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

(19) **World Intellectual Property Organization**
International Bureau

(43) **International Publication Date**
19 December 2024 (19.12.2024)

WIPO | PCT

(10) **International Publication Number**
WO 2024/256701 A1

(51) **International Patent Classification:**
A23L 29/231 (2016.01) *A23L 23/00* (2016.01)
A23L 35/00 (2016.01) *A23L 27/60* (2016.01)
A23D 7/005 (2006.01)

(21) **International Application Number:**
PCT/EP2024/066687

(22) **International Filing Date:**
14 June 2024 (14.06.2024)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
23179855.4 16 June 2023 (16.06.2023) EP

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(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,

(54) **Title:** PECTIN EMULSION GELS WITH IMPROVED MOUTHFEEL

Carrot emulgel – 25°C – 6 months

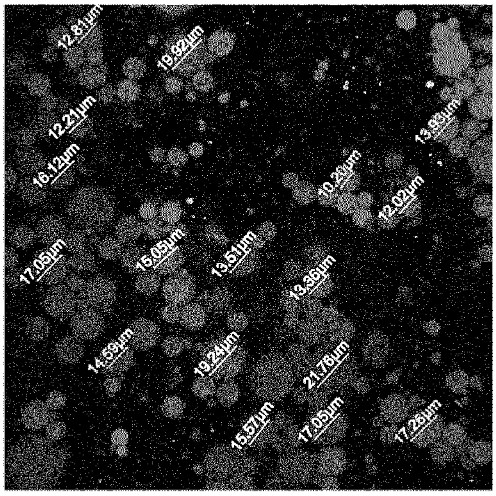

FIG. 28B

(57) **Abstract:** The present invention relates to a pectin based emulsion, said emulsion comprising between 0.5 and 6 wt% pectin, 3 and 40 wt% oil, and water, wherein the emulsion has a pH which is less than 5, an average oil droplet size in the emulsion is below 20 pm, and the pectin is high methoxy pectin with degree of methoxy (DM) > 60.

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[Continued on next page]

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).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

Pectin emulsion gels with improved mouthfeel

Background

Emulsions, emulgels (also known as emulsion-filled gels) are frequently used in food matrices to bring fat-like attributes such as mouthcoating and stickiness. Emulsions often consist in proteins as hydrocolloids and are very hydrophilic and not surface active. Chemically modified hydrocolloids such as cellulose, any by further example methyl- or ethylcellulose, are surface active and can lead to oleogel formation but they are not well perceived by consumers. Current emulsions used in cooking processes also have a tendency to not hold their shape during cooking and do not have good mouthcoating properties. There is a clear need to develop new emulsions that not only have an improved cooking performance but that also have better mouthcoating and stickiness attributes.

Summary of the invention

The present invention describes pectin emulsions comprising up to 40% oil with different pectin content. By adjusting the pH and ion content a wide range of textures could surprisingly be obtained. The emulsions can melt upon cooking, with or without oil release, and hold their shape depending on the composition. The emulsions also have an unexpectedly strong mouthcoating, much stronger than emulsion gels generated traditionally from protein. The pectin emulsions are suitable for use as an improved binder, a meltable filling or a flavor carrier.

By using pectin which is a natural ingredient derived from for example vegetables and fruits, a clean label food product with improved sensory aspects can be obtained without other existing emulsifiers such as ethyl- or methyl-cellulose, gum arabic and lecithin, which are often perceived as unfavorable by consumers.

The present invention provides a stable emulsion in which small oil droplets with the average size of less than 20 µm are uniformly dispersed and homogenized in a continuous aqueous phase. This stable emulsion can be clearly distinguished from a gelled matrix in which much bigger oil droplets are simply entrapped. Such gelled matrix generally requires other emulsifiers or addition of calcium ions to stabilize. As will be discussed in the following examples, the present invention enables an emulsion which can maintain improved stability even without other emulsifier or addition of calcium ion.

Brief description of figures

Figure 1. Force displacement-curve of a probe tack test measurement. Y-axis = Force (g).

Figure 2. Investigated parameters for emulgel formulation and stability results. Legend: black circles = stable emulsion ; strikes = unstable emulsion ; grey = stable only without calcium addition ; white = not tested.

Figure 3. Prediction of the measured parameters (tack force, G' at 40°C, tan delta during heating or cooling) as a function of the emulgel composition.

Figure 4A. Storage and loss modulus for 4% pectin system as a function of calcium concentration at 25 and 80°C.

Figure 4B. Storage and loss modulus for 6% pectin system as a function of calcium concentration at 25 and 80°C.

Figure 5A. Oil droplet measurement of emulgels formulated with 4% of pectin and 20% of sunflower oil before heat treatment.

Figure 5B. Oil droplet measurement of emulgels formulated with 4% of pectin and 20% of sunflower oil after heating at 80°C.

Figure 6A. Oil droplet measurement of emulgels formulated with 4% of pectin, 20% of sunflower oil and 20 mM of calcium salt before heat treatment.

Figure 6B. Oil droplet measurement of emulgels formulated with 4% of pectin, 20% of sunflower oil and 20 mM of calcium salt after heating at 80°C.

Figure 7A. Oil droplet measurement of emulgels formulated with 6% of pectin and 20% of sunflower oil before heat treatment.

Figure 7B. Oil droplet measurement of emulgels formulated with 6% of pectin, 20% of sunflower oil and 20 mM of calcium salt before heat treatment.

Figure 8. Storage modulus of emulsion gels with increasing concentrations of unsaturated Palm Stearin, as temperature is ramped from 25°C to 80°C.

Figure 9. Probe tack test results of samples P1 (Dissolution at 50 °C during 15 min) and P2 (Dissolution at 50 °C during 2 h) during the measurement.

Figure 10. Results of rheology heating and cooling ramp test for P1 and P2.

Figure 11. Probe tack test results during the measurement of samples P2 (Dissolution at 50 °C for 2 h), and P4 (Dissolution at 50 °C for 15 min and pH 2).

Figure 12. Results of rheology heating and cooling ramp test for P2 and P4.

Figure 13. Loss factor of emulsion gel containing 4% pectin, 20% high oleic sunflower oil, and additional fibers and starches.

Figure 14. Principal component (PC) analysis of the sensory attributes of the designed recipes in Example 2.

Figure 15. Impact of water content on sensory attributes of pectin emulgels in Example 2.

Figure 16. Impact of pectin content on sensory attributes of pectin emulgels in Example 2.

Figure 17. Impact of oil content on sensory attributes of pectin emulgels in Example 2.

Figures 18A. Storage and loss modulus for samples stored at 4°C by the rheological method modulating the frequency in Example 11.

Figure 18B. Storage and loss modulus for samples stored at 20°C by the rheological method modulating the frequency in Example 11.

Figure 19A. Storage and loss modulus for samples stored at 4°C by the rheological method modulating the amplitude in Example 11.

Figure 19B. Storage and loss modulus for samples stored at 20°C by the rheological method modulating the amplitude in Example 11.

Figure 20A. Viscosity for samples stored at 4°C in Example 11.

Figure 20B. Viscosity for samples stored at 20°C in Example 11.

Figure 21A. Texture analysis results of carrot emulgels stored at 4°C in Example 11: hardness (positive force) and tack force (negative force).

Figure 21B. Texture analysis results of carrot emulgels stored at 4°C in Example 11: positive and negative areas.

Figure 22A. Texture analysis results of carrot emulgels stored at 20°C in Example 11: hardness (positive force) and tack force (negative force).

Figure 22B. Texture analysis results of carrot emulgels stored at 20°C in Example 11: positive and negative areas.

Figure 23A. Tribology measurements of carrot emulgels stored at 4°C in Example 11.

Figure 23B. Tribology measurements of carrot emulgels stored at 20°C in Example 11.

Figure 24. Oil binding capacity of carrot emulgels stored at 4°C and at 20°C in Example 11.

Figure 25. Oil oxidation of carrot emulgels stored at 4°C and at 20°C in Example 11.

Figure 26. Oil droplet measurement of carrot emulgels of example 11 after heat treatment.

Figure 27A. Oil droplet measurement of carrot emulgels of example 11 after 2 months of storage at 4°C.

Figure 27B. Oil droplet measurement of carrot emulgels of example 11 after 6 months of storage at 4°C.

Figure 28A. Oil droplet measurement of carrot emulgels of example 11 after 2 months of storage at room temperature.

Figure 28B. Oil droplet measurement of carrot emulgels of example 11 after 6 months of storage at room temperature.

Figure 29A. Texture attributes of recipes R1 to R5 as described in example 12.

Figure 29B. Texture attributes of recipes R1 and R6 to R8 as described in example 12.

Figure 30A. Sensory attributes of recipes R1 to R5 as described in example 12.

Figure 30B. Sensory attributes of recipes R6 to R8 as described in example 12.

Figure 31. Sensory mapping of recipes R1 to R8 as described in example 12.

Figure 32. Rheology of emulgels C1 and C2 as described in example 15.

Figure 33A. Oil droplet size of emulsions C1 as described in example 15.

Figure 33B. Oil droplet size of emulsions C2 as described in example 15.

Figure 34. Acidity ranking of pectin emulgels as described in example 16.

Embodiments of the invention

The invention relates in general to pectin based emulsions.

In particular, the invention relates to a pectin based emulsion comprising pectin, oil, and water, wherein the emulsion has a pH which is less than 5.

In particular, the invention relates to a pectin based emulsion comprising pectin, oil, and water, wherein the emulsion has a pH which is less than the pKa of the pectin.

In particular, the invention relates to a pectin based emulsion comprising between 0.5 and 6 wt% pectin, oil, and water, wherein the emulsion has a pH which is less than 5.

In particular, the invention relates to a pectin based emulsion comprising pectin, between 3 and 40 wt% oil, and water, wherein the emulsion has a pH which is less than 5.

In particular, the invention relates to a pectin based emulsion comprising between 0.5 and 6 wt% pectin, between 3 and 40 wt% oil, and water, wherein the emulsion has a pH which is less than 5, an average oil droplet size in the emulsion is below 20 µm, and the pectin is high methoxy pectin with degree of methoxy (DM) > 60.

In one embodiment, the emulsion has a pH which is less than 4.5, or less than 4.2, or less than 4, or about 3.5.

In one embodiment, the average oil droplet size in the emulsion is below 19 µm, or below 18 µm, or below 17 µm, or below 16 µm, or below 15 µm.

In one embodiment, the pectin is high methoxy pectin with degree of methoxy (DM) of 70.

In one embodiment, the emulsion comprises multivalent ions. In one embodiment, the multivalent ions comprise calcium, magnesium or iron. In one embodiment, the multivalent ions are preferably calcium ions.

In one embodiment, the emulsion comprises up to 80 mM multivalent ions.

In one embodiment, the emulsion comprises between 5 and 40 mM multivalent ions.

In one embodiment, said emulsion comprises about 2 wt% pectin and about 15 wt% oil.

In one embodiment, the pectin is purified or non-purified. For example, the non-purified pectin is unrefined citrus fiber.

In one embodiment, said emulsion further comprising fruit powder, vegetable powder, for example pulse flour, purified fibers, or purified starch.

In one embodiment, the water is de-ionized water, tap water, or mineral water.

In one embodiment, the water is replaced by a cooked purée, for example a vegetable puree, or a fruit puree, or a pulse puree.

In one embodiment, the pectin is a citrus pectin, a sugar beet pectin, an apple pectin, or an amidated pectin.

In one embodiment, the pectin is a citrus pectin.

The invention further relates to a method of making the pectin based emulsion according to the invention, said method comprising heating pectin in water to at least 50°C, adding oil and high shear mixing for about 5 minutes.

The invention further relates to a method of making a pectin based emulsion, said method comprising:

- heating between 0.5 and 6 wt% pectin in water to at least 50°C to obtain a hydrated pectin solution,
- adding between 3 and 40 wt% oil to the hydrated pectin solution; and
- mixing the mixture of the hydrated pectin solution and the oil by high shear mixing for about 5 minutes,

wherein the emulsion has a pH which is less than 5, an average oil droplet size in the emulsion is below 20 µm, and the pectin is high methoxy pectin with degree of methoxy (DM) > 60.

In one embodiment, the high shear mixing is performed while heating the mixture to at least 50°C, preferably about 75°C.

In one embodiment, the high shear mixing is performed at a shear rate of between 170 and 3400 s-1. This shear rate corresponds to a rotational speed between 100 and 2000 RPM.

In one embodiment, the method further comprises adjusting pH of the pectin based emulsion to be less than pH 5, preferably less than pH 4.5, more preferably less than pH 4.2, more preferably less than pH 3.5.

In one embodiment, the pH is adjusted to about pH 3.5.

In one embodiment, the method further comprises adding multivalent ions, preferably calcium ions to the pectin based emulsion after the high shear mixing.

In one embodiment, multivalent ions are added to the pectin based emulsion after the high shear mixing, so that the final concentration of the multivalent ions in the pectin based emulsion reaches up to 80 mM, preferably between 5 and 40 mM.

In one embodiment, in the step of mixing the mixture of the hydrated pectin solution and the oil by high shear mixing, the oil is added at a constant flow of about 100 ml per minute.

The invention further relates to the use of a pectin based emulsion according to the invention, wherein said emulsion is

a. a binder;

b. a filling;

c. a flavor carrier;

d. a fat replacer;

e. a spreadable product;

f. a purée;

g. a dip;

h. a topping; or

i. a frozen dessert.

Detailed description of the embodiments

Pectin

The pectin may be a high methoxy pectin. The degree of methoxy (DM) may be between 60 and 70%. The degree of methoxy (DM) of the pectin may be 70%. The pectin may be a low methoxy pectin. The degree of methoxy may be about 33% methoxy. The pectin may be an amidated pectin. The degree of methoxy may be about 27% methoxy. The amidated pectin may comprise about 20% amides. The pectin may be a sugar beet pectin. The pectin may be an apple pectin. Low methoxy pectins were found to produce hard and less sticky gels.

The pectin based emulsion may comprise about 0.5 wt%, or about 1 wt%, or about 1.5 wt%, or about 2 wt% pectin, or about 3 wt% pectin, or about 4 wt% pectin, or about 5 wt% pectin, or about 6 wt% pectin, or about 7 wt% pectin, or about 8 wt% pectin, or about 9 wt% pectin, or about 10 wt% pectin. Preferably the pectin based emulsion comprises about 2 wt% pectin or about 4 wt% pectin.

Starch

The starch may be a waxy corn starch. The starch may be a potato starch.

Fibers

The fiber may be citrus fibers. The citrus fiber may have about 30% pectin. The fiber may be wheat fiber. The citrus fiber can be used in addition to or as the pectin source in the emulsion. The wheat fiber can also be used in addition to the citrus fiber.

Oil

For the purpose of the present application, the term "oil" and "fat" are used interchangeably. The fat or oil may comprise animal fat or oil, vegetable fat or oil, for example a coconut oil or fat, sunflower oil and milk fat.

The oil may be sunflower oil, for example high oleic sunflower oil. The pectin based emulsion may comprise palm stearin oil. The pectin based emulsion may comprise about 3 wt%, or about 5 wt%, or about 10 wt%, or about 15 wt%, or about 20 wt%, or about 30 wt%, or about 40 wt%, or about 50 wt% oil. Preferably, the pectin emulsion comprises between 3 and 40 wt% oil, or between 5 and 40 wt% oil, or between 5 and 30 wt%, or between 5 and 20 wt% oil, or between 10 and 30 wt% oil, or between 10 and 20 wt% oil, or between 10 and 15 wt% oil. The pectin based emulsion may comprise palm stearin oil and high oleic sunflower oil in the following approximate ratios: 25:75, 50:50, or 75:25 palm stearin oil : high oleic sunflower oil.

Multivalent ions

The pectin based emulsion may comprise multivalent ions, for example magnesium, iron, or calcium ions, preferably calcium chloride dihydrate. The pectin based emulsion may comprise about 1% calcium chloride dihydrate. The pectin based emulsion may comprise about 5mM, or about 6mM, or about 7mM, or about 8mM, or about 9mM, or about 10mM, or about 11mM, or about 12mM, or about 13mM, or about 14mM, or about 15mM, or about 16mM, or about 17mM, or about 18mM, or about 19mM, or about 20mM calcium chloride. Preferably, the pectin based emulsion comprises between 5 and 40 mM multivalent ions.

The multivalent ions, for example calcium ions may be added to the pectin based emulsion after mixing and emulsifying the oil with the pectin solution for example by high shear mixing. For example, multivalent ions, preferably calcium ions are added to the pectin based emulsion after mixing and emulsifying the oil with the pectin solution so that the final concentration of multivalent ions in the pectin based emulsion reaches up to 80mM, preferably between 5 and 40 mM.

When vegetable and/or fruit purée is used as an aqueous phase to replace at least part of water in the pectin based emulsion, the vegetable and/or fruit purée may comprise some multivalent ions, for example magnesium, iron or calcium ions, and at least part of the final concentration of the multivalent ions in the pectin based emulsion may originate from the vegetable and/or fruit purée.

For example, the content of calcium ions in the vegetable and/or fruit purée may be on average between 10 and 40 mg per 100 g, or between 0.2 and 0.8 mmol per 100 g.

Other pectin based emulsion ingredients

The pectin based emulsion may comprise about 50 wt% water, about 60 wt% water, about 70 wt% water, about 80 wt% water, about 90 wt% water, or between 50 to 90 wt% water. De-ionized water was found to provide a viscoelastic fluid. It was found to be useful for controlling melting properties. The use of mineral water provides a gel-like material. Mineral water can be used as a source of calcium.

The pectin based emulsion may comprise potato starch, for example about 3wt% potato starch. The pectin based emulsion may comprise waxy maize starch, for example about 3wt% waxy maize starch. The pectin based emulsion may comprise wheat fiber, for example about 3wt% wheat fiber, or about 6wt% wheat fiber. Preferred starches are waxy starch or potato starch. Starch was found to improve binding properties in both hot and cold applications. Potato starch was found to provide very good sensory attributes.

The pectin based emulsion may comprise pulse flour, preferably micronized pulse flour. Micronizing the flour was found to avoid graininess due to agglomeration.

Pectin based emulsion recipes

The pectin based emulsion may, for example, comprise about 1.5-2.0 wt% pectin and about 10-15 wt% oil. The pectin based emulsion may, for example, comprise about 4 wt% pectin and about 20 wt% oil. The pectin based emulsion may, for example, comprise about 4 wt% pectin and 20 wt% oil in deionized water. The pectin based emulsion has a pH less than 5, preferably less than 4.5, preferably less than 4.2, preferably less than 4, preferably less than 3.5. The pH may be about pH 2.

The pectin based emulsion may comprise about 3wt% pectin, about 8wt% soy flour and about 20wt% fat. The pectin based emulsion may comprise about 8wt% pectin, and about 10wt% fat. The pectin based emulsion may comprise about 4wt% pectin, and about 40wt% fat.

Food products comprising pectin based emulsion

The food product comprising the pectin based emulsion may be a vegetable puree spread. The puree may comprise red bell pepper puree, carrot puree, or broccoli puree. The food product may have a recipe substantially similar to that shown in table 16.

The food product may be a spreadable liquid like matrix, wherein the product comprises an emulsion with about 2wt% pectin and about 15wt% oil.

The pectin based emulsion may be used as a flavor enhancer. The flavor enhancer may have a recipe substantially similar to that shown in table 19 (R8).

The pectin based emulsion may be used as a purée, for example as a baby food purée. The example of baby food purée may comprise about between 0.5 and 1.5 wt% pectin and about between 3 and 7 wt% fat or oil.

The pectin based emulsion may be used as an ice cream, gelato or frozen dessert. The example of frozen dessert may comprise about between 1 and 2 wt% pectin, about between 3 and 20 wt% fat or oil, and about between 60 and 95 wt% vegetable and/or fruit purees. The example of frozen dessert may further comprise sugar.

Method of producing pectin based emulsion

The pectin can be hydrated with water. The water may be mineral water, for example Vittel water. The water may be tap water. The water may be deionized water. The pectin can also be hydrated with water contained in vegetable and/or fruit purée. The hydration step may last for about 15 min, and be done at about 50 °C. A pasteurization step may be done for about 5 min at about 75 °C. Both may be performed at about speed 2.5 in a Thermomix (350 RPM). The pasteurization step may optionally be performed only for the purpose of safety for consumption, and the pectin based emulsion according to the present invention is stable without such optional pasteurization step. After hydration, oil is added to the pectin solution, and the pectin solution can be emulsified for about 5 minutes, for example by high shear mixing. The high shear mixing may be performed while heating the mixture to at least 50°C, preferably about 75°C. The high shear mixing may be performed at a shear rate of between 170 and 3400 s-1, which corresponds to a rotational speed between 100 and 2000 RPM. The shear speed of the Thermomix may be increased to about 4.5 (1550 RPM) and the oil added in a constant flow of about 100 ml per minute. Depending on the sample formulation, calcium chloride may be added during the last minute of emulsification, or after the emulsification.

The method may further comprise a step of retorting the pectin based emulsion. The retorting step may be performed at 95°C for 5 min.

Use of pectin based emulsion

The pectin based emulsion may be used as (i) a binder, for example which holds upon cooking so the product can be flipped on the pan while cooking. Typically, the emulsion comprises calcium and starch; (ii) a filling, for example inside a matrix so the emulsion thins upon cooking but without phase separation (for example, croquette and burrata); (iii) a flavor carrier, for example by incorporating spices inside a food matrix; (iv) a fat replacer, for example where the emulsion destabilizes during cooking and enhances the juiciness in the final food product; (v) spreadable product; (vi) a purée; (vii) a dip; (viii) a topping; or (ix) a frozen dessert.

As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise.

The words “comprise,” “comprises” and “comprising” are to be interpreted inclusively rather than exclusively. Likewise, the terms “include,” “including” and “or” should all be construed to be inclusive, unless such a construction is clearly prohibited from the context.

The compositions disclosed herein may lack any element that is not specifically disclosed. Thus, a disclosure of an embodiment using the term “comprising” includes a disclosure of embodiments “consisting essentially of and “consisting of the components identified. Similarly, the methods disclosed herein may lack any step that is not specifically disclosed herein. Thus, a disclosure of an embodiment using the term “comprising” includes a disclosure of embodiments “consisting essentially of” and “consisting of” the steps identified.

The term "and/or" used in the context of "X and/or Y" should be interpreted “s "X," or "Y," or “X and Y.” Where used herein, the terms “example” and “such as,” particularly when followed by a listing of terms, are merely exemplary and illustrative and should not be deemed to be exclusive or comprehensive. Any embodiment disclosed herein can be combined with any other embodiment disclosed herein unless explicitly stated otherwise.

As used herein, “about” and “approximately” are understood to refer to numbers in a range of numerals, for example the range of -10% to +10% of the referenced number, preferably within -5% to +5% of the referenced number, more preferably within -1% to +1% of the referenced number, most preferably within -0.1 % to +0.1 % of the referenced number.

A vegan product is defined as being devoid of animal products, for example devoid of dairy products and meat products. A vegan analogue product of the invention has the look, taste, and texture which is close to real animal based product.

The invention will now be illustrated by way of examples, which should in no way be thought to limit the scope of the invention as herein described.

Examples

Emulsion preparation

In the following Examples, the pectins used were (i) high methoxy pectin (from citrus, degree of methoxy (DM) = 70%); (ii) low methoxy pectin (from citrus, DM = 33%); (iii) amidated pectin (from citrus, 27% methoxy and 20% amides); (iv) sugar beet pectin; and (v) apple pectin. Soy flour, starch (waxy corn and potato starch), citrus fibers (with 30% pectin), and wheat fiber were also used.

The first step of producing the emulgels was hydration of the pectin with water (Vittel or tap or deionized) for 15 min at 50 °C, and a pasteurisation step of 5 min at 75 °C in order to make the gels safe for consumption. Both were performed at speed 350 RPM. After the hydration process, the pectin solution was emulsified for 5 minutes by high shear mixing . During the high shear mixing, the shear speed was increased from 350 RPM to 1550 RPM, and the oil was added in a constant flow of 100 mL per minute. Depending on the sample formulation, $CaCl_2$ was added during the last minute of emulsification.

Analysis

Sample stickiness and hardness was assessed by an adaptation of a probe tack test method, using a texture analyser (TA HD plusC-, Stable Micro Systems Ltd, Godalming, UK). Cylindrical plates of altitude 12,5mm were filled with the samples right after their preparation until maximum capacity and with a flat surface. They were then covered and refrigerated at 4 °C for 24h before the analysis. In all the experiments each sample was measured eight times. A cylindrical plexiglass probe of 45mm of diameter moved downwards at 0.5 mm s-1 until it went down to 2mm into the sample. Then, the probe moved upwards at 10 mm s-1 for 5 s. The hardness (N) was measured as the peak force when the probe was 2 mm in the sample. The tack force Ftack (N), which is the maximum required strength for separating the binder and the adherent force obtained when separating the probe from the sample, and the work of adhesion Wadhesion (N*s), which is the total work necessary to separate the probe from the sample and also known as adhesiveness, were also obtained.

