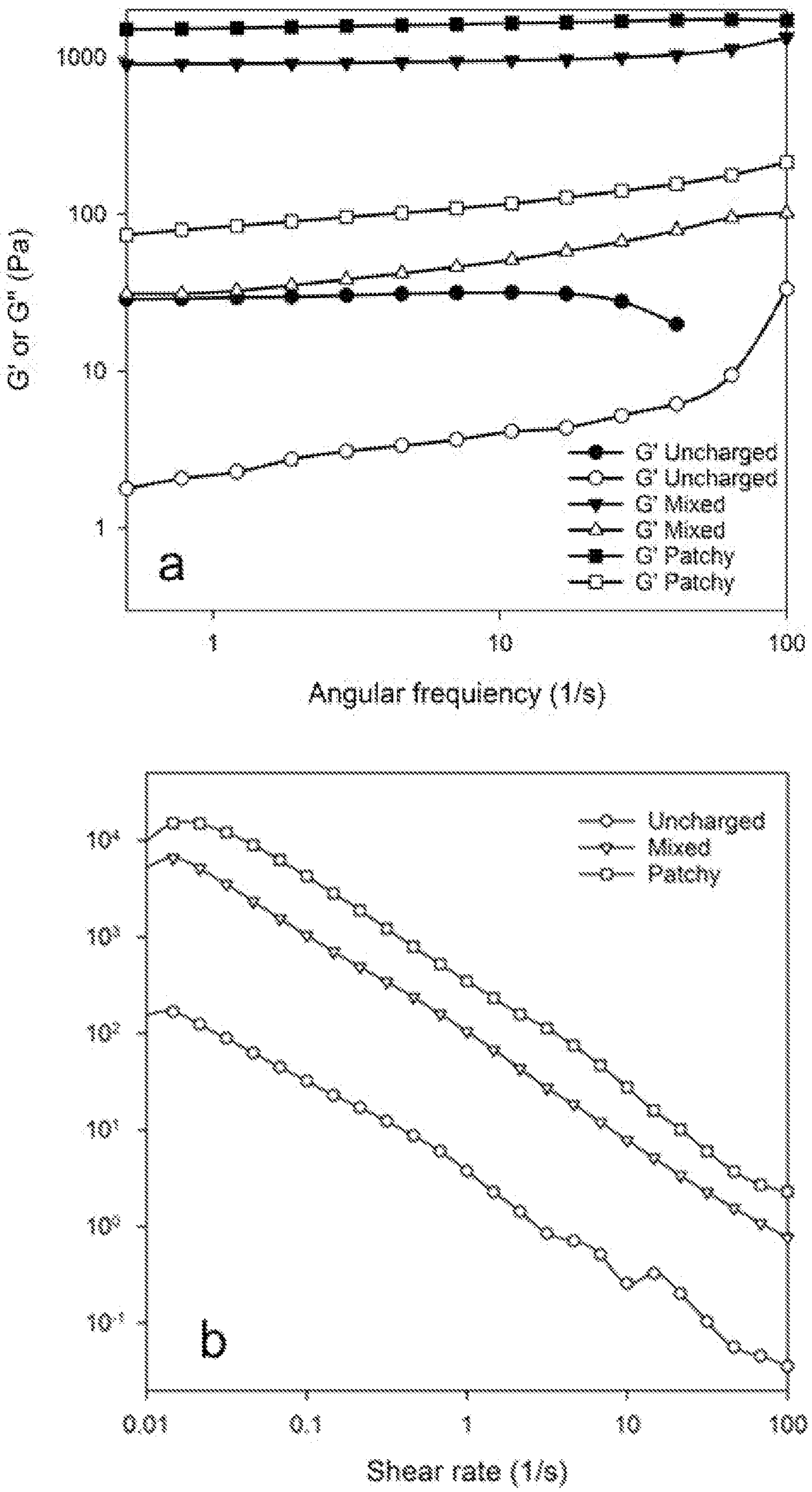

1000
100
10
1
G' or G" (Pa)
G' Uncharged
G' Uncharged
G' Mixed
G' Mixed
G' Patchy
G' Patchy
a
1
10
100
Angular frequency (1/s)
10⁴
10³
10²
10¹
10⁰
10⁻¹
Uncharged
Mixed
Patchy
b
0.01
0.1
1
10
100
Shear rate (1/s)