Figure 1 shows a force-displacement-curve of a probe tack test measurement in which the force (in g but converted to N during data treatment with the conversion factor 1 N=101,97 g) over time (s) and the different parameters that have been obtained from it (Hardness, Ftack and Wadhesion).

For the oil binding method, samples (4-4.5 g) were placed in 15 mL polypropylene tubes and centrifuged at 11000 g (7993 rpm) for 15 minutes at 20 °C with a Sorvall Lynx 6000 Centrifuge (ThermoFisher Scientific, Waltham, USA). After centrifugation, the exudative oil was removed and the OBC was calculated. This is the ratio, as a percentage, of oil retained by the emulsion-gel sample after centrifugation and the oil initially present on the sample.

$$OBC = \frac{(m_1 - m) * X_{oil} - (m_1 - m_2)}{(m_1 - m) * X_{oil}} * 100$$

In this equation, m is the mass of the empty tube, m_1 is the total mass of the tube with the added emulsion-gel sample, m_2 is the total mass of the emulsion-gel sample, and X_{oil} is the initial oil content in % of the initial sample.

Rheological analysis was carried out using a rotational rheometer (MCR 502, Anton Paar, Graz, Austria) with the following geometries:

- Solid-like samples: stainless-steel parallel plate geometry of 50 mm of diameter and serrated surface (PP50/SS/P2) to prevent a slippery effect with a gap distance of 1 mm. To prevent water evaporation from the samples, paraffin oil was applied and a cooling covering hood system was used.
- Liquid-like samples: CC-27 sanded cylinder

Samples were loaded at 4°C and were heated to 90°C (5°C/min, 0.2% strain, 1 Hz), cooked at 90°C for 1 min and cooled down to 60°C (5°C/min, 0.2% strain, 1 Hz ; holding time 3 min) then to 40°C (5°C/min, 0.2% strain, 1 Hz ; holding time 3 min). Frequency sweeps (0.02% γ, 0.01-10 Hz) were performed at 4°C and after cooling at 40°C. the storage modulus G', the loss modulus G'' and the loss factor tan delta were recorded at 4°C, 40°C in the heating step, 90°C and 40°C in the cooling step.

The impact of calcium on the heat stability was studied on a shorter ramp, where samples were heated from 25°C to 90°C (5°C/min, 0.2% strain, 1 Hz). A frequency sweep was performed at 25°C and at 90°C (0.02% γ, 100-0.1 Hz).

Colour was measured using a DigiEye system following the recommendations from the supplier. The equipment measured the clearness (L), the colour on the green-red (a) and on the blue-yellow axis (b). colour difference between 2 samples 1 and 2 is expressed by ΔE as:

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

Colour differences are perceived for ΔE >4.

Oil oxidation was measured using a ML Oxipress (MikroLab Aarhus A/S, Denmark). Briefly, the emulgel (50g) was weighted in a glass vessel and oxidized at 5 bar and 90°C. The oxidation curve was recorded as the pressure evolution over time. The breakpoint time when the pressure starts to drop was recorded as the time needed to detect oxidation and rancidity.

Oil droplet size was measured by confocal laser scanning microscopy, using Nile red to stain the oil droplets. Images were obtained using a LSM 710 microscope equipped with Airyscan from Zeiss with an excitation performed at 561 nm. Oil droplet size was measured using ImageJ.

Example 1

Pectin emulsion physical properties

A design of experiments was implemented to rationalize the impact of the oil, pectin and ion content on the emulgel properties. The high methoxy pectin (from citrus, DM = 70%) was varied between 2 to 10%, the oil between 10 to 50%, and additional $CaCl_2$ dihydrate at 0 or 1%. The emulgels were generated as described in the previous section. Emulgels could be generated in most of the formulations. The result of formulation tests is shown in figure 2.

The measured parameters were oil binding, TA (adhesion, tack force and hardness), and rheology (G' and tan delta at 4°C and 40°C after heating). Several relationships were observed. Texture Analyzer parameters were correlated (for instance, the Tack force was positively correlated with the Hardness (r=0.91) and positively correlated with the Adhesiveness (r=0.88)). The tack force could be predicted using a linear model (R2 = 0.76). The model coefficients indicated that a higher tack force (in absolute values) is achieved when (i) a high pectin level is used ($p<10^{-4}$); and (ii) a low oil content was used (p=0.06), although this effect only applied when a high pectin level was used (≥8%). Linear additive models were sufficient to describe the impact of formulation on gel properties. Good prediction accuracy was achieved for rheology and texture analysis (figure 3).

Possible routes to produce a gel with the desired properties were identified: (i) TA, high tack force and work of adhesiveness → High pectin level, coupled with low oil level; (ii) [Rheology] High G' and low tan delta at 40°C cooling → High oil level, coupled with calcium addition; and (iii) [Rheology] High G' and low tan delta at 90°C → High oil level, coupled with calcium addition.

Table 1 shows impact on increasing the content of the formulation parameters (pectin, oil and calcium) on the emulsion-gel properties and the R^2 values of the linear model regressions for each analytical parameter. Arrows pointing down mean a decrease on that parameter and pointing up an increase. The type and number of arrows indicates the level of significance.

Table 1

Parameter	Oil binding capacity	Water activity	Texture Analyzer		
			Hardness	Tack force	Adhesiveness
Pectin	↘	↘↘	↗↗	↗↗	
Oil	↘			↘	↘↘
Calcium	↘↘		↗		
R^2	0.42	0.60	0.84	0.76	0.58

↗↗ Highly significant (p<0.01)
↗ Significant (0.01<p<0.05)
↗ Trend (0.05<p<0.20)

Parameter	Rheology – G'				Rheology – Tan delta			
	4°C	40°C Heating	90°C	40°C Cooling	4°C	40°C Heating	90°C	40°C Cooling
Pectin	↗↗	↗↗	↗↗	↗↗	↘↘	↘	↗↗	↗↗
Oil	↗↗	↗↗	↗↗	↗↗	↘↘	↘↘		
Calcium	↗	↗↗	↗	↗	↘	↘↘	↘	↘
R^2	0.94	0.90	0.72	0.90	0.78	0.63	0.74	0.83

Overall results are shown in Tables 2 (texture analysis), 3a, and 3b (rheology).

Table 2

								TEXTURE ANALYSIS: PROBE TACK TEST					
Water (%)	Pectin (%)	Oil (%)	CaCl2 (%)	Final Tp	pH at final Tp	Water Activity	OBC (%)	TA Hardness (g)		TA tack force (g)		TA Wadhesion (g*sec)	
								Average	StDev	Average	StDev	Average	StDev
88	2	10	0	50				12,394	0,604	-13,980	0.386	-14,629	0,143
88	2	20	0	50				16,164	1,296	-22,816	1,693	-21,869	1,000
86	4	10	0	50	3,62	0,982	97,18	57,446	10,516	-85,033	8,574	-51,297	11,04
76	4	20	0	50	3,59	0,985	97,89	58,069	5,612	-110,212	6,985	-88,743	3,694
66	4	30	0	50	3,67	0,984	97,16	75,988	6,818	-147,141	9,047	-103,997	8,278
56	4	40	0	50	3,60	0,983	44,15	62,557	14,413	-68,21	15,242	-16,723	3,463
85	4	10	1	50	2,98	0,985	95,72	40,634	2,801	-65,136	3,858	-54,387	2,352
75	4	20	1	50	2,80	0,986	100,00	79,414	8,337	-115,399	4,869	-78,39	1,774
65	4	30	1	50	2,87	0,984	96,23	90,533	10,098	-140,101	10,1	-92,695	5,151
55	4	40	1	50	2,90	0,984	21,57	64,005	11,004	-61,548	7,41	-16,255	1,59
84	6	10	0	50	3,50	0,981	100,00	93,296	10,417	-207,613	18,444	-136,887	20,353
74	6	20	0	50	3,47	0,979	72,14	85,862	10,616	-173,146	10,453	-86,337	15,067
64	6	30	0	50	3,52	0,982	38,07	92,328	42,054	-132,09	42,272	-35,246	9,794

83	6	10	1	50	2,91	0,979	99,98	110,418	18,497	-209,743	21,319	-143,99	10,081
73	6	20	1	50	2,90	0,978	62,35	112,238	16,634	-192,406	20,956	-88,129	16,698
63	6	30	1	60	3,01	0,977	37,11	79,934	17,771	-88,479	16,225	-18,49	1,384
82	8	10	0	65	3,74	0,983	95,74	120,556	13,49	-292,21	10,697	-249,875	19,771
72	8	20	0	65	3,68	0,981	90,04	105,829	8,077	-196,875	21,776	-58,59	16,257
81	8	10	1	65	2,67	0,982	98,59	173,747	12,51	-316,899	21,092	-191,115	33,011
71	8	20	1	70	2,60	0,977	72,29	168,900	37,623	-176,557	39,219	-33,664	12,112
80	10	10	0	70	3,48	0,977	98,56	184,934	21,127	-415,832	20,665	-275,437	32,3
70	10	20	0	65	3,50	0,976	90,71	148,914	38,394	-226,731	56,211	-47,326	9,132
79	10	10	1	65	2,70	0,976	100,00	232,166	31,223	-460,586	36,85	-236,549	27,295

Table 3a

Water (%)	Pectin (%)	Oil (%)	CaCl2 (%)	Final Tp	G' 4 °C (Pa)		tan delta 4°C		G' 40 °C heating (Pa)		tan delta 40 °C heating	
					Average	StDev	Average	StDev	Average	StDev	Average	StDev
88	2	10	0	50	10,45	0,25	0,96	0,03	9,33	0,01	0,68	0,015
88	2	20	0	50	24,1	0.4	0,73	0,03	13,7	0,4	0,61	0,015
86	4	10	0	50	89,19	2,66	0,78	0,02	47,52	2,02	0,71	0,02
76	4	20	0	50	167,37	1,34	0,66	0,01	89,03	0,93	0,65	0,01
66	4	30	0	50	300,07	11,11	0,52	0,01	166,63	7,13	0,54	0,01
56	4	40	0	50	354,58	3,14	0,44	0,01	199,46	2,37	0,43	0,01
85	4	10	1	50	67,8	3,68	0,95	0,03	32,12	1,74	0,92	0,03
75	4	20	1	50	172,67	4,76	0,7	0,01	92,83	3,14	0,68	0,01
65	4	30	1	50	290,98	9,94	0,52	0,01	173,47	8,16	0,53	0,02
55	4	40	1	50	383,83	22,41	0,48	0	234,43	7,56	0,45	0,01
84	6	10	0	50	303,65	11,97	0,69	0,01	121,41	7,89	0,8	0,02
74	6	20	0	50	434,27	25,63	0,59	0,02	179,24	13,57	0,72	0,04
64	6	30	0	50	562	23,29	0,55	0,01	234,77	9,76	0,67	0,01
83	6	10	1	50	401,31	15,15	0,61	0,01	208,37	8,21	0,62	0,01
73	6	20	1	50	608,61	36,46	0,49	0,01	343,01	21,83	0,5	0,01
63	6	30	1	60	811,56	8,9	0,45	0,01	474,42	1,93	0,45	0,01
82	8	10	0	65	733,46	20,6	0,59	0,01	263,22	6,12	0,81	0,01
72	8	20	0	65	911,85	26,93	0,53	0	348,71	11,85	0,74	0,01
81	8	10	1	65	976,26	10,26	0,51	0	521,33	6,91	0,55	0
71	8	20	1	70	1241,57	2,91	0,44	0	707,67	2,64	0,46	0
80	10	10	0	70	1320,6	6,4	0,55	0	454,7	2,23	0,83	0
70	10	20	0	65	1559,03	12,31	0,48	0	601,57	1,42	0,7	0,01
79	10	10	1	65	1796	69,97	0,45	0,01	972,89	38,86	0,5	0,01

Table 3b

Water (%)	Pectin (%)	Oil (%)	CaCl2 (%)	Final Tp	G' 90 °C heating (Pa)		tan delta 90 °C heating		G' 40 °C cooling (Pa)		tan delta 40 °C cooling	
					Average	StDev	Average	StDev	Average	StDev	Average	StDev
88	2	10	0	50	7,07	0,53	0,41	0,005	9,55	0,45	0,435	0,005
88	2	20	0	50	12,8	112,8	0,31	0,3	35,15	3,65	0,285	0,015
86	4	10	0	50	153,77	110,67	0,26	0,02	198,37	13,35	0,27	0,01
76	4	20	0	50	100,54	5,8	0,27	0,01	212,73	7,24	0,32	0,01
66	4	30	0	50	164,39	6,37	0,25	0	310,75	18,91	0,29	0
56	4	40	0	50	205,03	11,15	0,22	0	380,7	12,69	0,28	0,01
85	4	10	1	50	63,7	7,91	0,31	0,01	140,42	18,36	0,33	0,02
75	4	20	1	50	116,67	3,01	0,28	0,01	258,18	5,33	0,31	0,01
65	4	30	1	50	177,17	7,84	0,25	0,01	345,49	17,81	0,29	0,01
55	4	40	1	50	256,9	34,08	0,25	0,01	550,83	75,76	0,28	0,01
84	6	10	0	50	149,24	13,56	0,31	0,01	359,73	10,28	0,37	0,01
74	6	20	0	50	212,63	36,3	0,33	0,02	511,98	75,78	0,35	0,03
64	6	30	0	50	254,54	28,34	0,33	0,01	577,3	36,92	0,36	0,01
83	6	10	1	50	281,1	71,14	0,28	0,01	582,1	71,32	0,31	0,02
73	6	20	1	50	304,37	15,75	0,29	0	613,64	9,83	0,33	0,01
63	6	30	1	60	453,51	34,67	0,28	0	902,75	44,05	0,3	0
82	8	10	0	65	223,41	21,73	0,43	0,02	648,54	94,99	0,41	0,02
72	8	20	0	65	338,71	184,05	0,43	0,08	936,14	285,07	0,38	0,05
81	8	10	1	65	377,94	8,34	0,34	0	908,46	11,9	0,37	0
71	8	20	1	70	512,43	2,05	0,32	0	987,69	39,3	0,36	0,01
80	10	10	0	70	262,18	67,14	0,61	0,06	865,56	105,14	0,49	0,05
70	10	20	0	65	278,75	31,18	0,62	0,05	1019,77	83,23	0,46	0,02
79	10	10	1	65	677,35	57,06	0,35	0	1373,73	91,35	0,37	0,01

Example 2

Sensory impact of pectin emulgel formulations

The impact of the pectin emulsion gel composition on the sensory attributes was studied systematically. The recipes are summarized in Table 4. A high methoxy pectin (DM 70%) derived from citrus was used. All formulations were prepared in mineral water, except for sample S15 in which deionized water was used.

Table 4. Recipes used for sensory assessment.

Sample code	Water (wt%)	Pectin (wt%)	Oil (wt%)	Potato starch (wt%)
S1	78	2	20	0
S2	86	4	10	0
S3	76	4	20	0
S4	66	4	30	0
S5	56	4	40	0
S6	84	6	10	0
S7	74	6	20	0
S8	64	6	30	0
S9	82	8	10	0
S10	72	8	20	0
S11	82	8	10	0
S12	70	10	20	0
S13	76	4	20	0
S14	73	4	20	3
S15	76 (DI water)	4	20	0

The samples were tasted at the ambient temperature (25°C) or in a heated state (60°C), and assessed by a trained panel using a rate all that apply methodology consisting in first listing all the attributes related to the sample, and then rate these attributes from 1 (slightly intense) to 5 (strongly intense). The sensory glossary used is given in Table 5.

Table 5. Sensory attributes used to describe the pectin-based emulgels.

Appearance (AP)	
Shiny	Smooth surface reflecting light
Compact	Refers to dense texture, non aerated resulting from a lack of air in the product
Homogeneity	Smooth surface (Homogeneous=5) vs presence of bubbles on the surface (Heterogeneous=0)

Humid	Degree of moisture on the surface
Texture (TX)	
Firm	The force required to deform a product using the molars
Slippery	Enhanced lubricating or friction reduction (refers to egg white which is highly slippery)
Sticky	Extent to which the product sticks to the teeth or palate during chewing
Powdery	Perception of fine particles
Crumbly	Extent to which the product falls apart into many pieces/crumbs on the first bite. Synonym: Brittle; Opposite: Pasty
Melting	Time necessary for a product melting in mouth. If a product melts immediately, it's very melting (=5)
Mouthcoating	Smooth, fatty film in the whole mouth that you can not remove with the tongue
Astringent	The complex sensation of shrinking, numb, drying or puckering in the mouth. Describes a dry/rough tongue and palate

Little differences were observed between hot (60°C) and ambient temperature (25°C) samples. All attributes were significantly different across samples (p value <0.001). Three main groups were obtained, as shown on Figure 14:

- Group 1: more melting and slippery
- Group 2: more compact, sticky and homogeneous
- Group 3: more crumbly, firm, and oily surface

The impact of each single component on the sensory attributes were reviewed individually (figures 15 to 17). As seen in Figure 15, higher water content was strongly correlated to higher homogeneity and fewer bubbles, less oily surface, and more compact textures.

As seen in figures 16 and 17, the same exercise performed on pectin and oil showed that higher pectin content resulted in firmer textures, higher heat stability, higher stickiness and higher mouthcoating. On the other hand, higher oil content promoted an oily and shiny surface while reducing the appearance homogeneity.

Furthermore, the use of demineralized water was shown to strongly increase the slipperiness and melting, while decreasing the oil leaking, firmness, stickiness and mouthcoating. Therefore, filling formulations should favor the use of demineralized water, when the presence of minerals favour heat-stability and are better suited for binding applications.

Example 3

Impact of calcium addition and heating

In this example 3, the following recipes in Table 6 were used.

Table 6

	Recipe 1	Recipe 2
Pectin (high methoxy, citrus)	4	6
Sunflower oil	20	20
Water	76	74

To better visualize the effect of calcium concentration on the heat stability of the gel, the storage modulus at a frequency of 68 rad/s was selected as a single point of reference. This was motivated by the interest in the elastic solid-state properties, which was visible in the G’ value. The G’ values from 0mM to 80mM addition of calcium at temperatures of 25°C and 80°C can be seen in figures 4A and 4B. Figure 4A shows results of samples with 4% pectin (Recipe 1), and figure 4B shows results of samples with 6% pectin (Recipe 2).

At values of 25°C with no calcium added, the gel exhibits more liquid state behavior as the loss modulus was greater than the storage. This manifests as a much less viscous fluid like emulsion, rather than a more solid like gel seen at higher additions of calcium. Upon addition of 10mM calcium solution, a dramatic increase in solid like behavior is observed, as the storage modulus increases by greater than a factor of three from 91 Pa to 289 Pa in the 4% mixture. Notably, the rheological results demonstrate a storage modulus greater than the loss, now indicating that the gel exhibits a more solid like behavior. This dramatic increase is attributed to the formation of dimers within the pectin, as the positively charged divalent calcium electrostatically binds to the negatively charged carboxyl groups within the pectin backbone. This reaction leads to the formation of a network which follows the egg-box model, ultimately exhibiting a much more rigid structure than that of pectin without cationic charges present. It is clear from rheological results, that addition of as little as 10mM can be sufficient to initiate this gelling mechanism.

For each system of 4 and 6% pectin at 25°C, the highest G' values were observed at 20mM. For both percentages, it was clear that addition of excess calcium beyond 20mM, did not have a beneficial effect on the strength of the gel. While these higher concentrations of 40, and 80mM did exhibit higher storage moduli values than the gels without calcium, the values were lower than the lower concentrations of 10 and 20mM. The presence of this maximum quantity of cationic charges can likely be attributed to the tendency of pectin to localize within the aqueous matrix. Aggregation of pectin as a result of excess positive charges, would prevent the formation of a continuous long-range network, and would result in weaker gels than those at lower calcium concentrations.

Upon heating from 25°C to 80°C, an overall drop in G' and G'' was visible for every concentration of calcium as gel strength was decreased upon the application of heat. The measure of heat resistance was interpreted as the highest G' value at 80°C, as this would correspond to the most solid-like behavior at the higher temperature. Similar to the G' values seen at 25°C, the strongest gels, and most heat resistance, were seen again at concentrations of 10mM and 20mM calcium for the 4 and 6% pectin systems, respectively. This behavior would be consistent with the observation that lower concentrations of calcium result in stronger gels.

The impact of heating and calcium addition on the emulsion stability was also assessed by confocal microscopy, measuring the oil droplet size. Surprisingly, the oil droplet size was found to be very small, way below 20 µm, and this diameter was hardly impacted by the addition of calcium or by heat treatment. Oil droplet diameters are shown on figure 5A and 5B (4% pectin, 20% oil, no calcium – before and after heat treatment to 80°C), figure 6A and 6B (4% pectin, 20% oil, 20 mM Ca – before and after heat treatment to 80°C), and on figure 7A and 7B (6% pectin, 20% oil, no calcium or 20 mM Ca, before heat treatment). Increasing pectin concentrations generated smaller oil droplets, from about 15 µm (4% pectin) down to below 10 µm (6% pectin).

This example 3 shows that the pectin based emulsion according to the present invention provides a fluid-like emulsion in which small oil droplets with the average size of less than 20 µm are well dispersed and homogenized in the continuous aqueous phase. In contrast to a gelled matrix in which much bigger oil droplets are merely entrapped, the emulsion according to the present invention enables improved stability, versatility for e.g. liquid or fluid applications, as well as more controllable texture. Remarkably, the present invention provides such stable and homogenous emulsion even without calcium addition. The fact that the small oil droplet sizes were not significantly impacted by heating and calcium addition means that the present invention may be used for several applications to provide stable food products even without high temperature heat treatment, and that such stability may not be compromised by any heat treatment which may be required for food safety or operational reasons in some applications. Calcium addition after emulsifying oil and pectin would advantageously tune the texture of the emulsion while maintaining the stable emulsion state.

Example 4

Impact of pectin type

The high methoxy pectin derived from citrus used was replaced by: a low methoxy pectin derived from citrus, an apple pectin, a sugar beet pectin, an amidated pectin derived from citrus, and an unrefined citrus fiber. The citrus fiber may be considered as non-purified pectin compared to the purified high methoxy pectin derived from citrus. The emulsion was generated from 4% pectin and 20% oil in MQ water.

Table 7a. Impact of the pectin type on pH, oil binding and TA data.

	pH at final Tp	**Oil binding capacity (%)**	**TA Hardness (N)**	**TA tack force (N)**	**TA work of adesivness (N*s)**
High methoxy	3,49	100	0,098	-0,328	-0,503
Low methoxy	2,47	100	0,179	-0,502	-0,645
Amidated	4,03	100	0,078	-0,129	-0,187
Citrus fiber	3,33	100	0,469	-1,188	-1,311
Sugar beet pectin	2,96	100	0,094	-0,193	-0,295
Apple pectin	4,84	*13,45*	*NA*	*NA*	*NA*
Apple pectin	Corrected to pH 3.5		0.091	-0.082	-0.083

All formulations had very good oil binding capacities. No emulsion could be generated with apple pectin, because of its higher pH, but when pH was lowered to 3.5 stable emulsions could be formulated, although they were very liquid and thin compared to the citrus pectin ones. It was very surprising that emulsions could be generated from citrus pectins, but also with pectins of different methoxylation and amidation pattern. The sugar beet pectin gels had low hardness and tack force compared to citrus derivatives.

Table 7b. Impact of pectin type on emulgel rheological properties.

	Rheology G' 4 °C (Pa)	Rheology tan delta 4°C	Rheology G' 40 °C heating (Pa)	Rheology tan delta 40 °C heating	Rheology G' 40 °C cooling (Pa)	Rheology tan delta 40 °C cooling
High methoxy	50,04 ± 1.18	1,68 ± 0.01	6,70 ± 0.08	4,11 ± 0.07	1,74 ± 0.5	6,15 ± 2.1
Low methoxy	132,73 ± 15.6	0,85 ± 0.01	49,83 ± 6.02	1,34 ± 0.04	7,51 ± 3.23	1,49 ± 0.49
Amidated	4,06 ± 0.2	3,89 ± 0.2	0,57 ± 0.02	8,24 ± 0.21	0,13 ± 0.09	25,50 ± 17.5
Citrus fiber	610,19 ± 37	0,67 ± 0.02	364,23 ± 31.9	0,72 ± 0.04	343,75 ± 26.9	0,68 ± 0.07
Sugar beet pectin	14,67 ± 0.2	1,90 ± 0.03	4,59 ± 0.08	2,12 ± 0.04	7,31 ± 0.31	1,11 ± 0.01
Apple pectin (pH 3.5)	2.31 ± 0.9	1.84 ± 0.4	1.00 ± 0.6	2.38 ± 1.0	1.42 ± 0.1	0.46 ± 0.2

The emulgels were heated up to 90°C and cooled down to 40°C to assess the stability. High methoxy and sugar beet pectin emulgels have a strong liquid-like behaviour (tan delta > 1) whereas citrus fiber or low methoxy pectins are gels. All materials thinned with cooking (increase in tan delta) but the sugar beet formulation was the least affected of all. Using a pectin-rich citrus fiber (40% pectin) allowed strongly improved the gel-like character and the heat stability. This suggests the emulgel properties and heat resistance can be tuned by modifying the pectin structure and degree of methoxylation in addition to the calcium content. None of the emulgel phase separated with heating but the apple pectin ones turned very thin.

Example 5

Impact of oil on the composition

The following recipes in Table 8 were investigated in this example 5.

Table 8

	Recipe 1	Recipe 3	Recipe 4	Recipe 5	Recipe 6
Pectin (high methoxy, citrus)	4	4	4	4	4
Sunflower oil (HOSO)	20	15	10	5	
Palm stearin (PSO)		5	10	15	20
Water	76	76	76	76	76

*Recipe 1 is the same as Recipe 1 in Table 6 in Example 3.

To determine the impact of oil saturation on the heat stability and strength of the gel system, a saturated fat was selected to be added to the emulsion gel at various concentrations. Palm stearin contains up to 50% palmitic acid, a fully saturated fatty acid which allows for the oil to retain a solid form at room temperature. This contrasts with the high oleic sunflower oil, which is comprised almost entirely of unsaturated oleic acid and exists as a liquid at room temperature. To incorporate the solid fat into the gel, the oil mixtures were heated to 55°C, well above the melting point of palm stearin. The oils were then incorporated under high shear in an identical fashion to the gels containing only high oleic sunflower oil.

Rheological data highlighting the impact of saturated oil addition to the gel strength at room temperature, and high temperature can be seen in figure 8. The storage modulus (G’) is selected for plotting as it represents the solid behavior of the gel. Notable is the different storage modulus values at room temperature as the amount of saturated oil is increased in the gel matrix. As the temperature is fixed at 25°C, the lowest G’ values are observed for the 0, and 25% additions of palm stearin to high oleic oil. At values greater than 25% addition, a trend is observed where the more saturated fat added, the greater the G’ value, with the 100% palm stearin gel displaying a dramatically higher G’ value at 25°C. The solid nature of the fat was found to lend rigidity to the gel matrix at temperatures below the melting point. As the temperature is ramped to 80°C the solid fat begins to melt, which manifests as a drop in the G’ values. At the 80°C final temperature the inverse trend is seen. Gels containing higher amounts of saturated fats display lower G’ values.

These behaviours show the importance of fatty acid saturation on the gel rigidity at both high and low temperatures. In order to maintain strength at both high and low temperatures, a mixture of both saturated and unsaturated may be needed.

Example 6

Impact of pH, temperature, and longer dissolution time

The potential impact of an extended solubilization time on the conformation of pectin chains and, consequently, the functional properties of the emulsion gels was investigated using the following recipes in Table 9.

Table 9

	P1	**P2**	**P3**	**P4**

Pectin (high methoxy, citrus) (%)	7	7	7	7
Sunflower oil (%)	20	20	20	20
Water (%)	73	73	73	73
Hydration T (°C)	50	50	50	50
Hydration t (hrs)	0.25	2	0.25	0.25
Final pH	3.5	3.5	5	2
Oil binding capacity	76.8	90.8	0	100

Figure 9 illustrates the results of the probe tack test and the visual appearance of the samples. Samples P1 and P2 differ in dissolution time to hydrate the pectin, for P1 dissolution was at 50 °C during 15 min with Vittel water, and for P2 dissolution was at 50 °C during 2 h with Vittel water. Although there were no visual differences in the gels, sample P2 exhibited significantly higher adhesiveness (1.617±0.27 N*s) compared to P1 (1.10±0.14 N*s), which had a shorter solubilization time, while the tack force remained similar.

Moreover, the sample with a longer solubilization time (P2) exhibited a higher oil binding capacity (90.8±3.1%) compared to P1 (76.8±3.3%) (table 9). Therefore, higher hydration time directly improved the emulsion properties of the pectin emulgels.

The higher oil binding capacity observed in this study could be attributed to the increased polymer extension of the pectin chains, which is a result of the longer hydration time. The extended polymer chains may expose methyl groups that could be previously confined within the pectin structure, creating chain configurations that can be described as "hydrophobic pockets." With a longer solubilization time, these pockets are displaced and become available to interact with the oil droplets. The intensified interaction between the exposed hydrophobic pockets and the oil droplets leads to enhanced binding and stabilization within the gel structure.

However, as shown in Figure 10, the rheological properties during heating and cooling did not exhibit significant differences between the samples.

To investigate the impact of pH on the stability of pectin emulgels, samples P3 and P4 were prepared, modifying pH to 2 or 5 (reference samples have pH around 3.5). P3 (pH = 5) did not generate a stable emulsion and immediately phase separated. As the pKa of the pectin is typically around 3.5 – 4 the carboxylic groups of pectins will be deprotonated, which decreases their oil affinity, and hence the emulsion stability.

On the other hand, at pH 2 (sample P4) generated a stable emulsion but with very different physical property compared to P1 or P3. As seen in figure 11, P4 presented a higher adhesiveness ($W_{adhesion}$) and a decreased hardness of the emulgel compared to P2. As pH is now below the pectin pKa, all chains will be fully protonated and loose their calcium binding affinity, which explains the weaker gel strength measured. This is further confirmed by rheology measurements (figure 12), where P4 shows G''>G', showing an increased liquid behaviour compared to P2 where G'>G'', typical of a gel material. In addition, the oil binding capacity was strongly improved for P4 over P2 (P2=90.8±3.1% and P4=100.0±0.0%, see table 9), further highlighting the oil affinity of the pectin compared to its gelling ability.

This would confirm that a higher presence of ionic bridges leads to a lower oil binding capacity. Long junction regions of calcium bridges in the pectin chains may create areas of rigidity with reduced molecular mobility that, as a result, reduce the availability of hydrophobic groups to interact with and stabilise oil droplets.

Moreover, it highlights that the formation of ionic bridges at higher pH, when the carboxylic groups are charged, might be more thermodynamically favourable compared to the hydrophobic interactions between pectin chains and oil droplets.

The results demonstrated that pH plays a crucial role in the overall properties of the system. Higher pH values led to the potential formation of ionic bridges, resulting in lower oil binding capacity and even emulsion breakdown by phase separation. A decrease in pH resulted in increased adhesiveness and decreased hardness, suggesting changes in the gelling mechanism and a shift towards hydrogen bond interactions. This pH-induced variation led to enhanced oil entrapment and stabilization properties in cold temperature.

Example 7

Addition of other ingredients

Several starches and fibers were added at varying concentrations in order to identify the effect on rigidity of the gel, as well as the texture. Figure 13 shows the loss factor of a 4% pectin, 20% oil emulsion gel with varying fibers and starches. Addition of these fibers has a notable effect on the rigidity of the gel as seen by the drop in loss factor at room temperature. Potato starch showed the least significant decrease, followed by wheat fiber. Waxy maize starch showed the most significant decrease in loss factor at both low and high temperatures. Additionally, from the wheat fiber additions, it is seen that increasing the amount of fiber decreases the loss factor further. These results demonstrate that addition of fibers and starches to the emulsion gels improve rigidity and can potentially improve heat stability.

In addition to the effects on rigidity, the addition of starches and fibers also affect the texture of the emulsion gels. Addition of these fibers have notable impacts on the hardness, tack force, and work of adhesion. Seen in table 10, the addition of starch and fiber results in similar trends seen in the rheological results. Potato starch shows the smallest change, followed by the wheat fiber, and the waxy maize. These results indicate that addition of fibers and starches can increase the stickiness of the gels, and can lead to overall much firmer textures.

Table 10. Texture analysis values for emulsion gels containing added fibers and starches.

	Hardness (N)	**Ftack (N)**	**Wadhesion (N*s)**
No Fiber	0.245 ± 0.015	-0.458 ± 0.025	-0.586 ± 0.024
Potato Starch 3%	0.585 ± 0.052	-1.126 ± 0.078	-1.101 ± 0.061
Waxy Maize 3%	0.831 ± 0.045	-1.471 ± 0.092	- 0.976 ± 0.111
Wheat Fiber 3%	0.565 ± 0.021	-1.038 ± 0.039	-0.938 ± 0.063
Wheat Fiber 6%	0.654 ± 0.021	-1.245 ± 0.032	-1.236 ± 0.068

Example 8

Formulation and mouthfeel

In this example the following recipes in Table 11 were prepared.

Table 11

Ingredients (wt%)	Recipe A	Recipe B	Recipe C
High methoxy pectin (citrus)	3	8	4
Sunflower oil	20	10	40
Salt	1	1	1
Water	68	81	55
Soy flour	8		

Six internal participants were used for the study. The samples were served at ambient temperature and they were not heated before.

The panelists were asked to tick on the attribute(s) that applied to describe each sample. The panelists had to then determine, out of the 3 samples, which one was the most intense and which one was the least intense. The panelists were also asked to give comments on the attribute(s) that was/were not listed into the glossary.

Based on the data collected from the whole panel, the following conclusions could be drawn:

Table 12

Samples	**Main sensory characteristics**
Recipe A	More Powdery, More Compact, Less Shiny
Recipe B	More Shiny, Firmer, More Sticky, More Mouthcoating
Recipe C	Less Firm, Slippery, Short melting time, oil leaking

Table 13. Number of selection of each sample as “the most” and “the least” intense for each attribute

		The most		
	Attributes	A	B	C
Appearance	Shiny		x x x x x	x
	Compact	x x x	x x	x
Texture	Firm	x x	x x x	
	Slippery	x x	x	x x
	Sticky	x	x x x x	
	Powdery	x x x x x		
	Crumbly	x x		x
	Melting time	x	x x x x	
	Mouthcoating		x x x x x	x
	Astringent	x x x	x	x
		The least		
	Attributes	A	B	C
Appearance	Shiny	x x x x x		x
	Compact	x x x		x x x
Texture	Firm	x	x	x x x x
	Slippery	x x	x x	x
	Sticky	x x x	x	x
	Powdery		x x x	x
	Crumbly	x	x x	
	Melting time	x x	x x	x x x
	Mouthcoating	x x x x	x	
	Astringent	x x	x x	

Example 9

Recipe for meltable fillings and binders

The following recipes were prepared as binders or fillings as described in the experimental section by hydrating the pectin in a mix of purée and water.

Table 14

Ingredients (wt%)	**Filling**	**Binder**
Pectin (high methoxy, citrus)	3	7
Red bellpepper purée	41	
NaCl	1	
Sunflower oil	20	20
Vittel Water	30	73
Lemon juice	2.5	
Nutritional yeast	2.5	

An example of a food product with a meltable core is given herein. A soy protein gel was prepared by hydrating 20% of soy protein in water for 15 min. The soy protein dough was placed on a plastic film to make a layer, then emulgel filling (whose recipe is disclosed in table 14) was added in the middle and the film was closed to make a small ball which was cooked in a steam oven. After cooking the ball could be open and cut through to let a liquid filling flow out. The sample had the appearance of a burrata, with a liquid core entrapped in a solid shell. It could be heated without melting.

In another example, the recipe given for a filling in table 14 was placed in half-sphere silicon moulds and frozen overnight. The following days spheres were demolded and assembled to make a single sphere, which breaded with egg and breadings then deep fried. The croquettas could be successfully fried and presented a liquid core. Vegetable pieces could be included into the ball.

In another example, a binder was prepared as disclosed in table 14, then combined with the ingredients disclosed in table 15 to form a wet dough, which was shaped as a croquette and pan fried. The croquetta could be pan fried and flipped over, while still maintaining its shape and without losing vegetable or TVP pieces, confirming the binding properties of pectin emulgels. It presented a very indulgent mouthfeel from the pectin, unlike the dry mouthfeel often felt for plant-based meat analogs.

Table 15

Ingredient	wt%
Pectin emulsion-gel (binder recipe of table 14)	38.1
Vegetables	28.6
TVP (texturized vegetable proteins)	26.7
Herbs and spices	4.0
Yellow pea starch	1.9
Salt	0.8

Example 10

Healthy spreads with high vegetable content

Table 16

Ingredient (wt%)	Red bell pepper recipe	Carrot recipe	Broccoli recipe	Red bell pepper - control
10% vinegar		2,34	3,10	
High methoxy pectin (citrus)	2	1,95	1,94	
Purée	82	80,08	79,46	84
Salt	1	0,98	0,97	1
Oil	15	14,65	14,53	15
Final pH	4.2	4.2	4.2	4.2

Emulsion gels with high purée content were prepared as described earlier using purée instead of water. The pH was adjusted to 4.2 with vinegar to ensure emulsion formulation, because vegetables with higher pH (higher than pH 5, for example) may not be efficiently emulsified and led to oil separation as reported in previous sections.

The emulsions presented vibrant colours, very good stability and an indulgent mouthfeel due to the pectin mouthcoating. Samples prepared using only the vegetables and oil felt oily but without the strong mouthcoating and indulgence feeling.

Example 11

Shelf Life Stability of vegetable spreads

The following recipe in Table 17 was tested for the healthy vegetable spreads.

Table 17

Ingredient (wt%)	**Carrot emulgel**
80% Lactic acid	0.57
High methoxy pectin	2
Carrot purée	81.43
Salt	1
Oil	15
Final pH	**3.5**

The spread was prepared as described in Example 10. The amount of acid was increased to ensure food safety. The emulsion was transferred to glass jars, sealed, and retorted in a steam oven so that the core temperature reached 95°C for 5 min.

The glass jars were stored either in a fridge at 4°C or at room temperature at 25°C over 6 months. The stability was assessed before and after heat treatment, after 2 weeks, 1 month, 1.5 month, 2 months, 3 months and 6 months. Stability of the gel was probed throughout the shelf life test with the following methods:

- rheological method modulating the frequency to monitor the storage and loss modulus for both the samples stored at 4°C, and the samples stored at 20°C (figures 18A and 18B).
- rheological method modulating the amplitude to monitor the storage and loss modulus for both the samples stored at 4°C, and the samples stored at 20°C (figures 19A and 19B).
- viscosity for both the samples stored at 4°C, and the samples stored at 20°C (figures 20A and 20B)
- texture analysis (figures 21A, 21B, 22A, 22B)
- tribology (figures 23A and 23B)
- oil binding (figure 24)
- oil oxidation (figure 25)

Overall, the samples showed little variation in these properties freshly after production and following heat treatment, with only a slight drop in viscosity and gel strength. No further deviation was observed upon time for up to 6 months when stored at room temperature.

The oil droplet size in a carrot purée was measured right after heat treatment and at 2 or 6 months shelf life with storage at room temperature (25°C) or at 4°C. Right after heat treatment the oil droplet size was about 10 µm (figure 26) and hardly evolved for the first 2 months, with a slight increase over 6 months (figures 27A and 27B). On the other hand, samples stored at room temperature showed a higher increase in oil droplet size to about 15 µm already visible at 2 months (figures 28A and 28B). However, the average oil droplet size for the samples stored at room temperature is still below 20 µm, even after 6 months. As discussed in the above example 3, the pectin based emulsion according to the present invention enables an emulsion which can maintain the good stability even after 6 months under the room temperature condition.

Table 18. Water activity evolution of samples stored at 4°C or at room temperature

Storage Temp	Week	Water Activity
	T0 No Heating	0.985
	T0	0.986
4°C	T2	0.987
	T4	0.987
	T6	0.987
	T8	0.988
	T12	0.986
	T24	0.982
20°C	T2	0.987
	T4	0.987
	T6	0.987
	T8	0.987
	T12	0.987
	T24	0.983

Example 12

Pectin emulgels and impact on flavour and texture perception

The sensory attributes of acidified pectin emulgels were assessed on the following recipes in Table 19.

Table 19

Ingredient wt%	R1	R2	R3	R4	R5	R6	R7	R8
Carrot purée	99	98.43	83.43	96.43	81.43	81.93	94.93	79.93
Pectin (high methoxy, citrus)				2	2		2	2

Sunflower oil			15		15	15		15
NaCl	1	1	1	1	1	1	1	1
80% Lactic acid		0.57	0.57	0.57	0.57	0.57	0.57	0.57
Curry spice mix						1.5	1.5	1.5

A panel of 10 people was trained on the product category and on the different attributes in Table 20.

Table 20

Flavour (FL)	FL_OverallFlavour	Describes the total intensity of all types of notes perceived.
	FL_Acid	Describes the intensity of the basic taste characterized by solutions of acids such as citric acid.
	FL_Bitter	Describes the intensity of the basic taste characterized by solutions of caffeine or quinine.
	FL_Sweet	Describes the intensity of the basic taste characterized by solutions of sucrose.
	FL_Salt	Describes the intensity of the basic taste characterized by solutions of salt.
	FL_OverallVegetable	Describes the intensity of all the vegetables perceived.
	FL_Spicy	Describes the intensity of the spicies (i.e. curry, paprika, curcumin).
	FL_Oil	Describes the intensity of oil note.
	FL_Other	Describes the intensity of any additional note characters not mentioned in the list.
Texture (TX)	TX_Smooth	Describes the silky perception in the mouth generated by a product which is free from roughness, lumps, ridges, irregularities or particles.
	TX_Thick	Describes the strength necessary for the tongue to move/squeeze the product in mouth against the palate.
	TX_Sticky	Describes the extent to which the product sticks to the palate during the mastication.
	TX_Oily	Describes the perception of a oil texture in mouth.
	TX_Mouthcoating	Describes the perception of a film coating/enrobing the mouth.
	TX_Astringent	Describes the complex sensation of shrinking, drying or puckering in the mouth. Describes a dry/rough tongue and dry/rough palate.
	TX_Other	Describes the intensity of any additional texture characters not mentioned in the list (to specify in comment).

Samples were stored in the fridge and tasted at ambient temperature.

Samples prepared with oil but without pectin phase separated, an oil layer was clearly visible at the top.

As seen in figure 29A the addition of pectin had a significant impact on the texture of the recipes by increasing the thickness, stickiness and mouthcoating compared to carrot purée (R4 and R5 against

R1, R2 and R3). However, the pectin emulgel provided an additional benefit in reducing the astringency and the bitterness perception against pectin-only thickened purée (R4 and R5, Figures 29A and B). The addition of curry spices did not affect the texture attributes of the emulgel recipes (figure 29B).

Pectin addition reduced the overall flavour perception, including the bitterness induced by lactic acid and the vegetable flavour. Emulgel samples (R5) were perceived slightly less acidic than acidified purée, but the differences were not significant. (figure 30A). The addition of pectin in curry-flavoured purée (R7) increased the spiciness perception but also the bitterness, whereas pectin emulgels were significantly less bitter while maintaining a strong curry flavour (figure 30B). A grouping of all products showed that pectin samples were not described as acidic unlike acidified purees (figure 31). This demonstrates the benefit of pectin emulgels in masking off-flavours.

Example 13

Recipes for frozen dessert

Pectin emulgels could also be formulated using fruit purées. Example recipes are described in Table 21. The emulgels were prepared as described in the previous examples and were successively frozen. Frozen desserts were freshly prepared using a Pacojet. The pectin used in this example was a high methoxy pectin from citrus with a degree of methoxylation around 70%.

Table 21. Pectin fruity frozen dessert recipes

Ingredient (wt%)	**Recipe D**	**Recipe E**	**Recipe F**	**Recipe G**
Pectin	1.7	2	1	1
Sunflower oil	12.8	20	4	
Coconut fat		10		4
Raspberry purée			95	95
Mango and maracuja purée	85.5	68		

Recipe D was shiny and perceived as fruity and fatty, rich, hearty.

Recipe E was very aerated and hearty. It could be used as a coating.

Recipes F and G presented nice indulgent textures and intense fruity taste. Coconut fat provided a more aerated texture than sunflower oil and was preferred over all other recipes.

Example 14

Baby purées

Baby purées were prepared from pectin emulgels to improve stability and texture. The pectin used in this example was a high methoxy pectin from citrus with a degree of methoxylation around 70%. To adapt the texture to indulgent purées low pectin concentrations were preferred in formulations. The recipes are summarized in table 22.

Table 22. Pectin emulgel recipes for baby food applications

Ingredient (wt%)	**B01**	**B02**	**B03**	**B04**	**B05**	**B06**
Pectin	0.5	1	1.5	0.5	1	1.5
Sunflower oil	3	5	7	5	7	3
Lemon juice concentrate	1.9	2	1.9	0.7	0.8	0.7
Carrot purée	94.6	92	89.6	93.8	91.2	94.8
Final pH	**3.5**	**3.5**	**3.5**	**4.2**	**4.2**	**4.2**

The emulgels were prepared as described earlier, then the samples were heated to 90°C for 5 min and filled in a glass jar which was closed and inverted for 90 sec to ensure shelf stability.

The samples were assessed for 2 weeks following heat treatment in terms of colour and viscosity.

The colour results are presented in table 23. Colours differences of the heat-treated purées were expressed against the non-treated purée. Colour differences can be perceived for ΔE values higher than 4, with higher ΔE values reflecting greater colour differences. The reference carrot purée was strongly affected by the heat treatment (ΔE > 12) compared to emulgel recipes (ΔE between 6 and 8). The lower the oil content and the lower the impact on colour.

Table 23. Colour variation of emulgel purées after heat treatment (HT)

ΔE	**Ref**	**B01**	**B02**	**B03**	**B04**	**B05**	**B06**
After HT	12.8	2.98	6.79	6.81	8.78	6.90	3.09
2 weeks after HT		4.62	8.56	8.27	8.78	6.48	2.29

The reference carrot purée clearly formed 2 phases after heat treatment, whereas the emulgel purées remained homogeneous. As seen in table 24, immediately after heat treatment, the viscosity decreased slightly and remained stable over 3 weeks. This demonstrates the superiority of emulgel purées for the stability of baby food purées.

Table 24. Viscosity variation of pectin emulgel formulations after heat treatment (HT)

Viscosity @ 100 s^{-1}	**B01**	**B02**	**B03**	**B04**	**B05**	**B06**
Before HT	646	926	1440	703	1310	1750
After HT	611	879	1360	704	1250	1740
2 weeks after HT	619	878	1380	676	1330	1790

Example 15

Healthy and indulgent spicy cooking sauces

Cooking sauces were prepared according to the recipe disclosed in table 25.

Table 25

Ingredient wt%	**Red bell pepper recipe**	**Carrot recipe**	**Broccoli recipe**
Lactic acid 80%	0.6	0.6	0.6
High methoxy pectin (citrus)	1.5	1.5	1.5
Purée	83.9	82.2	84.2
Salt	1	1	1
Oil	10	10	10
Spice mix	3	4.7	2.7

Emulsion gels with high purée content were prepared as described earlier with lactic acid the pH was adjusted to about 3.5. The spice mix used for each recipe is disclosed in table 26.

Table 26. Spice mix of each variant.

	Red bell pepper recipe	**Carrot recipe**	**Broccoli recipe**
Ingredients (wt%)	Fresh red chilli (1%)	Curry madras (1.23%)	Fresh emongrass (0.06%)
	Fresh garlic (0.56%)	Fresh turmeric (0.41%)	Fresh galanga (0.28%)
	Fresh ginger (1.4%)	Fresh red chilli (2.05%)	Fresh green chilli (1.4%)
	Cayenne pepper (0.04%)	Fresh garlic (0.55%)	Fresh garlic (0.56%)
		Fresh lemon zest (0.03%)	Fresh combawa zest (0.01%)
		Fresh ginger (0.41%)	Fresh ginger (0.35%)
		Cayenne pepper (0.03%)	Fresh lime zest (0.04%)
Total	3	4.71	2.7

The products obtained with these recipes had a lower viscosity than the dips given in example 10. The products were less sticky and mouthcoating. The mouthfeel was rich and indulgent and the spices were long perceived in mouth. The texture and viscosity was close to that of a barbecue sauce or a ketchup.

Example 15

Impact of process on oil droplet size and emulsion stability

To assess the impact of the process parameters, the following recipes (table 27) were prepared:

Table 27.