Figure 6

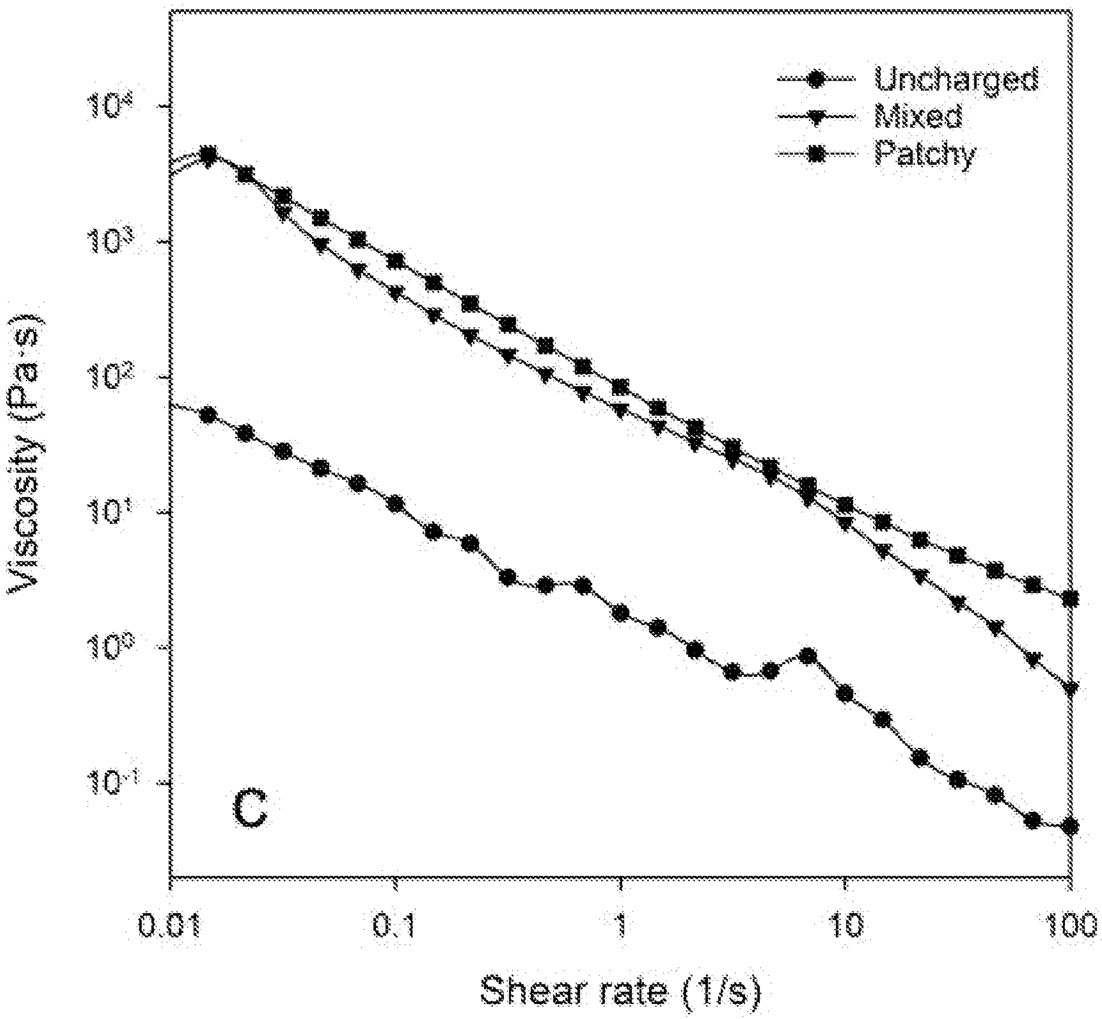


Figure 6 (continued)