Ingredient (wt%)	**C1**	**C2**
Pectin (high methoxy DM=70, citrus)	2	2
Oil	15	15
Water	83	83
$CaCl_2$ (mM)	5	5
pH	3.5	3.5
Hydration temperature (°C)	25	50
Emulsification temperature (°C)	25	75

Samples were prepared as described previously with minor modification:

- In C1, the pectin was hydrated at room temperature (25°C) then a solution of $CaCl_2$ 1M was added to reach a final concentration of 5 mM; finally, the emulsification was performed at 25°C.
- In C2, the pectin was hydrated at 50°C and the emulsification was performed at 75°C; the $CaCl_2$ solution was added after the emulsification was performed.

Samples C1 and C2 presented different viscoelastic properties, as seen in Figure 32. Cold emulsified samples (C1) had a weak gel-like behavior while C2 behaved like a viscoelastic fluid. Such a big difference in rheological properties was not expected by a simple variation in emulsification temperature. The oil droplet size was compared for both samples. While hot emulsification samples (C2) provided oil droplet sizes below 20 µm, the samples with emulsification at 25°C (C1) provided bigger oil droplet dimensions of about 25 µm (Figures 33A and 33B). Hot emulsification allows for lower viscosity of the pectin continuous phase and for the oil phase, which will be easier to disperse under shearing, resulting in smaller oil droplets which have a significant impact on the material properties.

Example 16

Acidity masking of emulgel purées

In this example, the following recipes (table 28) were prepared as described earlier:

Table 28.

Ingredient (wt%)	**D01**	**D02**	**D03**
Pectin (high methoxy DM=70, citrus)		0.8	1.6
Sunflower oil		3.0	3.0
Lemon juice concentrate	0.5	0.4	0.4
Carrot purée	99.5	95.8	95
Final pH	**4.2**	**4.2**	**4.2**

All products have the same acidity (pH target at 4.2).

A panel of 9 people was trained on the product category and on acidity. Panelists were asked to rank the acidity on a linear scale from 0 (no acid) to 10 (maximum acidity). The products were consumed at room temperature (20°C) in a random order under red light.

The scores are shown on Figure 34. * indicates ANOVA significant at 1% product significantly different than product D03 (lower score). ** indicates ANOVA significant at 1% product significantly different than product D02 and D01.

Sample D01 was the most acidic (score 7.1) while both emulgels samples were significantly less acidic (score 4.4 for D02 and 2.1 for D03). D03 was significantly less acidic than D02.

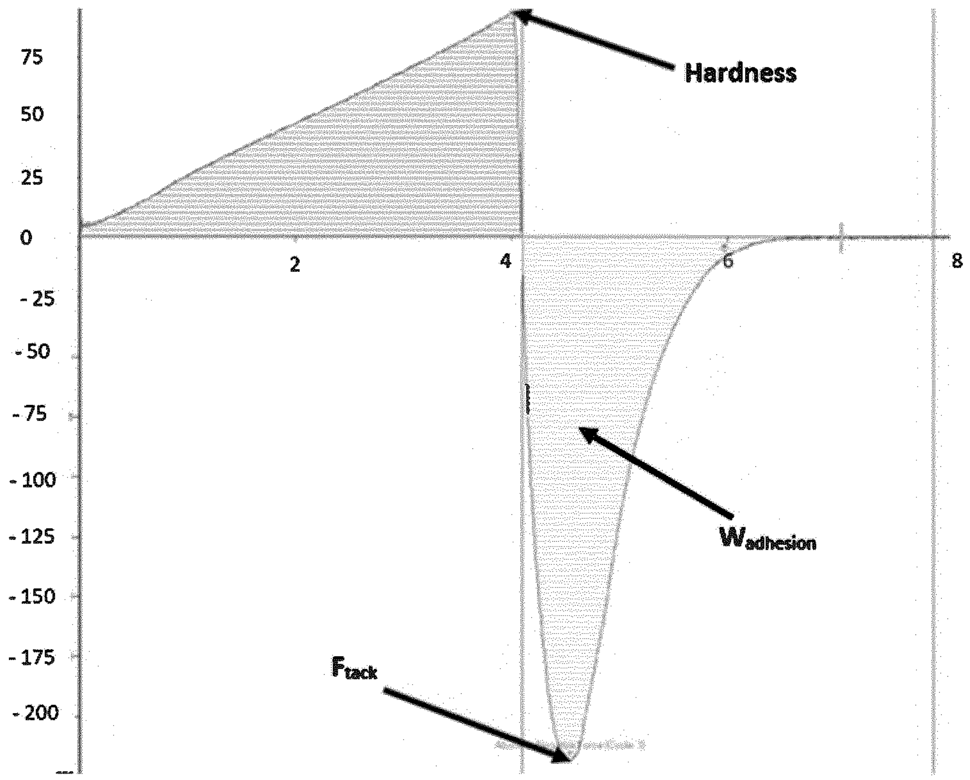
For a given pH (4.2), increasing the amount of pectin and sunflower oil significantly decreases the perceived acidity in sensory evaluation.

This example 16 shows that the pectin based emulsion according to the invention provides significant acidity masking effect.

Claims

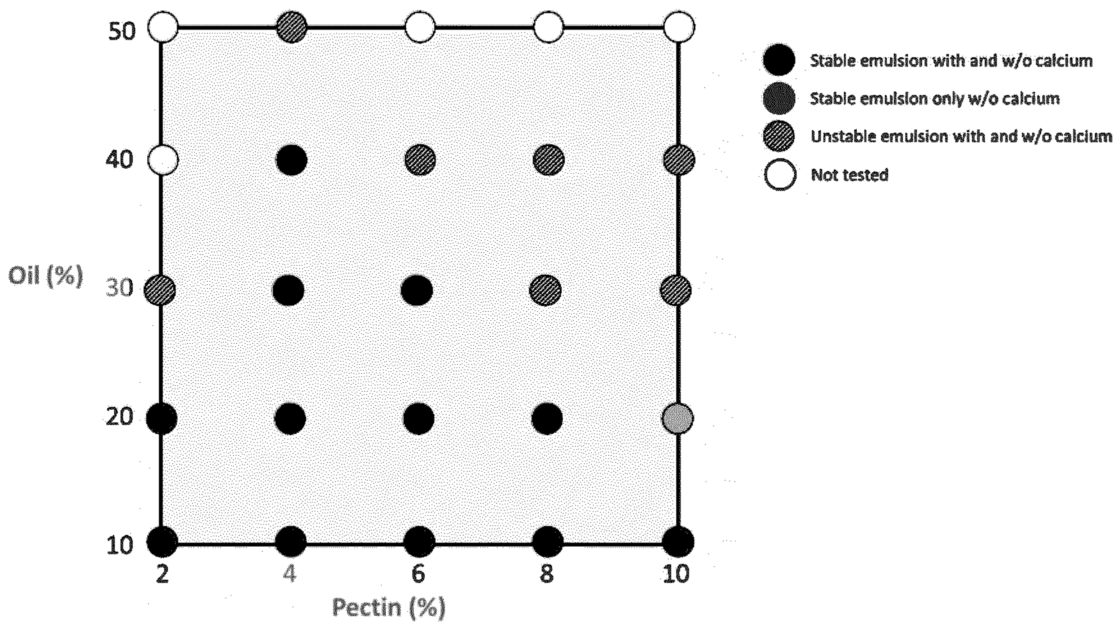
1. A pectin based emulsion, said emulsion comprising between 0.5 and 6 wt% pectin, between 3 and 40 wt% oil, and water, wherein the emulsion has a pH which is less than 5, an average oil droplet size in the emulsion is below 20 µm, and the pectin is high methoxy pectin with degree of methoxy (DM) > 60.
2. The pectin based emulsion according to claim 1, wherein the emulsion has a pH which is less than 4.5, preferably less than 4.2, more preferably about 3.5.
3. The pectin based emulsion according to claim 1 or 2, wherein said emulsion comprises about 1.5-2.0 wt% pectin and about 10-15 wt% oil.
4. The pectin based emulsion according to any one of claims 1 to 3, wherein the pectin is high methoxy pectin with DM of 70.
5. The pectin based emulsion according to any one of claims 1 to 4, said emulsion further comprising fruit powder, vegetable powder, for example pulse flour, purified fibers, or purified starch.
6. The pectin based emulsion according to any one of claims 1 to 5, wherein the water is de-ionized water, tap water, or mineral water.
7. The pectin based emulsion according to any one of claims 1 to 6, wherein the water is replaced by a purée, for example a vegetable puree, or a fruit puree, or a pulse puree.
8. The pectin based emulsion according to any one of claims 1 to 7, wherein the pectin is a citrus pectin, a sugar beet pectin, an apple pectin, or an amidated pectin.
9. The pectin based emulsion according to any one of claims 1 to 8, wherein the pectin is a citrus pectin.
10. A method of making a pectin based emulsion according to any one of claims 1 to 9, said method comprising heating pectin in water to at least 50°C, adding oil and high shear mixing for about 5 minutes.
11. The method according to claim 10, wherein the high shear mixing is performed while heating the mixture of the pectin and the oil to at least 50°C, preferably about 75 °C.
12. The method according to claim 10 or 11, wherein the high shear mixing is performed at a rotational speed of between 100 and 2000 RPM.
13. The method according to any one of claims 10 to 12, further comprising adjusting pH of the pectin based emulsion to be less than pH 5, preferably less than pH 4.5, more preferably less than pH 4.2, more preferably about pH 3.5.

14. The method according to any one of claims 10 to 13, further comprising adding multivalent ions, preferably calcium ions to the pectin based emulsion after performing the high shear mixing, so that the final concentration of multivalent ions in the pectin based emulsion reaches up to 80 mM, preferably between 5 and 40 mM.
15. Use of a pectin based emulsion according to any one of claims 1 to 9, wherein said emulsion is
    a. a binder;
    b. a filling;
    c. a flavor carrier;
    d. a fat replacer;
    e. a spreadable product;
    f. a purée;
    g. a dip;
    h. a topping; or
    i. a frozen dessert.



Hardness
75
50
25
0
-25
-50
-75
-100
-125
-150
-175
-200
2
4
6
8
$W_{adhesion}$
F_{tack}

FIG. 1



50
40
30
20
10
Oil (%)
2
4
6
8
10
Pectin (%)
Stable emulsion with and w/o calcium
Stable emulsion only w/o calcium
Unstable emulsion with and w/o calcium
Not tested

FIG. 2

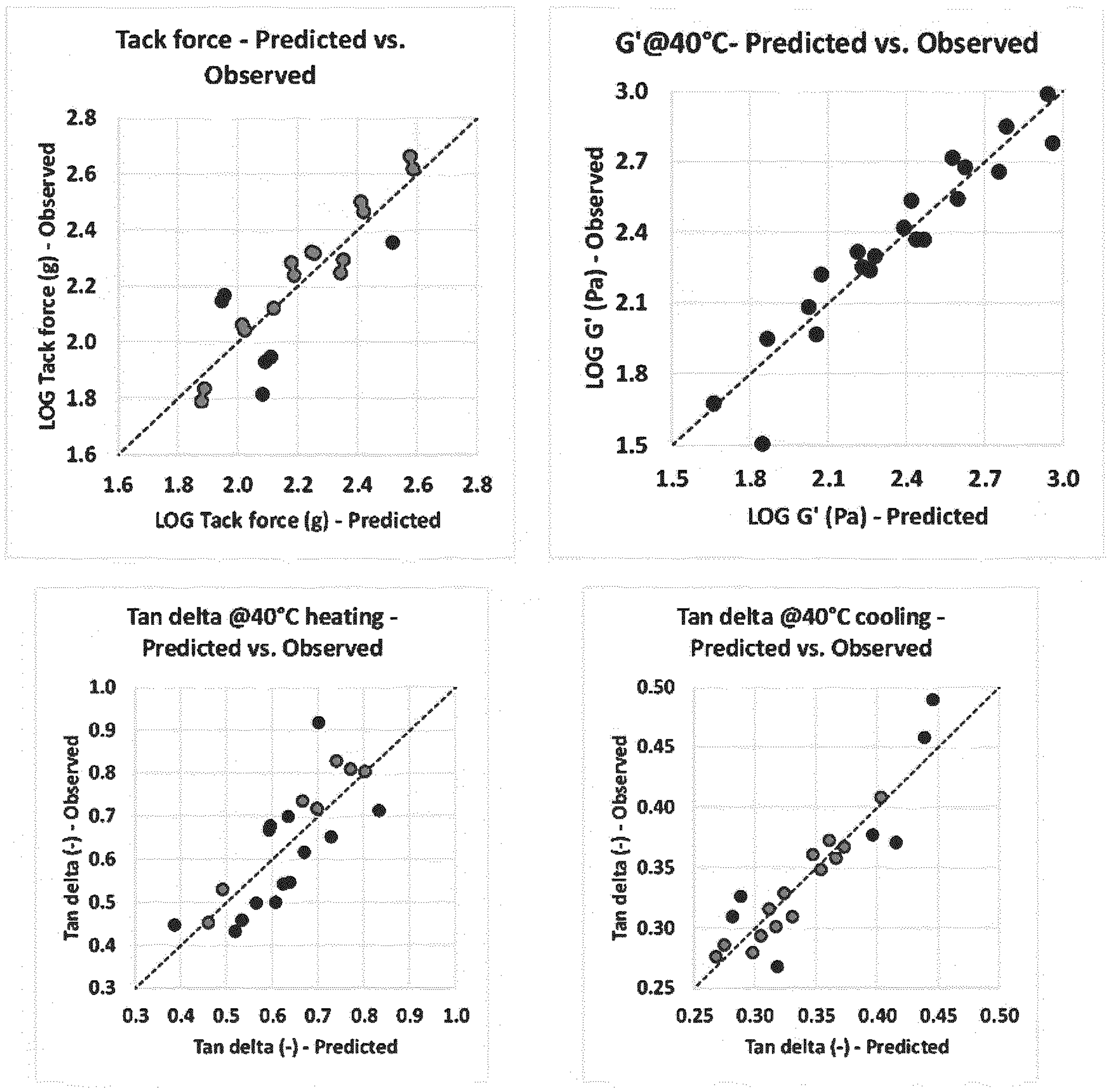

Tack force - Predicted vs. Observed
LOG Tack force (g) - Observed
LOG Tack force (g) - Predicted
1.6 1.8 2.0 2.2 2.4 2.6 2.8
G'@40°C- Predicted vs. Observed
LOG G' (Pa) - Observed
LOG G' (Pa) - Predicted
1.5 1.8 2.1 2.4 2.7 3.0
Tan delta @40°C heating - Predicted vs. Observed
Tan delta (-) - Observed
Tan delta (-) - Predicted
0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Tan delta @40°C cooling - Predicted vs. Observed
Tan delta (-) - Observed
Tan delta (-) - Predicted
0.25 0.30 0.35 0.40 0.45 0.50

FIG. 3

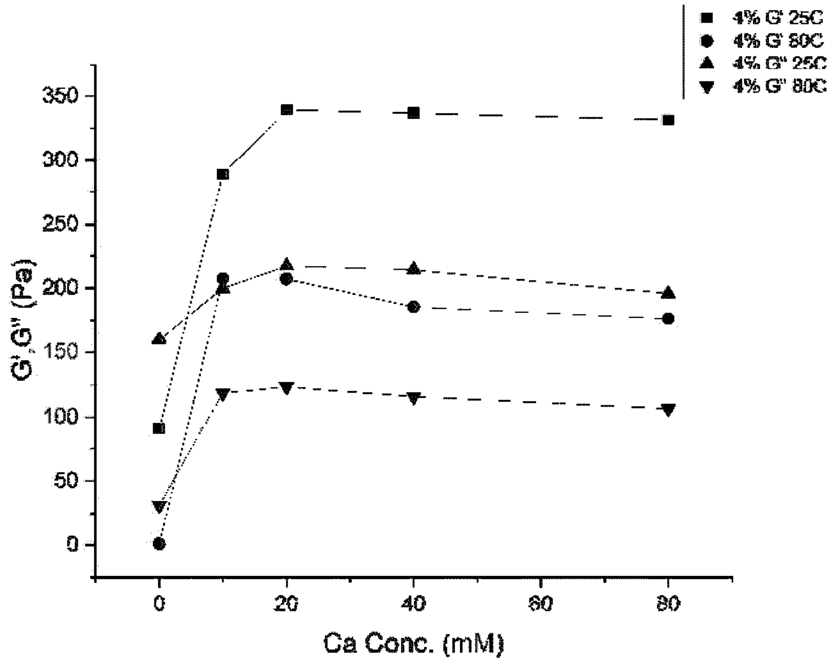

4% G' 25C
4% G' 80C
4% G" 25C
4% G" 80C
G',G" (Pa)
350
300
250
200
150
100
50
0
0
20
40
60
80
Ca Conc. (mM)

FIG. 4A

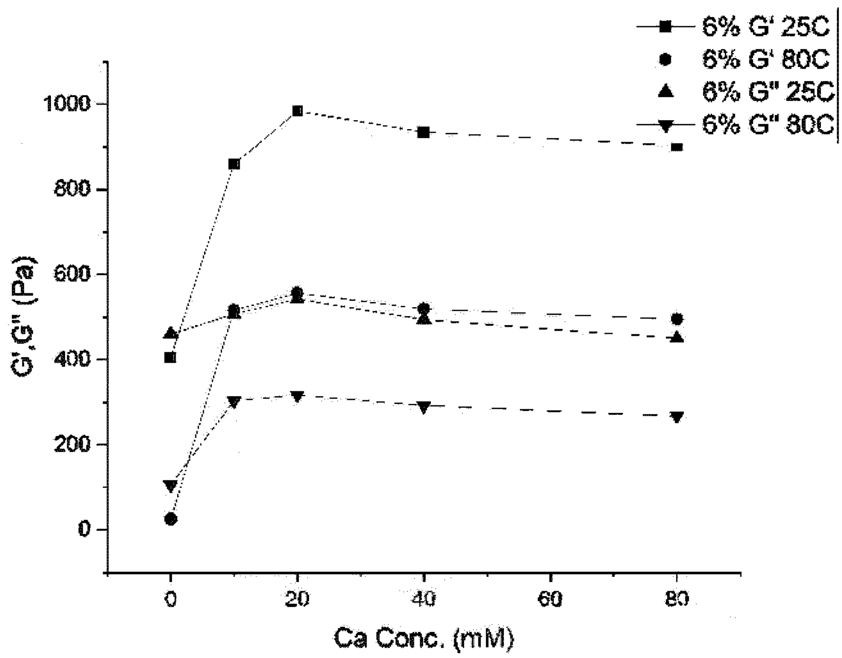

6% G' 25C
6% G' 80C
6% G" 25C
6% G" 80C
G',G" (Pa)
1000
800
600
400
200
0
0
20
40
60
80
Ca Conc. (mM)

FIG. 4B

4% pectin 20% oil no Ca no heat

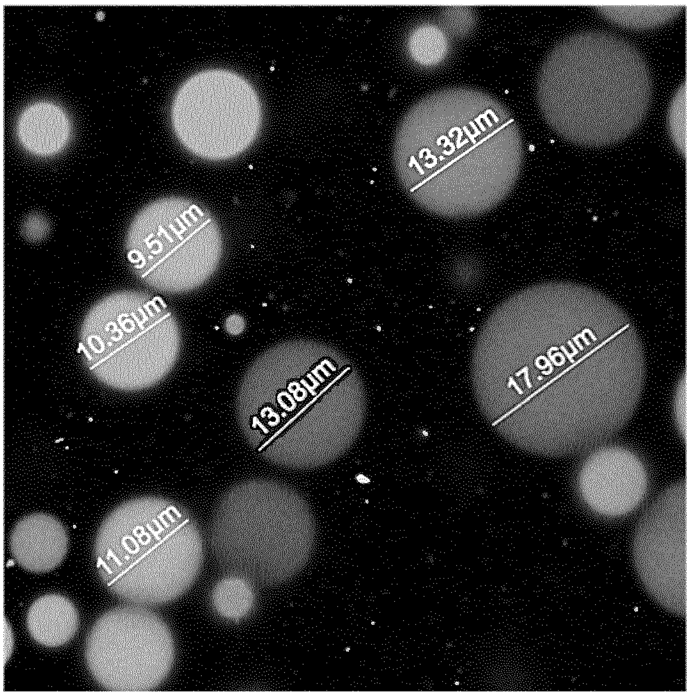


FIG. 5A

4% pectin 20% oil no Ca 80°C heat

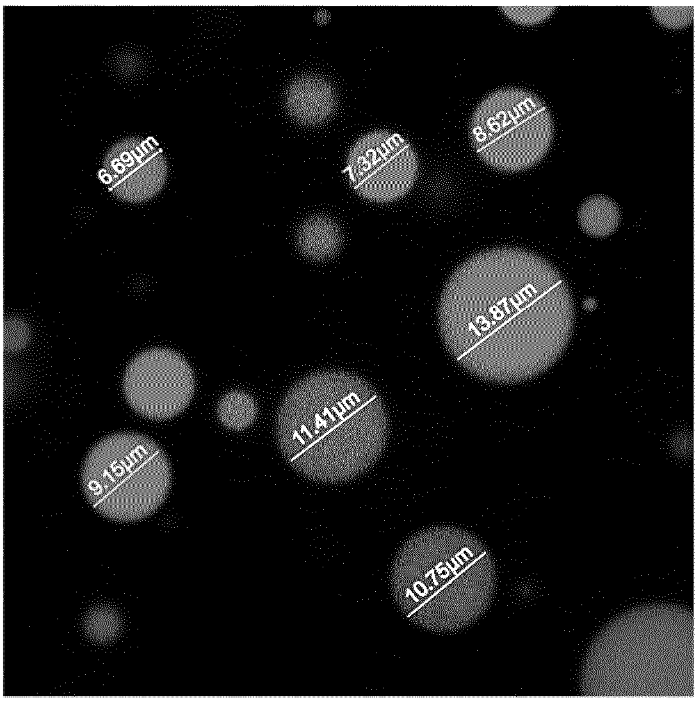


FIG. 5B

4% pectin 20% oil 20 mM Ca
no heat

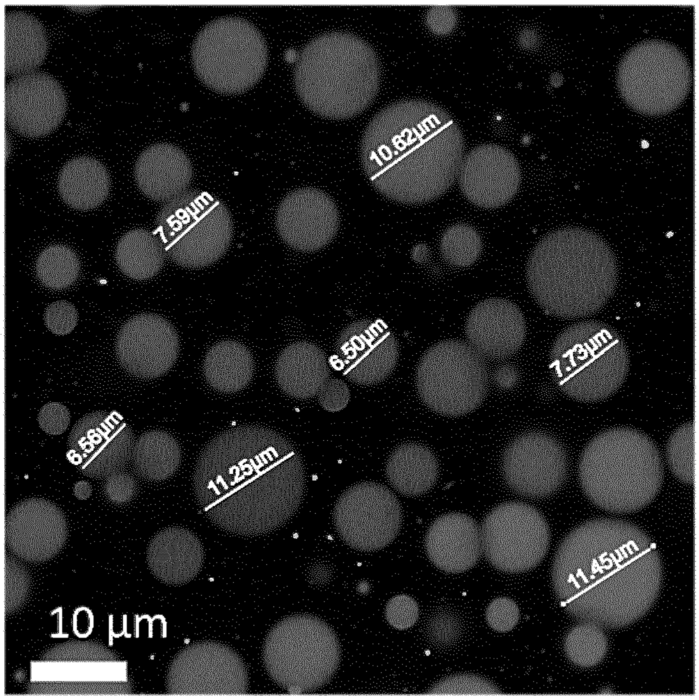


FIG 6A

4% pectin 20% oil 20 mM Ca
80°C heat

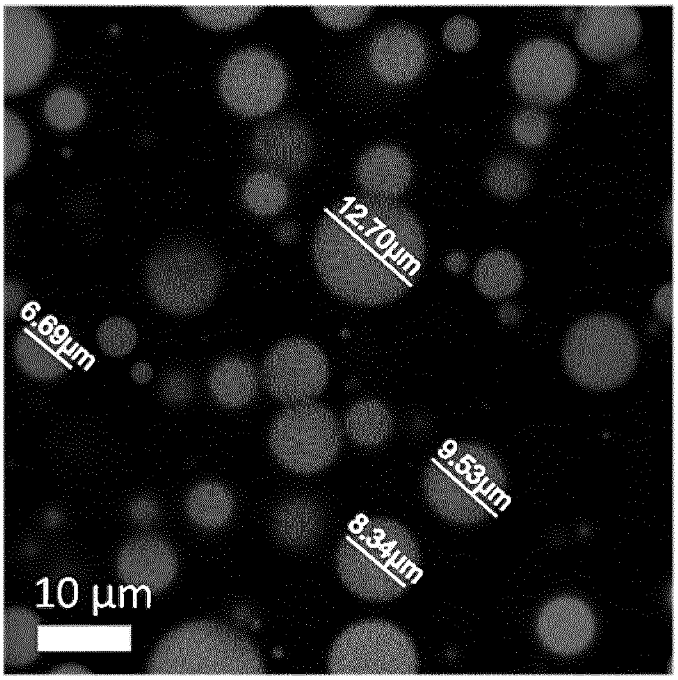


FIG. 6B

6% pectin 20% oil no Ca no heat

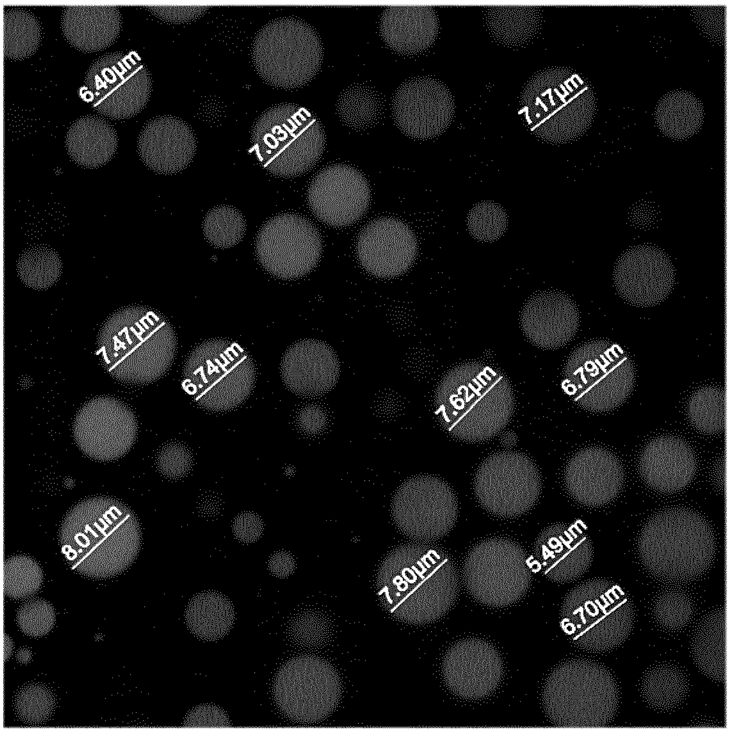


FIG. 7A

6% pectin 20% oil 20 mM Ca no heat

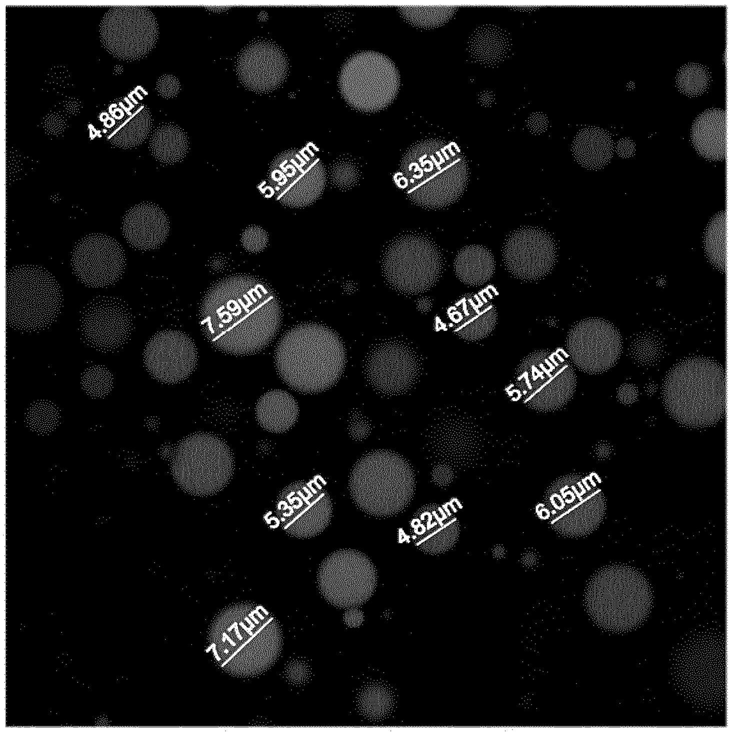
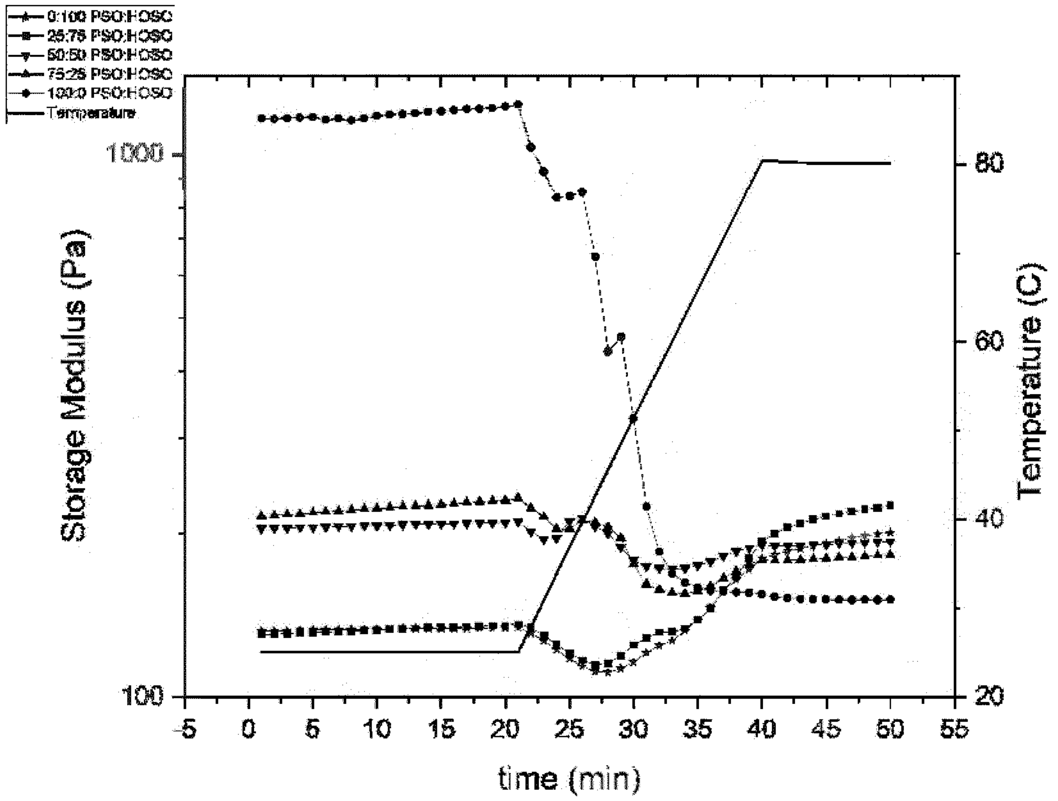
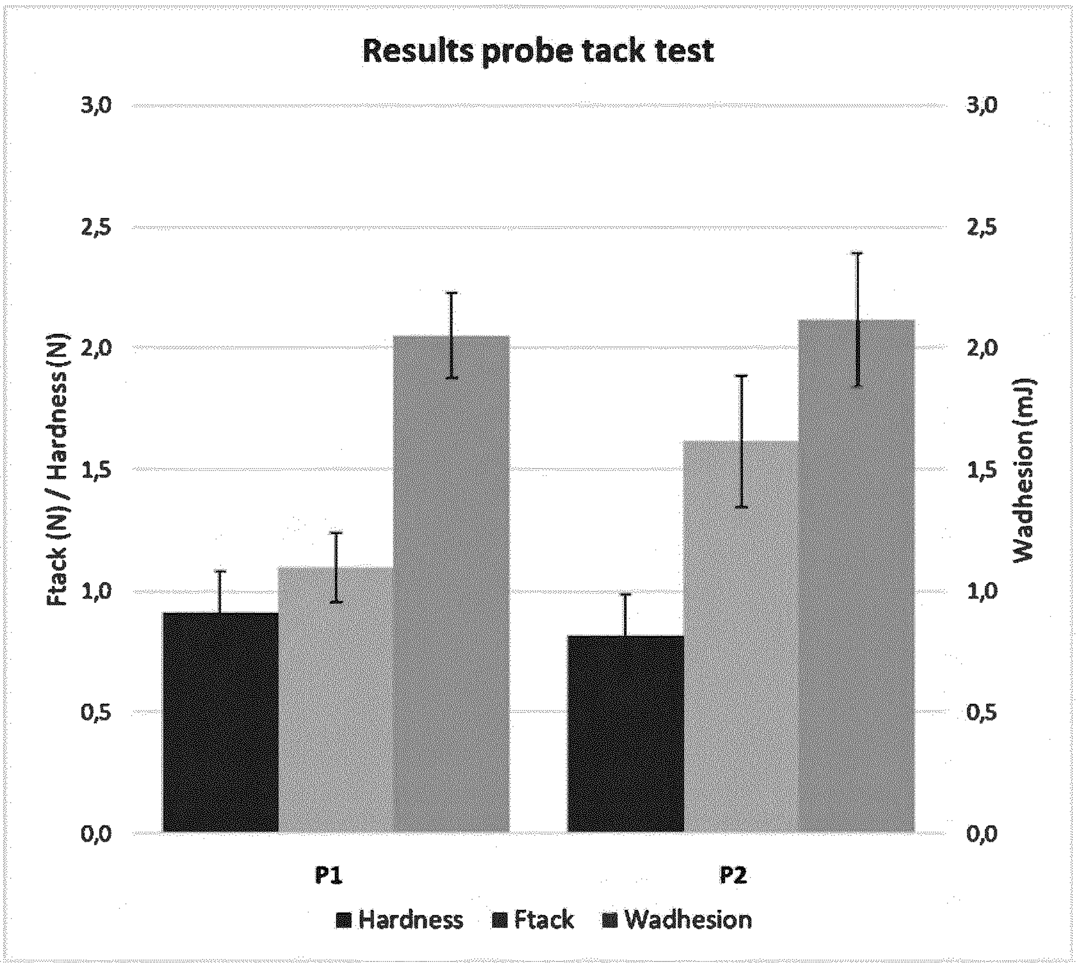


FIG. 7B



0:100 PSO:HOSO
25:75 PSO:HOSO
50:50 PSO:HOSO
75:25 PSO:HOSO
100:0 PSO:HOSO
Temperature
Storage Modulus (Pa)
Temperature (C)
time (min)
1000
100
80
60
40
20
-5
0
5
10
15
20
25
30
35
40
45
50
55

FIG. 8



Results probe tack test
3,0
2,5
2,0
1,5
1,0
0,5
0,0
Ftack (N) / Hardness (N)
Wadhesion (mJ)
P1
P2
Hardness
Ftack
Wadhesion

FIG. 9

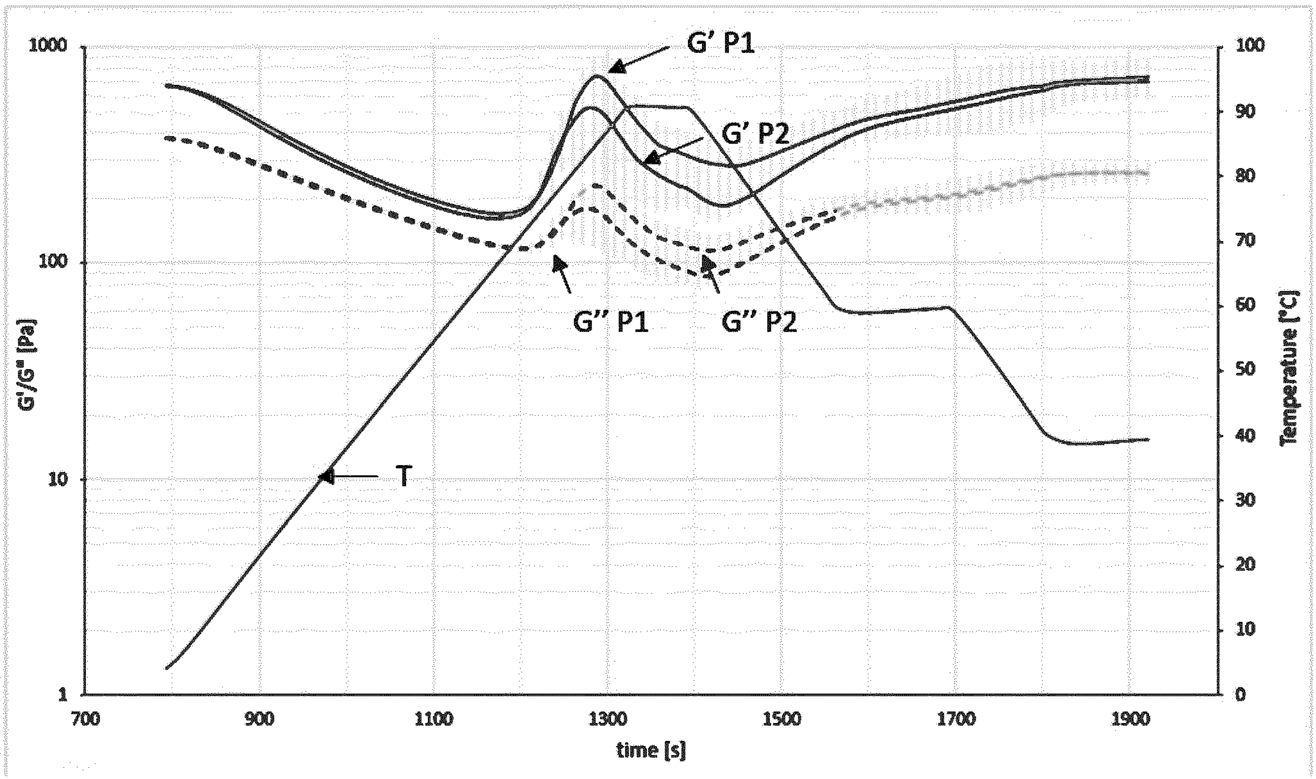

G' P1
G' P2
G'' P1
G'' P2
T
1000
100
10
1
G'/G" [Pa]
700
900
1100
1300
1500
1700
1900
time [s]
100
90
80
70
60
50
40
30
20
10
0
Temperature [°C]

FIG. 10

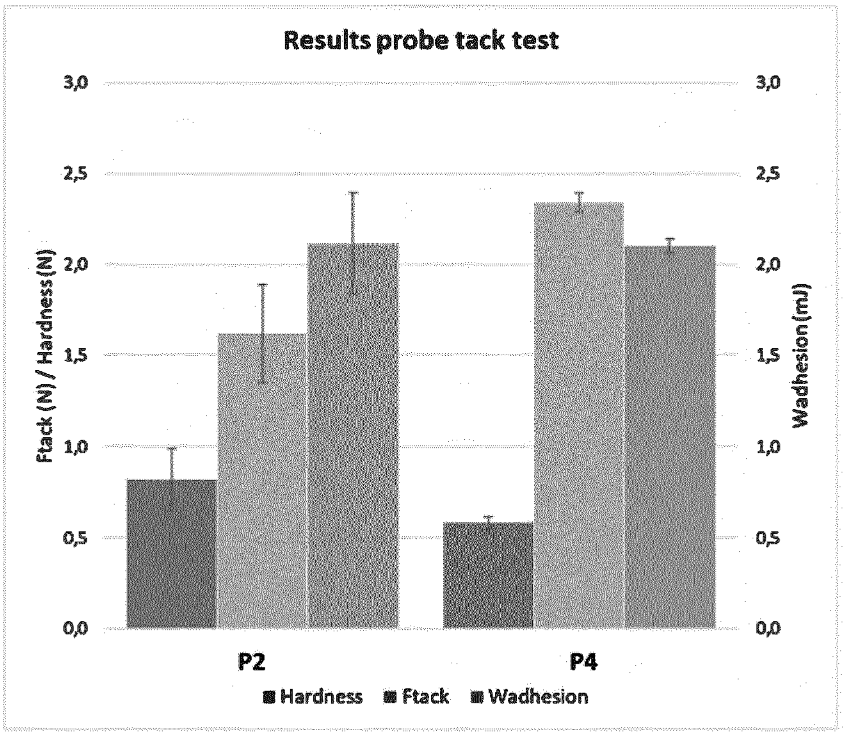

Results probe tack test
3,0
2,5
2,0
1,5
1,0
0,5
0,0
Ftack (N) / Hardness (N)
Wadhesion (mJ)
P2
P4
Hardness
Ftack
Wadhesion

FIG. 11

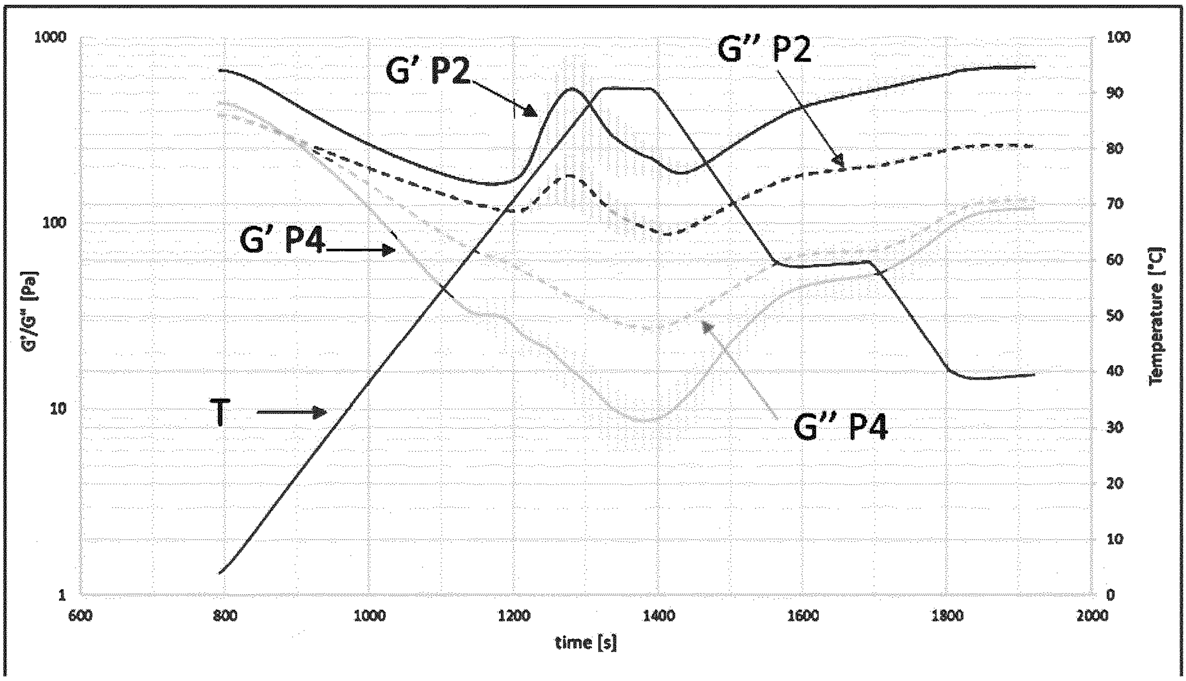
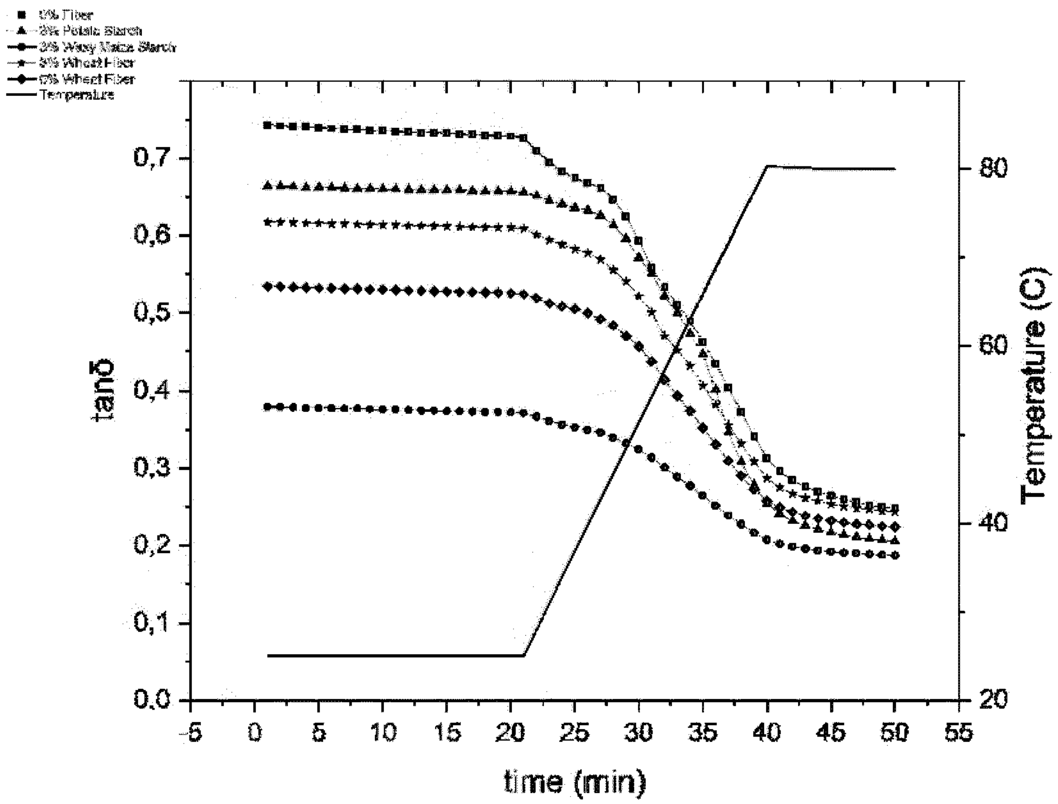

G' P2
G'' P2
G' P4
G'' P4
T
1000
100
10
1
G'/G" [Pa]
600
800
1000
1200
1400
1600
1800
2000
time [s]
100
90
80
70
60
50
40
30
20
10
0
Temperature [°C]

FIG. 12



Potato Starch
Waxy Maize Starch
Wheat Fiber
Wheat Fiber
Temperature
tanδ
0,0
0,1
0,2
0,3
0,4
0,5
0,6
0,7
Temperature (C)
20
40
60
80
time (min)
-5
0
5
10
15
20
25
30
35
40
45
50
55

FIG. 13

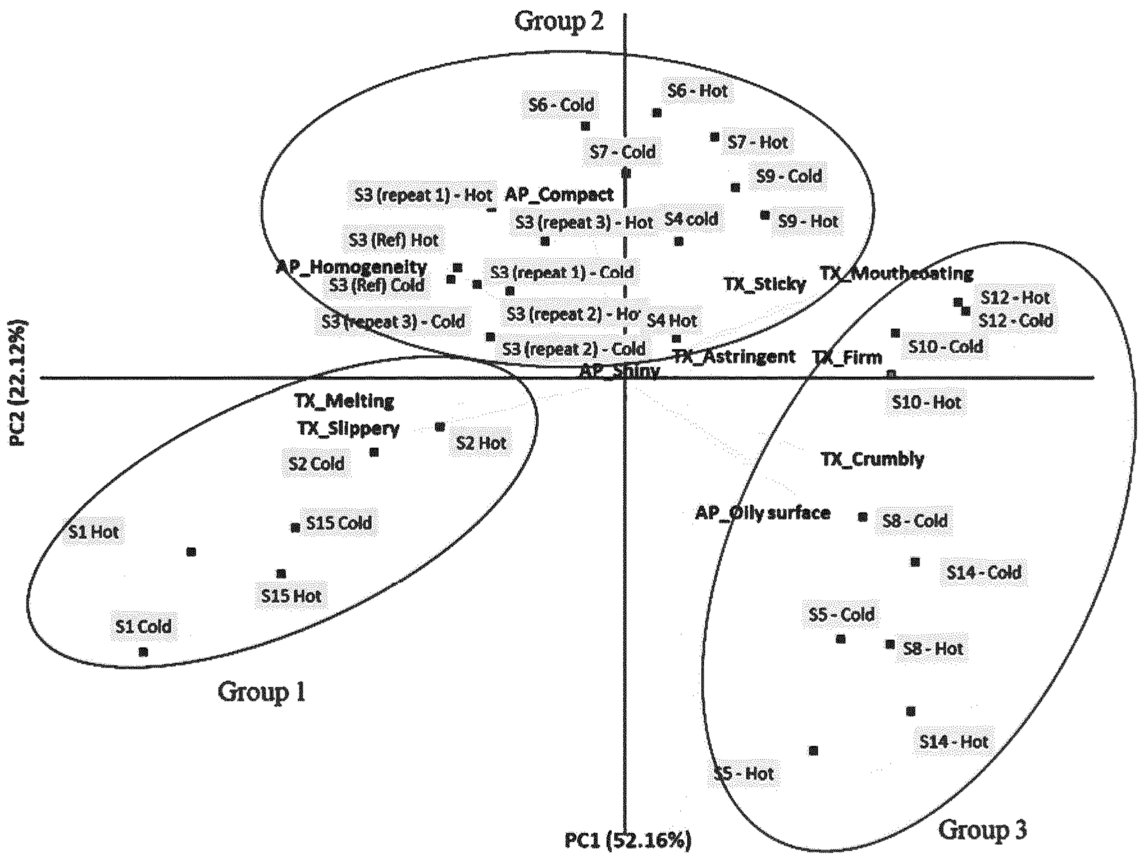

Group 2
S6 - Hot
S6 - Cold
S7 - Hot
S7 - Cold
S9 - Cold
S3 (repeat 1) - Hot
AP_Compact
S3 (repeat 3) - Hot
S4 cold
S9 - Hot
S3 (Ref) Hot
AP_Homogeneity
S3 (repeat 1) - Cold
S3 (Ref) Cold
TX_Sticky
TX_Mouthcoating
S12 - Hot
S12 - Cold
S3 (repeat 3) - Cold
S3 (repeat 2) - Hot
S4 Hot
S10 - Cold
S3 (repeat 2) - Cold
TX_Astringent
TX_Firm
AP_Shiny
PC2 (22.12%)
TX_Melting
S10 - Hot
TX_Slippery
S2 Hot
S2 Cold
TX_Crumbly
AP_Oily surface
S8 - Cold
S1 Hot
S15 Cold
S14 - Cold
S15 Hot
S5 - Cold
S1 Cold
S8 - Hot
Group 1
S14 - Hot
S5 - Hot
Group 3
PC1 (52.16%)