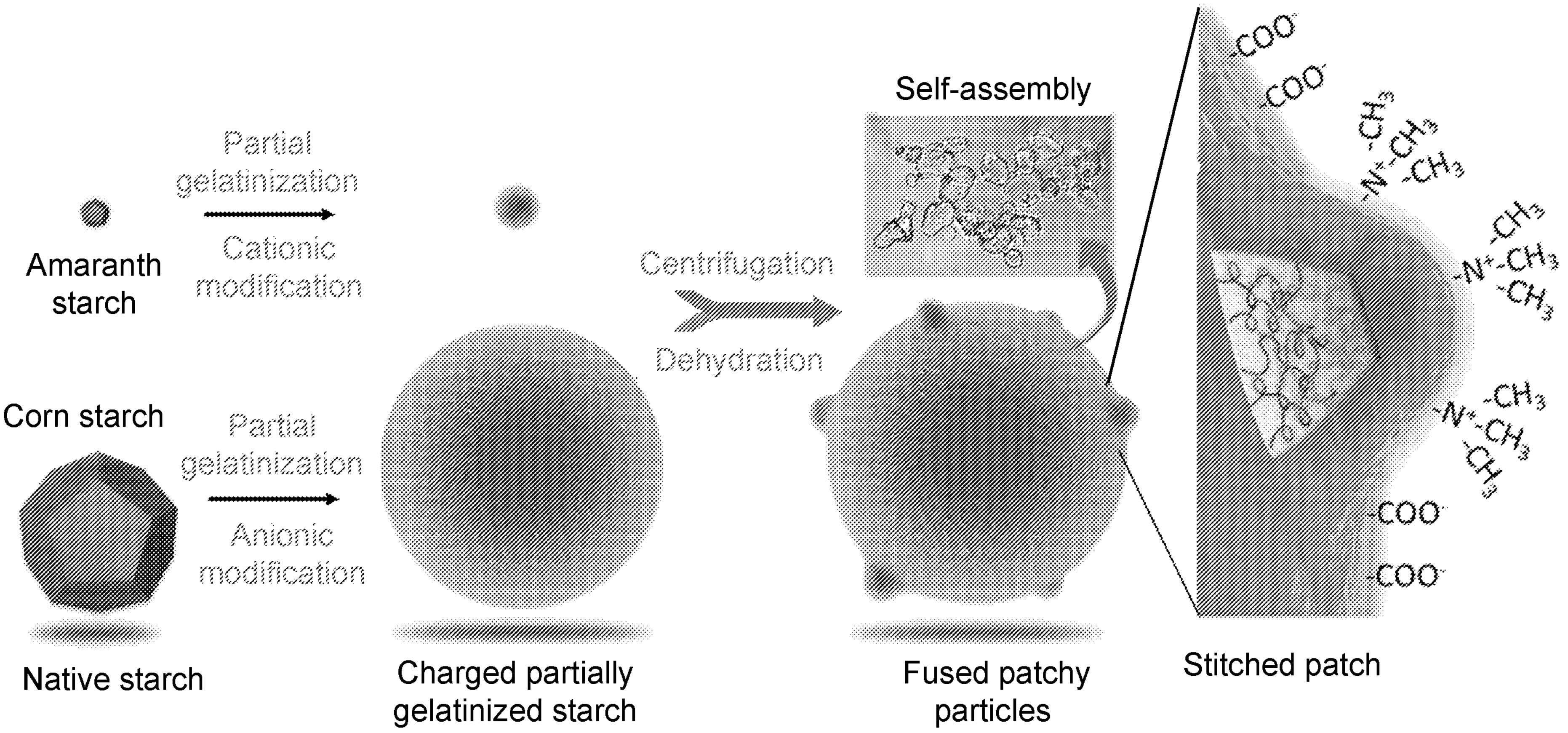

Amaranth starch
Corn starch
Native starch
Partial gelatinization
Cationic modification
Partial gelatinization
Anionic modification
Charged partially gelatinized starch
Centrifugation
Dehydration
Self-assembly
Fused patchy particles
Stitched patch
-COO⁻
-COO⁻
-N⁺-CH₃ -CH₃ -CH₃
-N⁺-CH₃ -CH₃ -CH₃
-N⁺-CH₃ -CH₃ -CH₃
-COO⁻
-COO⁻