FIG. 14

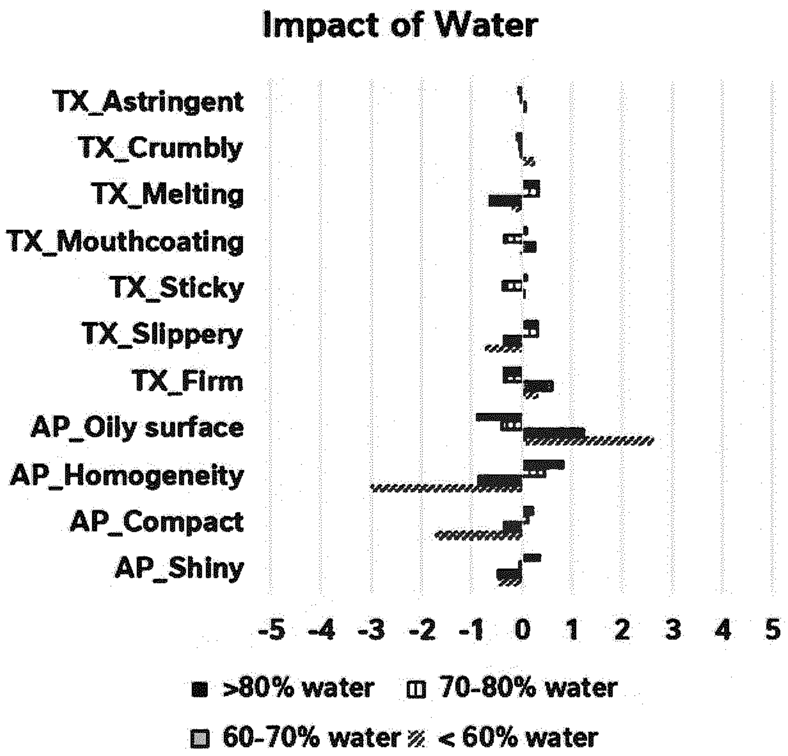

Impact of Water
TX_Astringent
TX_Crumbly
TX_Melting
TX_Mouthcoating
TX_Sticky
TX_Slippery
TX_Firm
AP_Oily surface
AP_Homogeneity
AP_Compact
AP_Shiny
-5 -4 -3 -2 -1 0 1 2 3 4 5
>80% water
70-80% water
60-70% water
< 60% water

FIG. 15

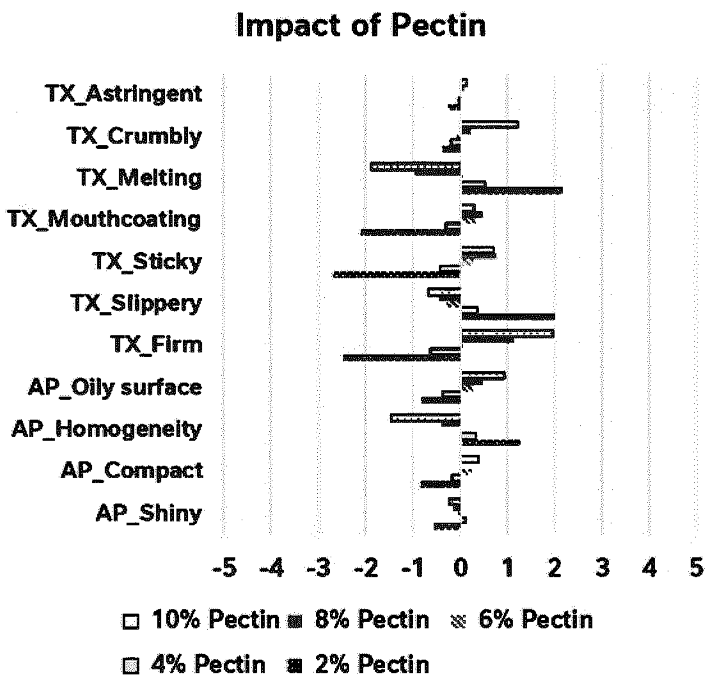

Impact of Pectin
TX_Astringent
TX_Crumbly
TX_Melting
TX_Mouthcoating
TX_Sticky
TX_Slippery
TX_Firm
AP_Oily surface
AP_Homogeneity
AP_Compact
AP_Shiny
-5 -4 -3 -2 -1 0 1 2 3 4 5
10% Pectin
8% Pectin
6% Pectin
4% Pectin
2% Pectin

FIG. 16

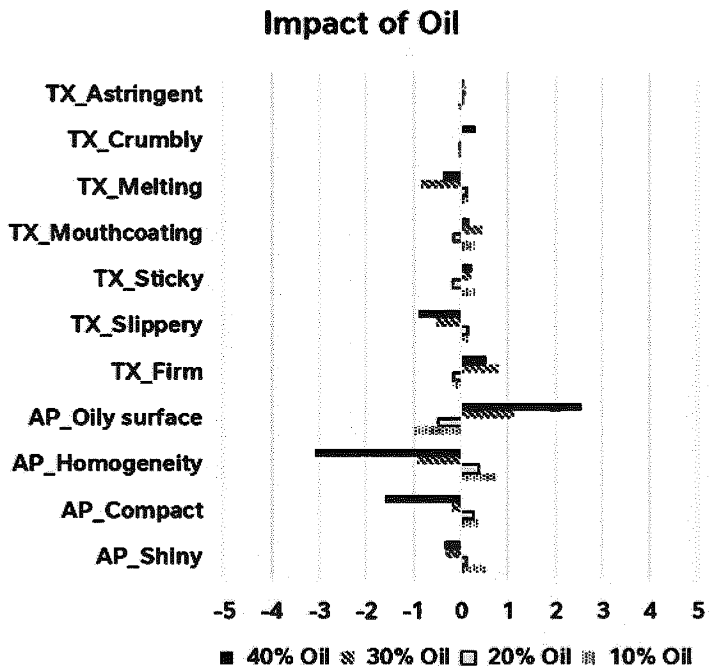

Impact of Oil
TX_Astringent
TX_Crumbly
TX_Melting
TX_Mouthcoating
TX_Sticky
TX_Slippery
TX_Firm
AP_Oily surface
AP_Homogeneity
AP_Compact
AP_Shiny
-5 -4 -3 -2 -1 0 1 2 3 4 5
40% Oil 30% Oil 20% Oil 10% Oil

FIG. 17

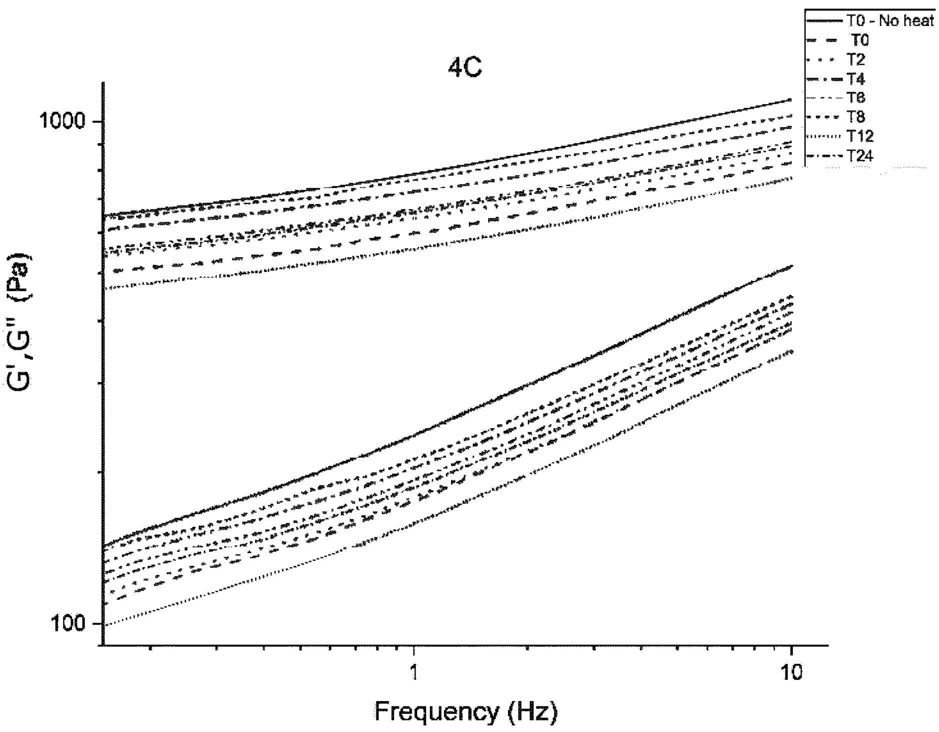


FIG. 18A

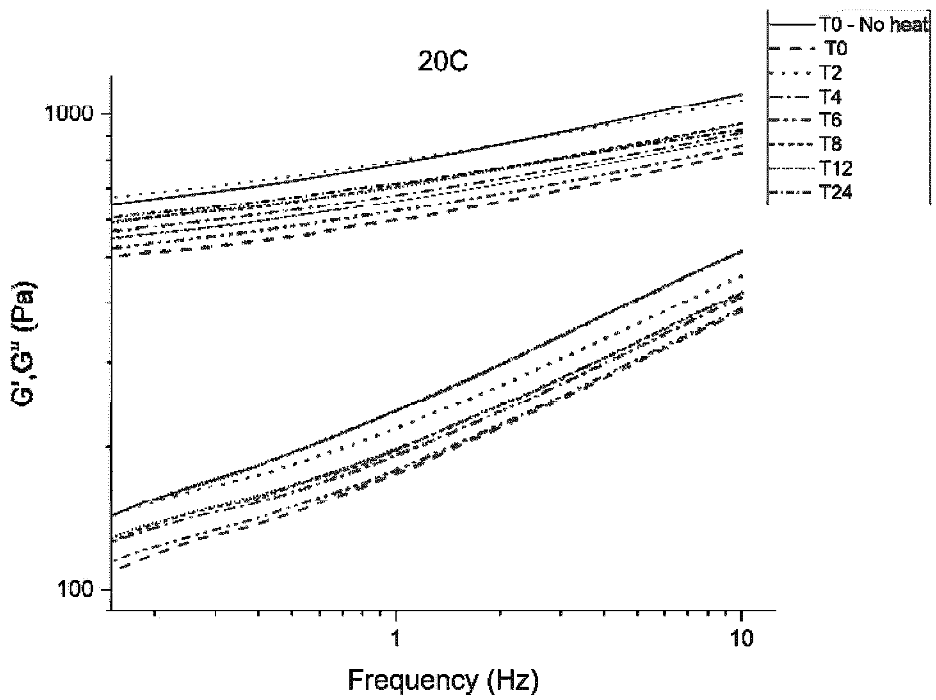


FIG. 18B

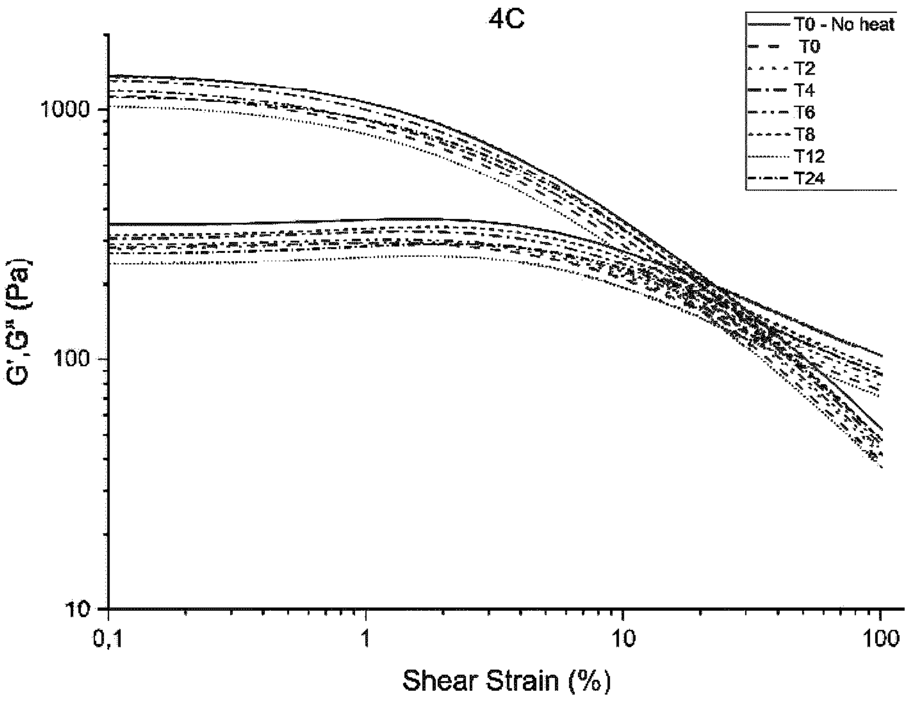


FIG. 19A

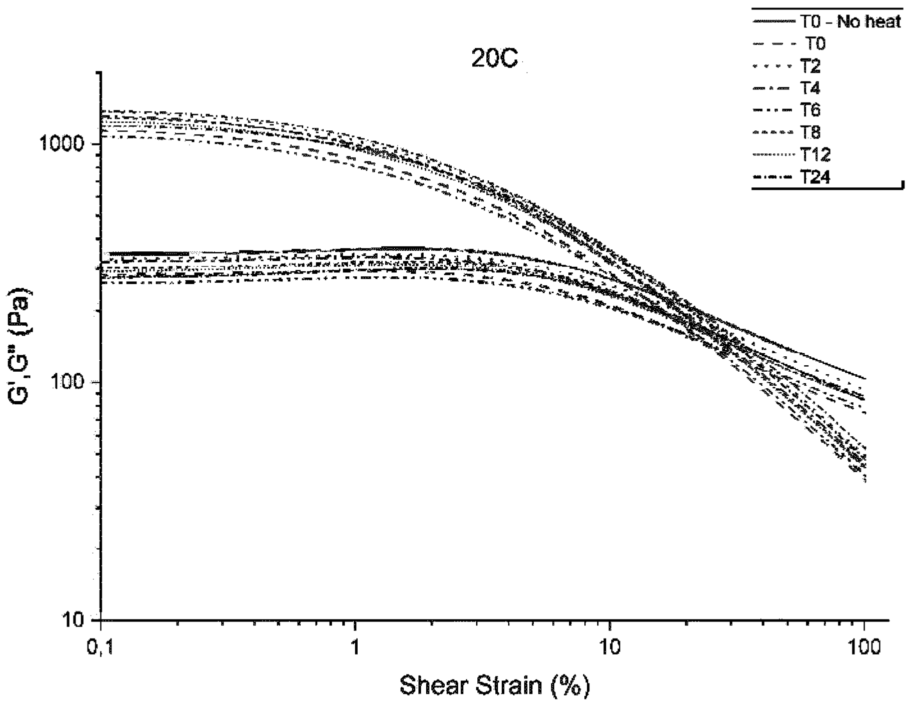


FIG. 19B

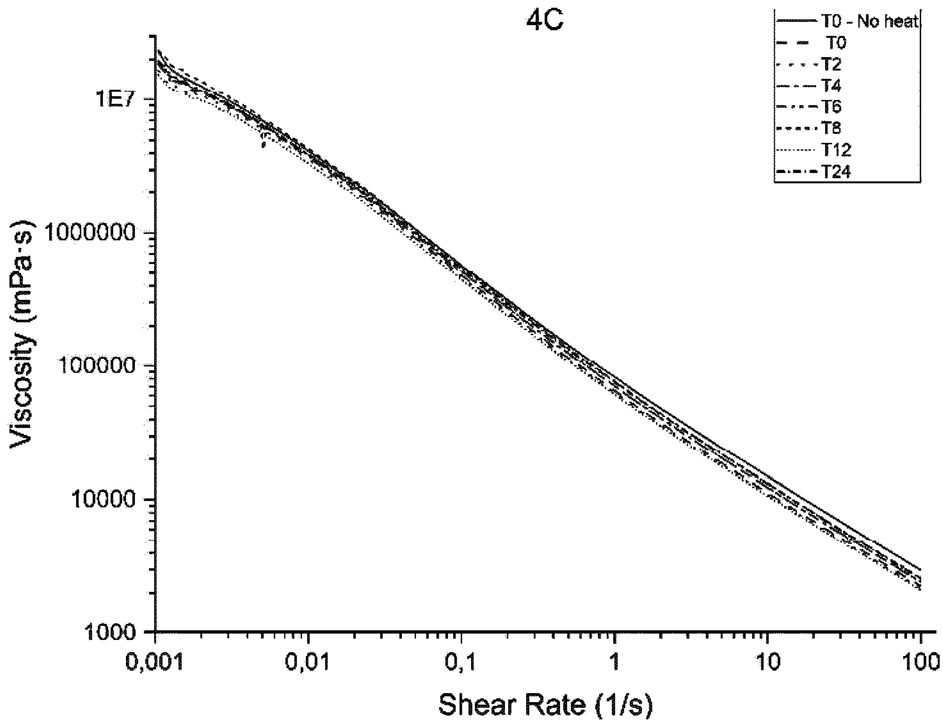


FIG. 20A

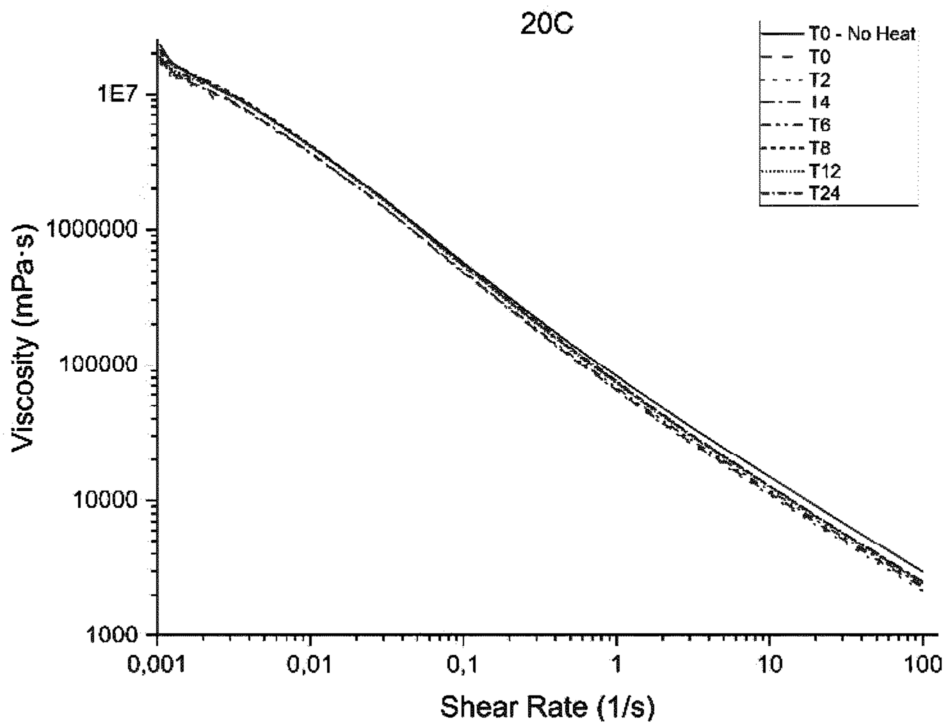


FIG. 20B

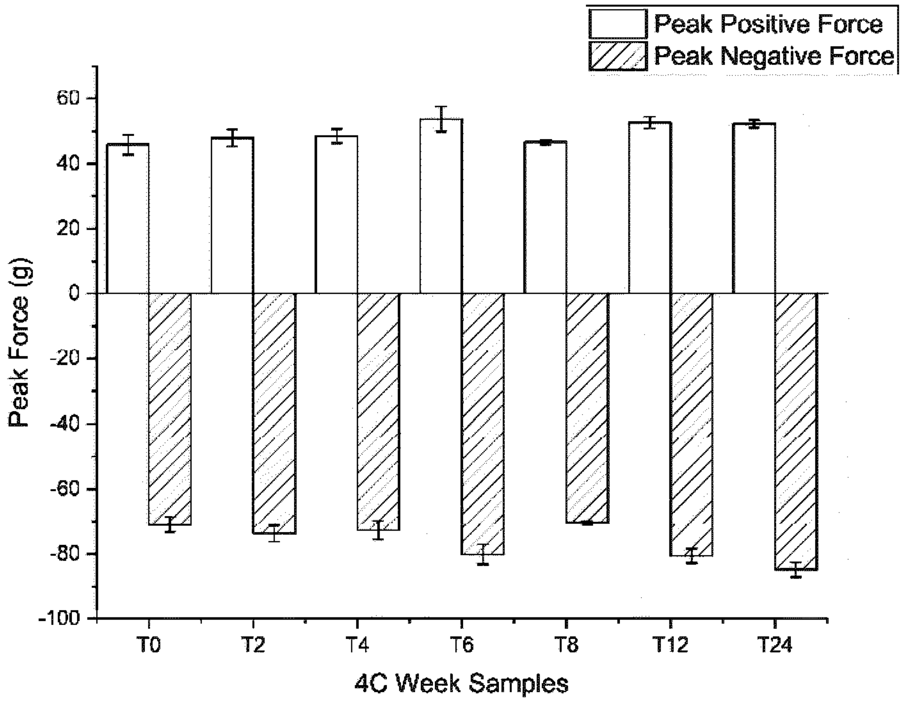


FIG. 21A

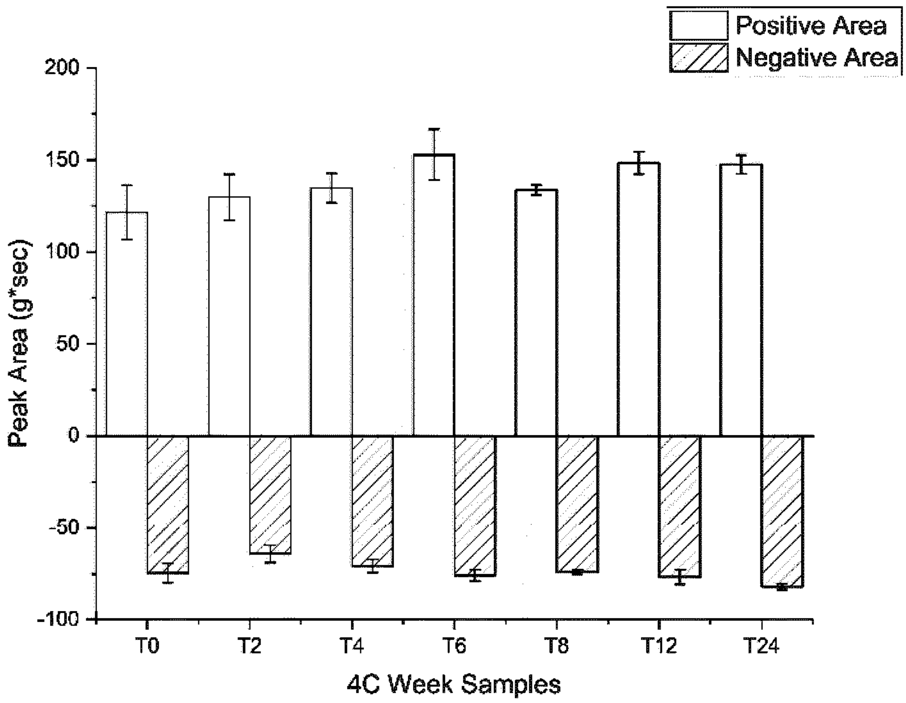


FIG. 21B

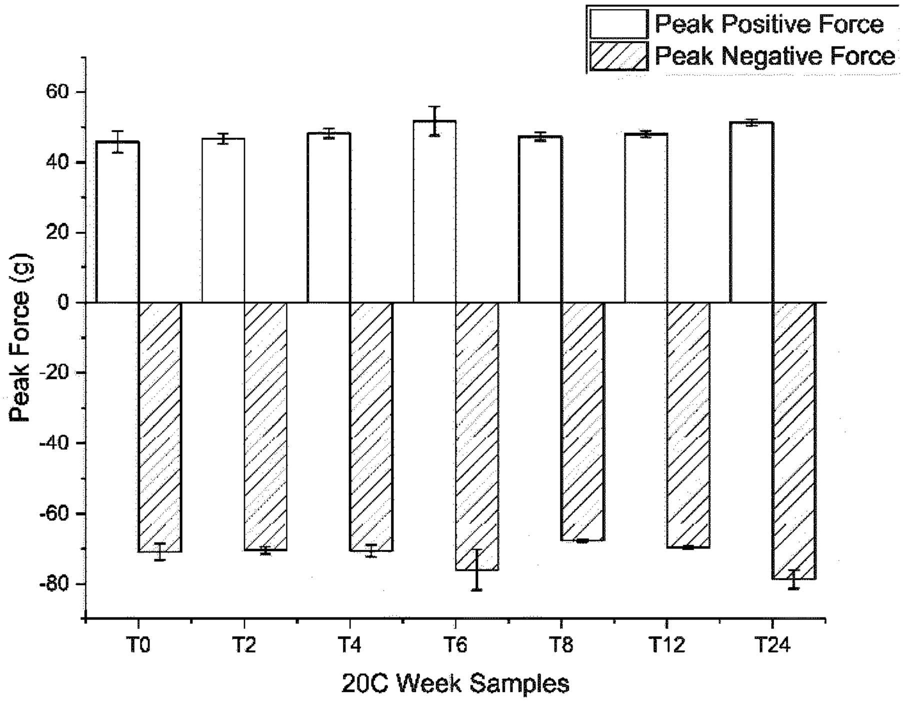


FIG. 22A

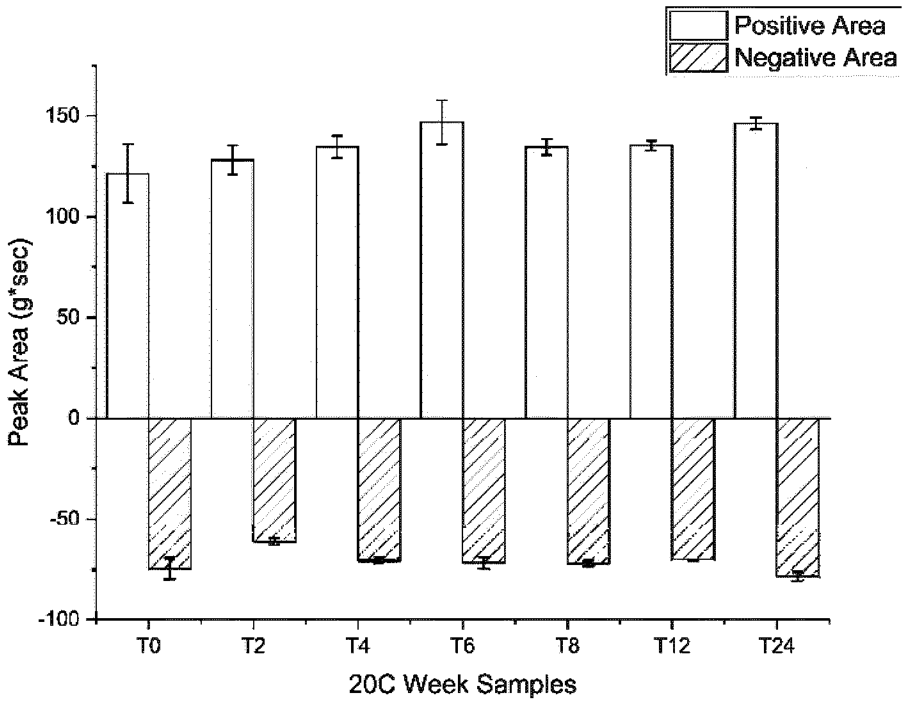


FIG. 22B

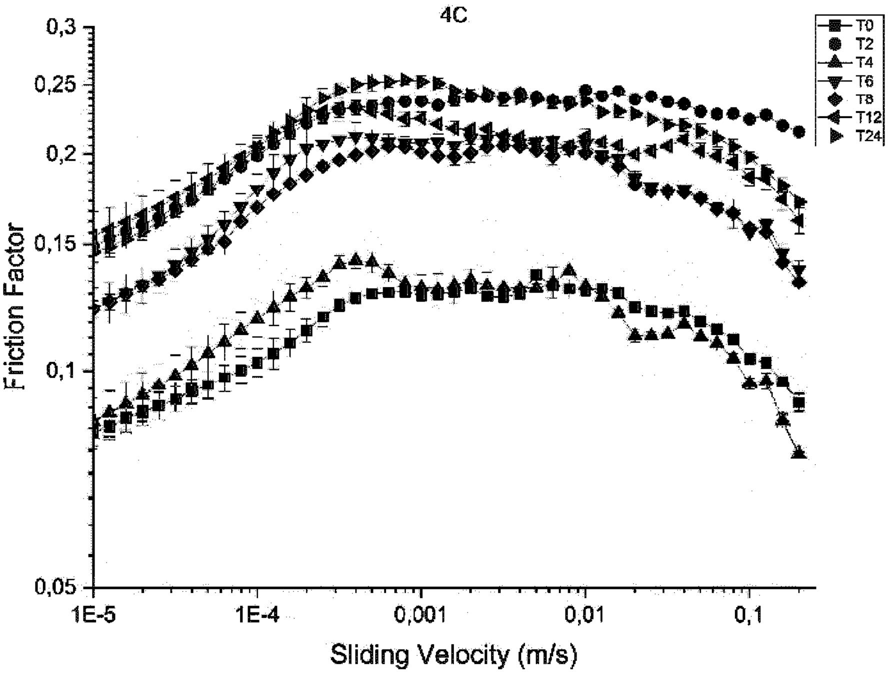


FIG. 23A

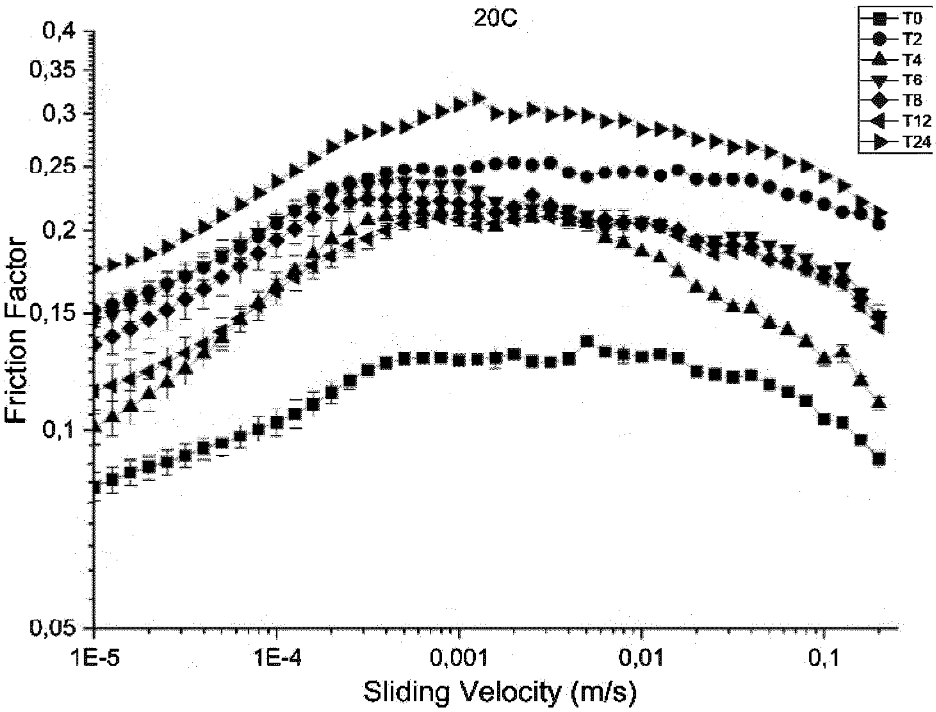


FIG. 23B

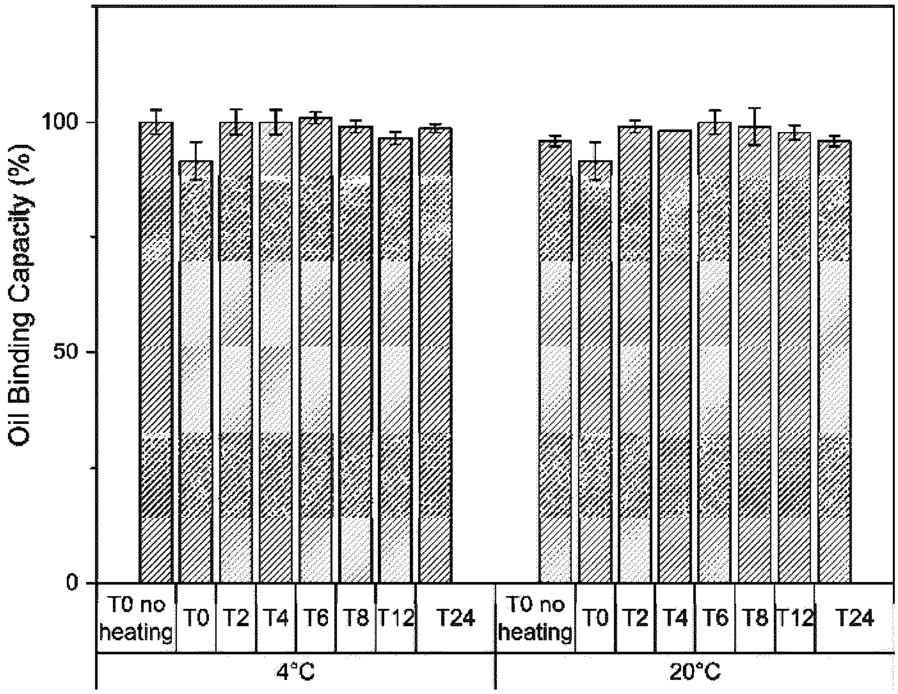

Oil Binding Capacity (%)
100
50
0
T0 no heating
T0
T2
T4
T6
T8
T12
T24
T0 no heating
T0
T2
T4
T6
T8
T12
T24
4°C
20°C

FIG. 24

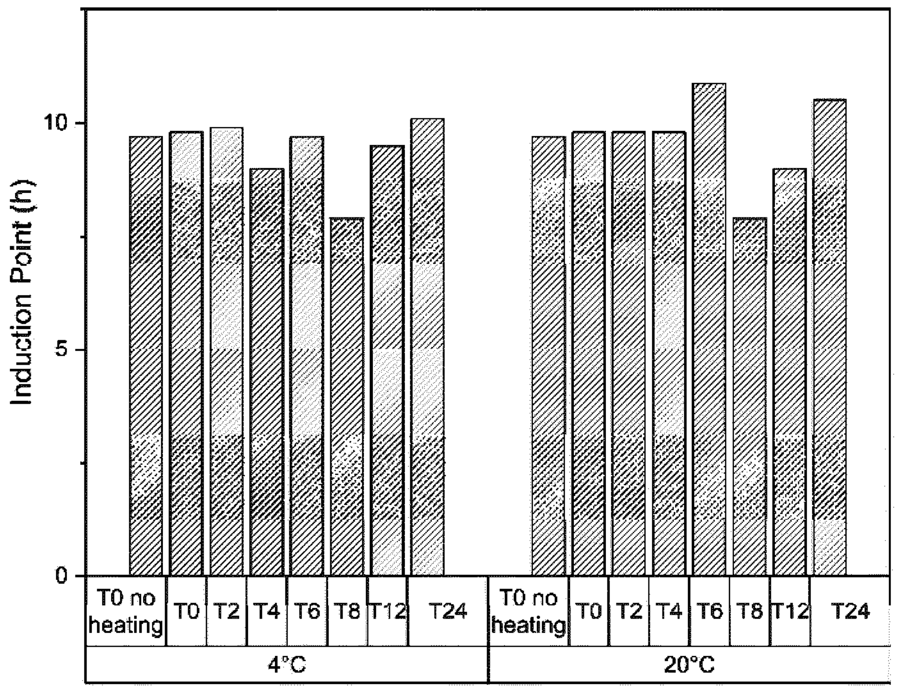

Induction Point (h)
10
5
0
T0 no heating
T0
T2
T4
T6
T8
T12
T24
T0 no heating
T0
T2
T4
T6
T8
T12
T24
4°C
20°C