Figure 7

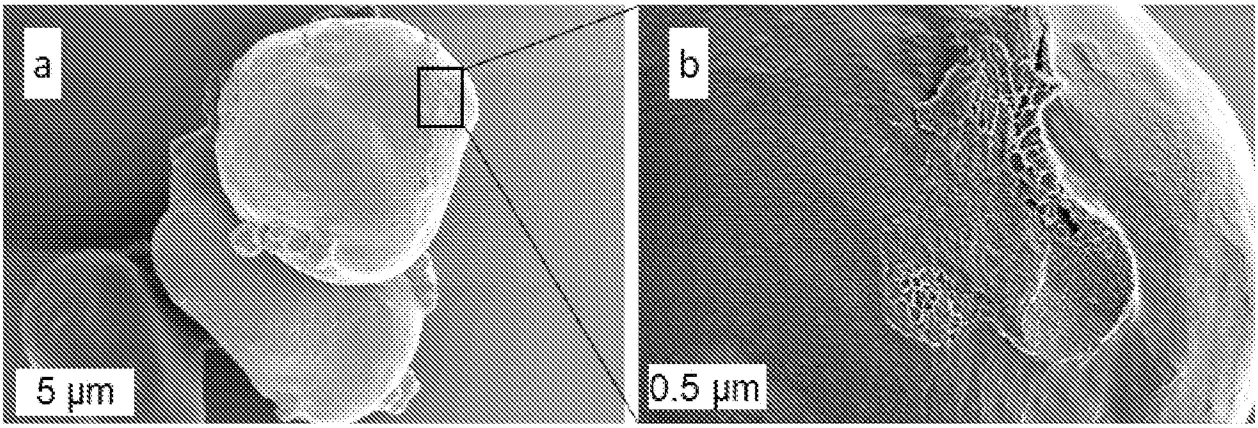


Figure 8

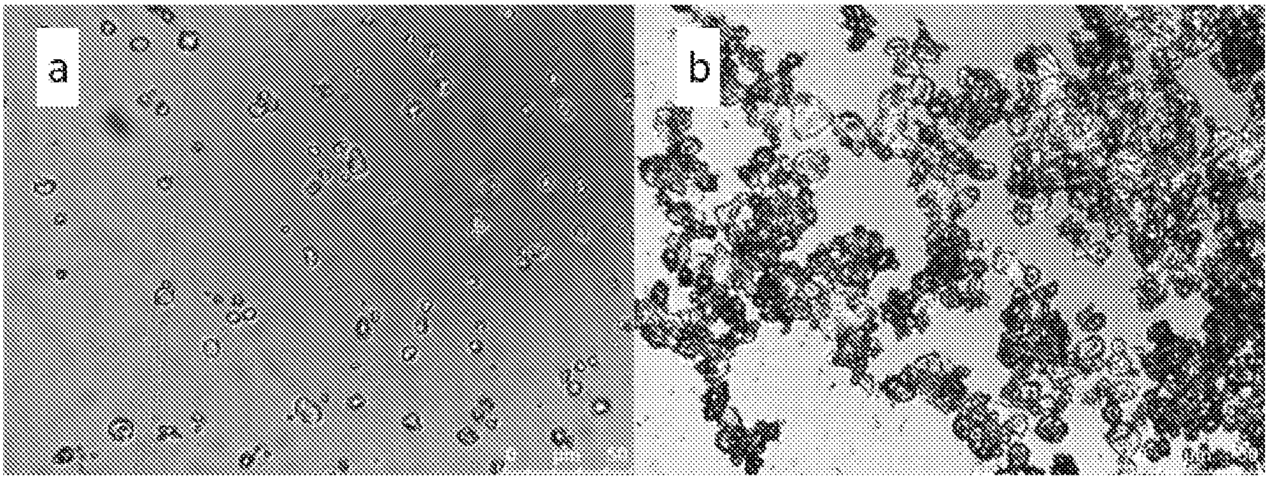


Figure 9