FIG. 25

Carrot emulgel – just after heat treatment

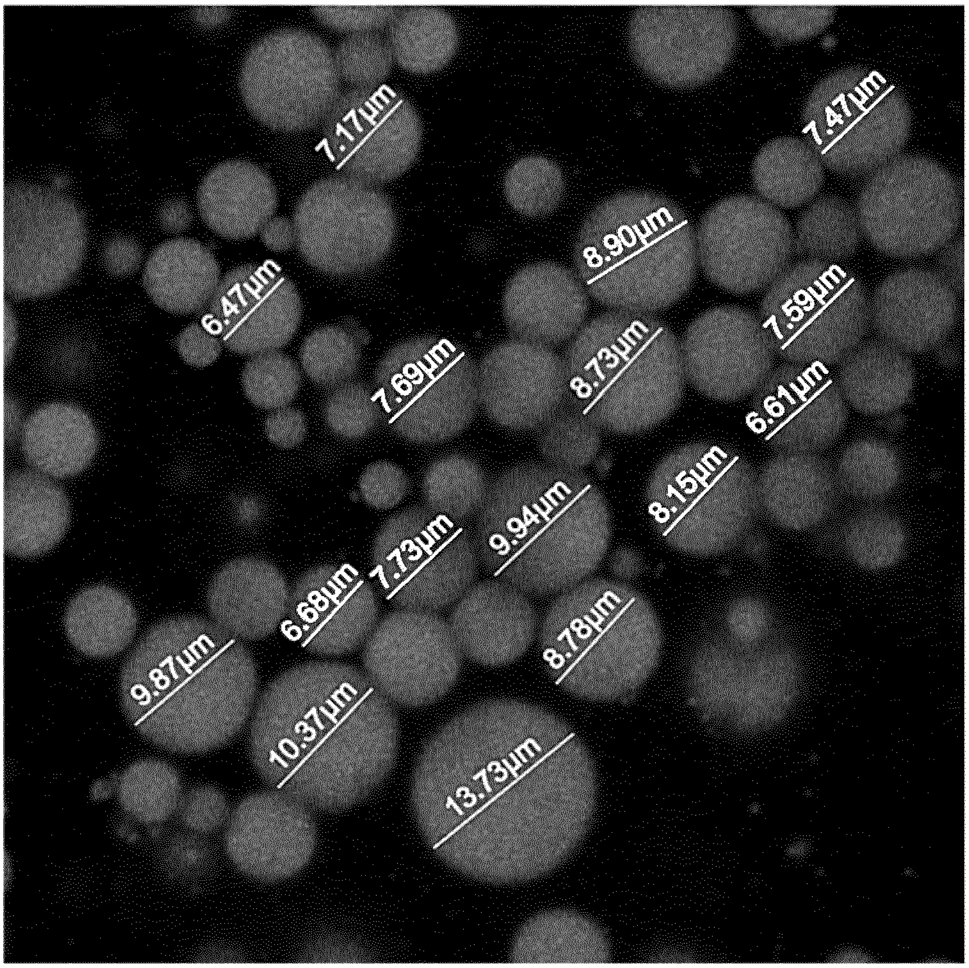


FIG. 26

Carrot emulgel – 4°C – 2 months

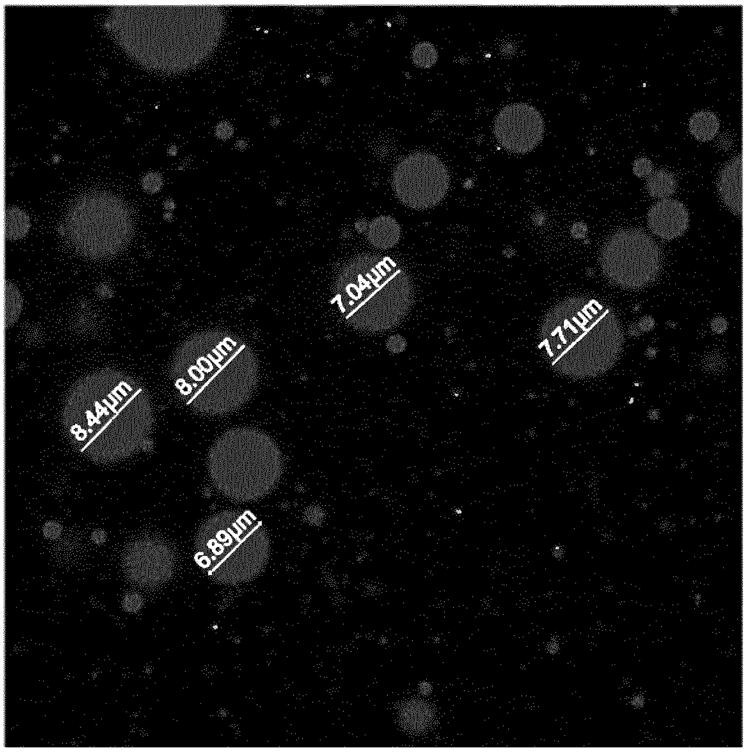


FIG. 27A

Carrot emulgel – 4°C – 6 months

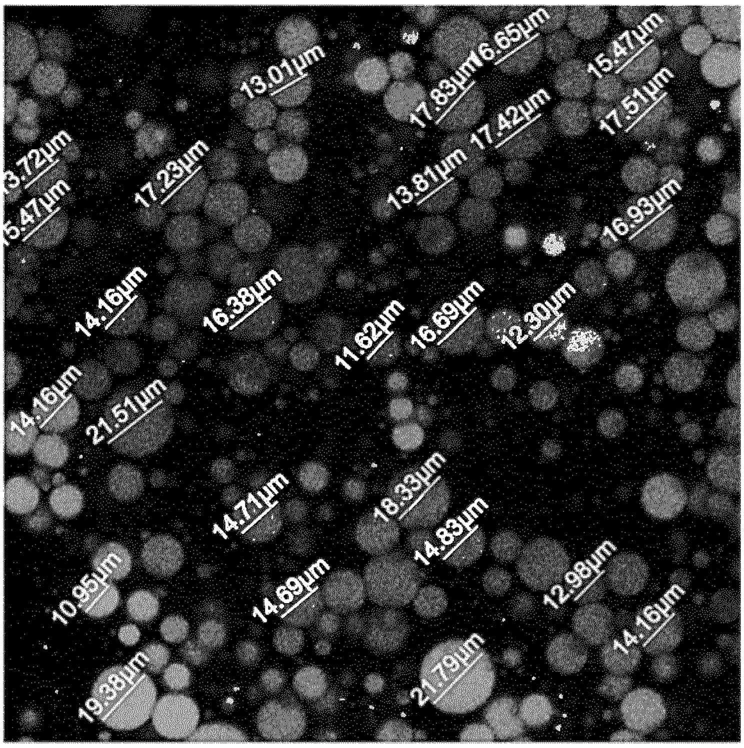


FIG. 27B

Carrot emulgel – 25°C – 2 months

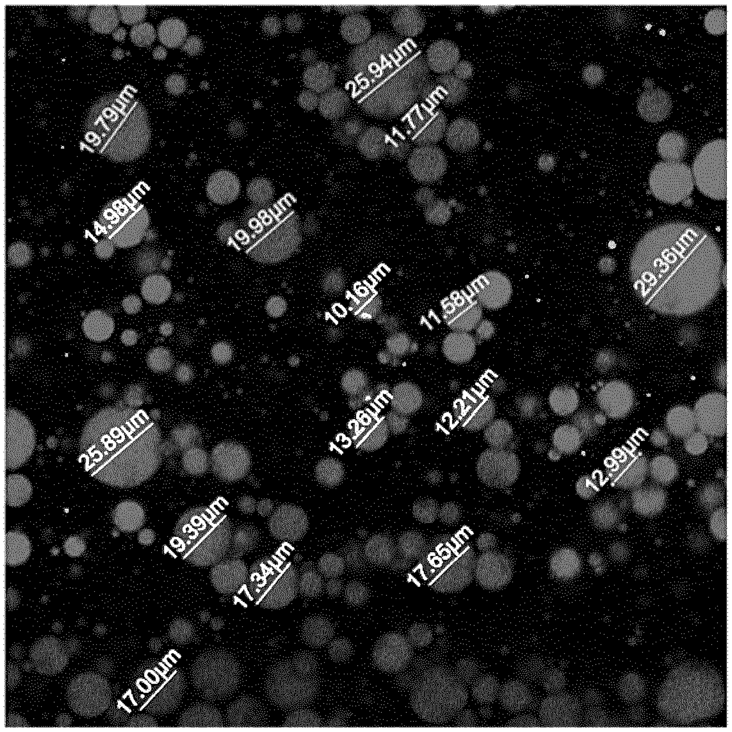


FIG. 28A

Carrot emulgel – 25°C – 6 months

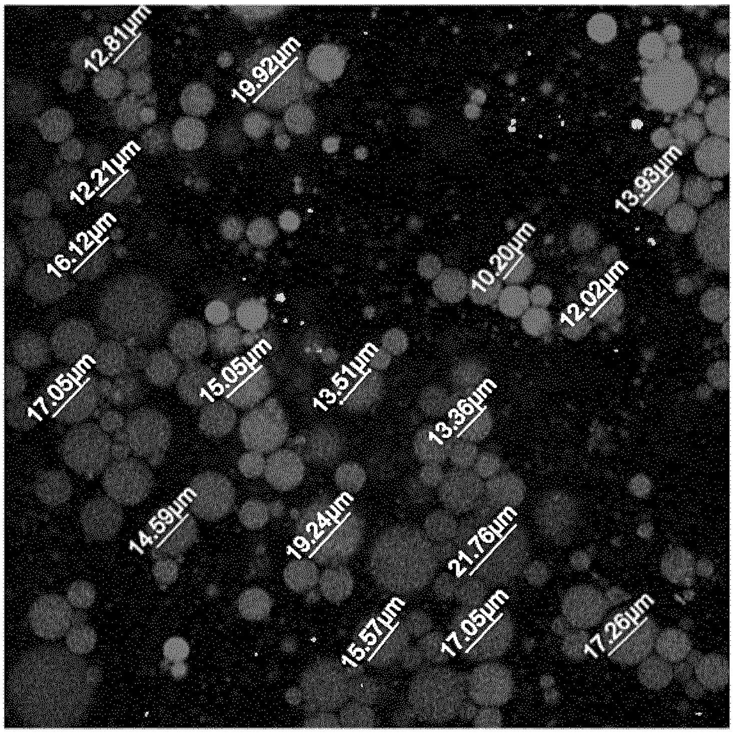


FIG. 28B

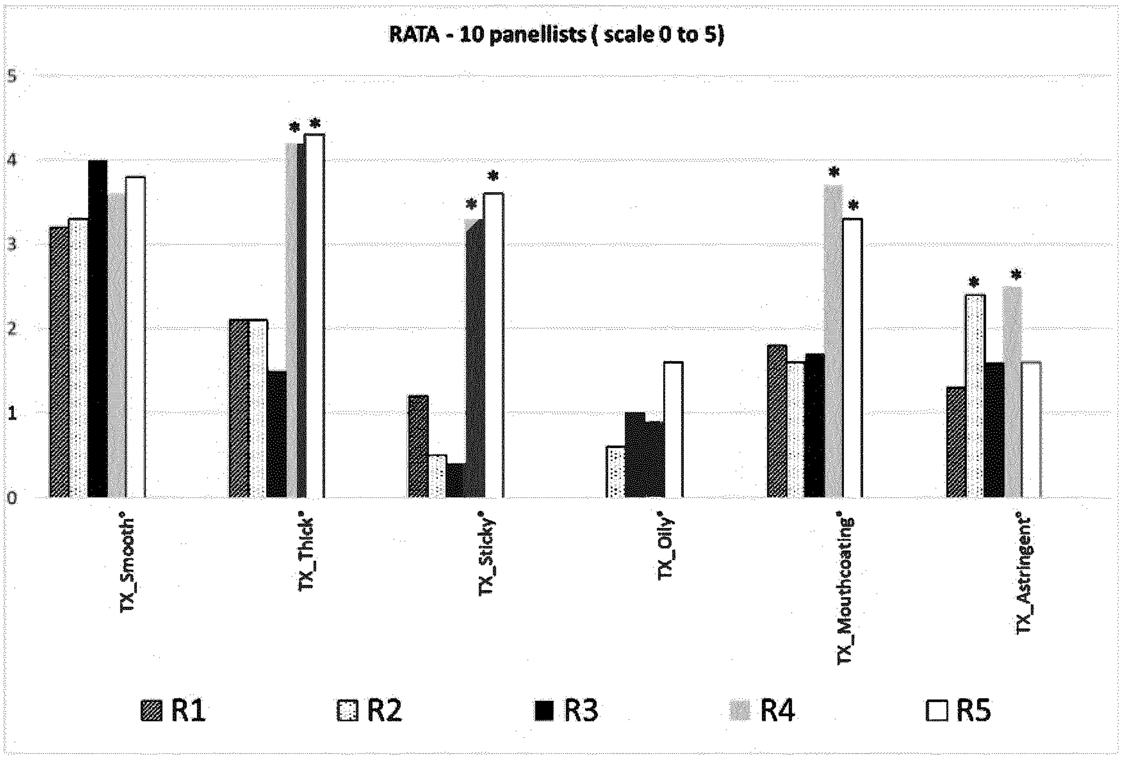


FIG. 29A

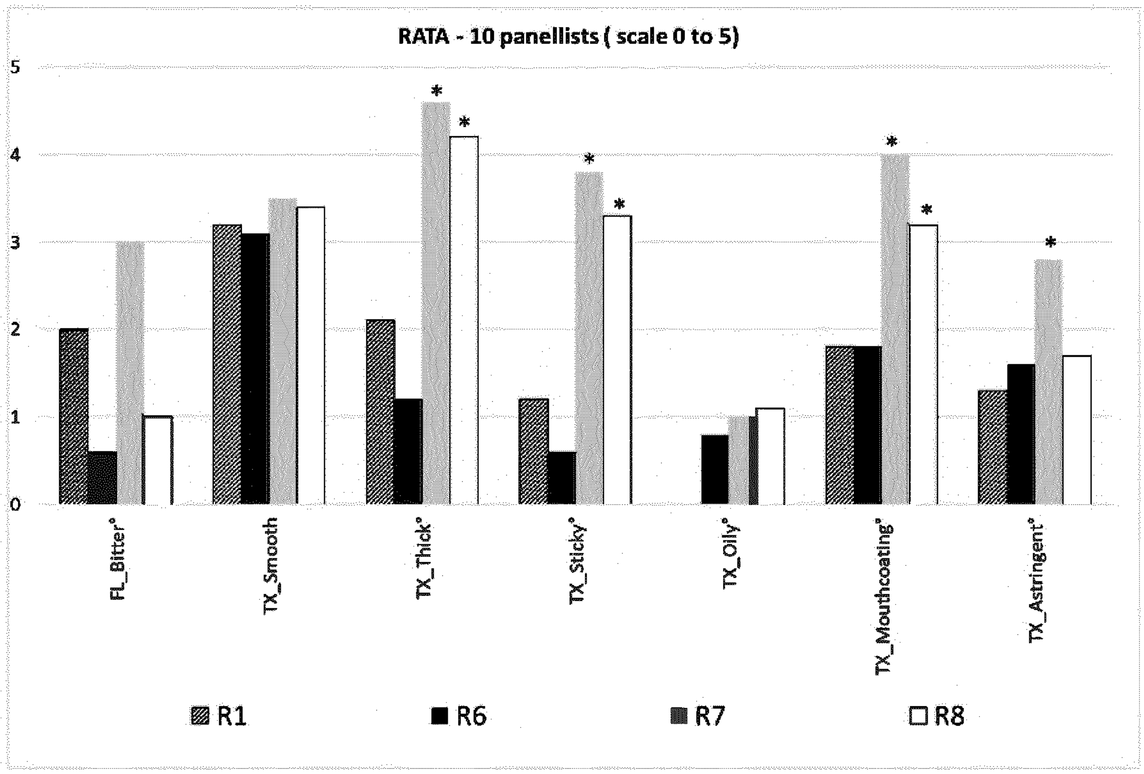


FIG. 29B

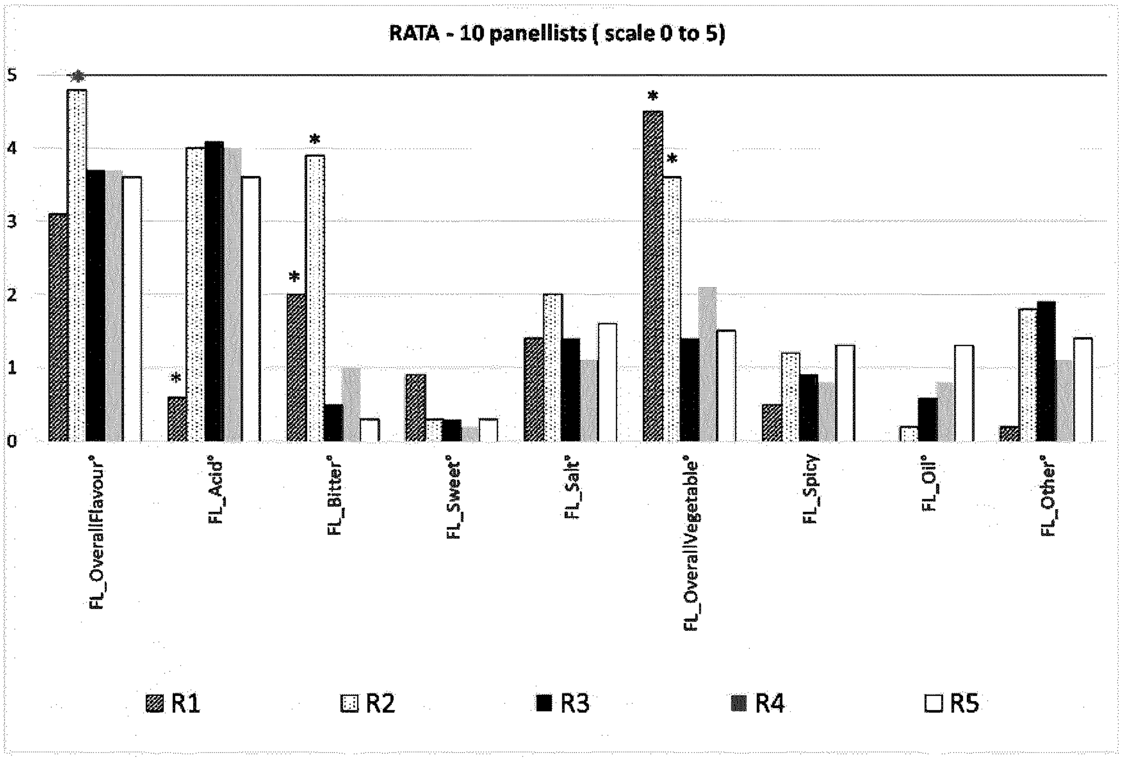


FIG. 30A

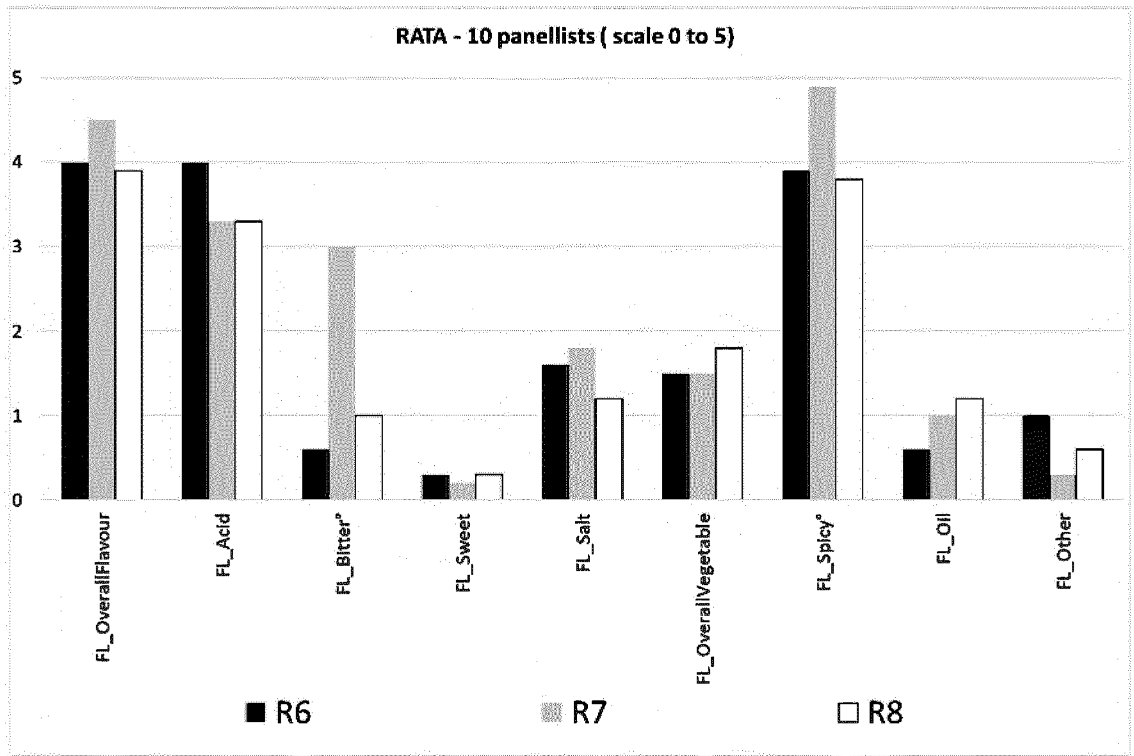


FIG. 30B

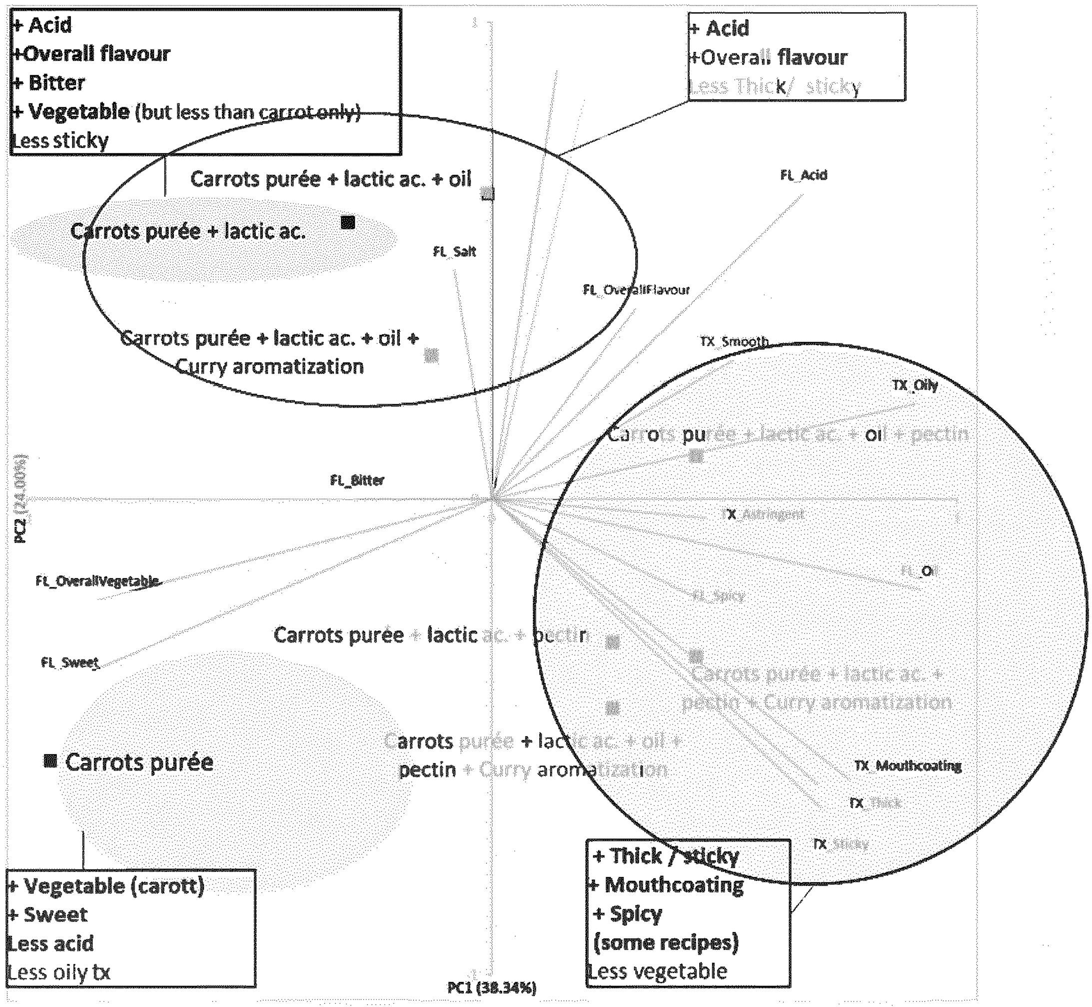

+ Acid
+Overall flavour
+ Bitter
+ Vegetable (but less than carrot only)
Less sticky
+ Acid
+Overall flavour
Less Thick / sticky
Carrots purée + lactic ac. + oil
Carrots purée + lactic ac.
FL_Salt
FL_Acid
FL_OverallFlavour
Carrots purée + lactic ac. + oil + Curry aromatization
TX_Smooth
TX_Oily
Carrots purée + lactic ac. + oil + pectin
FL_Bitter
PC2 (24.00%)
TX_Astringent
FL_OverallVegetable
FL_Oil
FL_Spicy
Carrots purée + lactic ac. + pectin
FL_Sweet
Carrots purée + lactic ac. + pectin + Curry aromatization
Carrots purée
Carrots purée + lactic ac. + oil + pectin + Curry aromatization
TX_Mouthcoating
TX_Thick
TX_Sticky
+ Vegetable (carott)
+ Sweet
Less acid
Less oily tx
+ Thick / sticky
+ Mouthcoating
+ Spicy
(some recipes)
Less vegetable
PC1 (38.34%)

FIG. 31

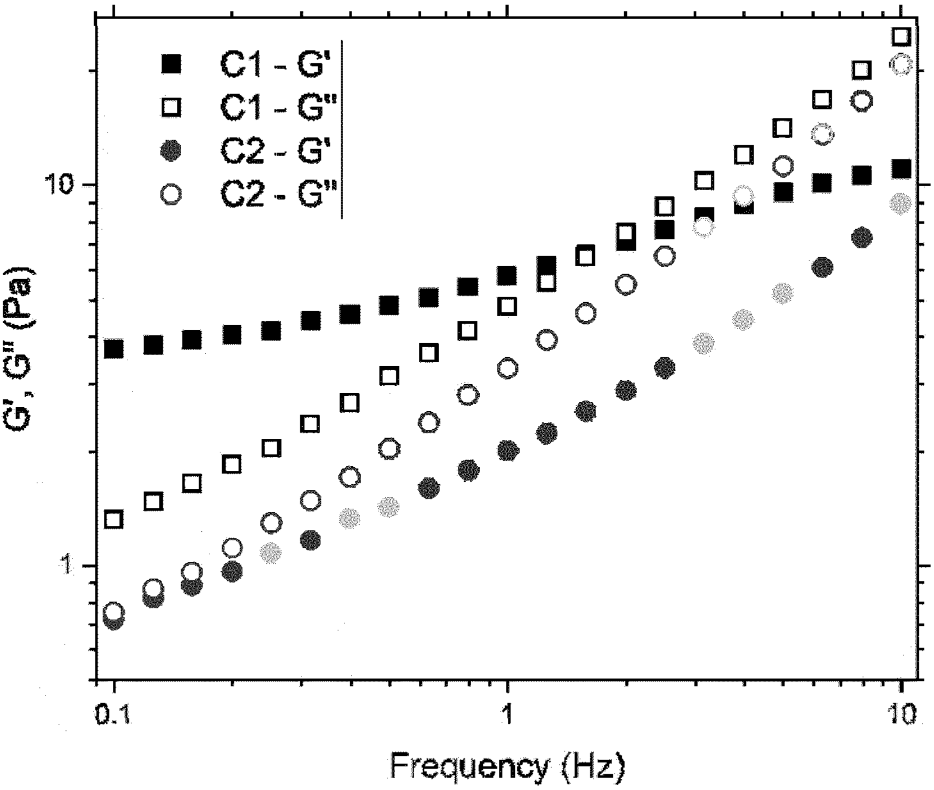


FIG. 32

C1

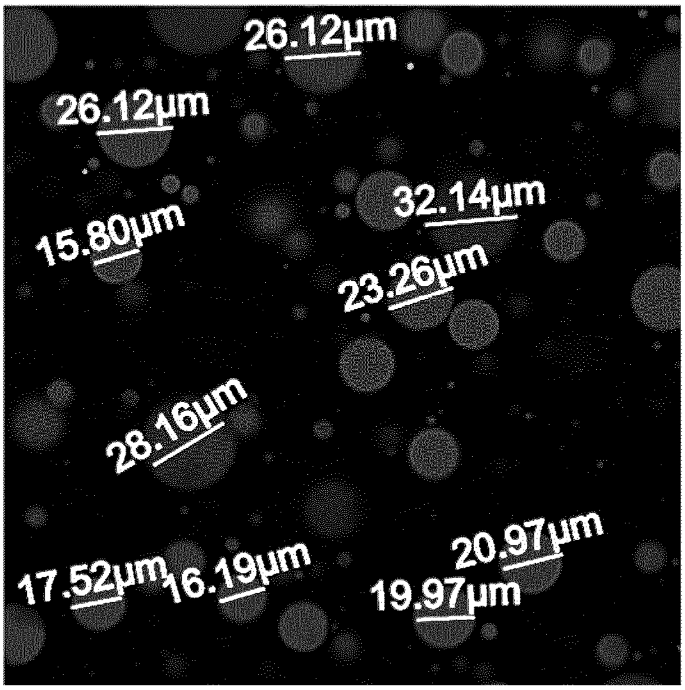


FIG. 33A

C2

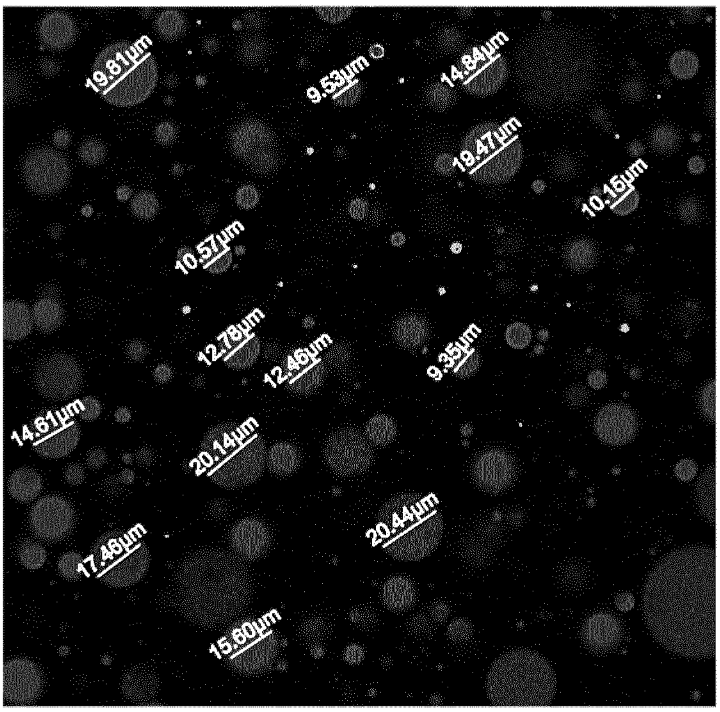


FIG. 33B

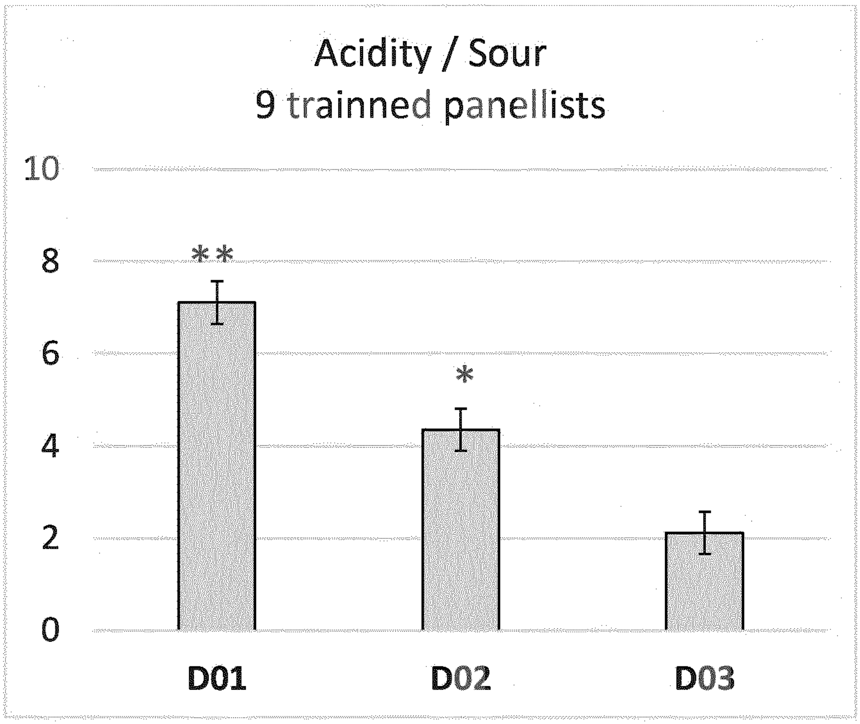


FIG. 34

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/066687

A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L29/231 A23L35/00 A23D7/005 A23L23/00 A23L27/60
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A23L A23D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 113 475 707 A (JIANGXI LAIMENG BIOLOGICAL TECH CO LTD ET AL.) 8 October 2021 (2021-10-08)	1-6,8, 10-15
Y	claims 1,5,10; examples 1-3	7,9

X	CN 112 056 544 A (UNIV HUAZHONG AGRICULTURAL) 11 December 2020 (2020-12-11)	1-6,8, 10-15
Y	claims 1,4-7; examples 1-3	7,9

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Y	page 5, line 38 - page 6, line 55; claims 1,4,6; examples 1,3	7,9

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[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 August 2024	02/09/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Tallgren, Antti

3

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2022/266588 A1 (WHITEWAVE SERVICES INC [US]) 22 December 2022 (2022-12-22) paragraphs [0002], [0010], [0027] - [0030], [0075], [0090] - [0094], [0102], [0110]; claims 1,17,18; examples 1-5 -----	1,6-10, 15
Y	WO 2014/001030 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; CONOPCO INC DBA UNILEVER [US]) 3 January 2014 (2014-01-03) page 12, paragraph 5; claims 1,14; examples 1-6 -----	7,9
X	US 2005/048181 A1 (GELIN JEAN-LUC [FR]) 3 March 2005 (2005-03-03) paragraphs [0001], [0009], [0011] - [0013], [0018], [0024]; claims 1,3,11,18-20; examples 1-5 -----	1-9,15
X	DU LE HOANG ET AL: "Pectin emulsions for colon-targeted release of propionic acid", FOOD HYDROCOLLOIDS, ELSEVIER BV, NL, vol. 103, 25 December 2019 (2019-12-25), XP086077394, ISSN: 0268-005X, DOI: 10.1016/J.FOODHYD.2019.105623 [retrieved on 2019-12-25] page 1, paragraph 1 page 2, right-hand column, paragraph 1-3 page 5, right-hand column, paragraph 3; table 1 -----	1-4,6, 8-14

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/066687

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