

(43) International Publication Date
28 June 2012 (28.06.2012)(10) International Publication Number
WO 2012/084441 A1

(51) International Patent Classification:

A23L 1/00 (2006.01) A61K 8/64 (2006.01)
A23L 1/0534 (2006.01) A61K 8/73 (2006.01)
A23L 1/10 (2006.01) A23D 7/005 (2006.01)

(21) International Application Number:

PCT/EP2011/071409

(22) International Filing Date:

30 November 2011 (30.11.2011)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PCT/CN2010/002128

22 December 2010 (22.12.2010)

CN

(71) Applicant (for all designated States except AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, QA, RW, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; a company registered in England and Wales, under company no.41424 of Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).

(71) Applicant (for IN only): **HINDUSTAN UNILEVER LIMITED** [IN/IN]; Unilever House, B.D. Sawant Marg, Chakala, Andheri East, Maharashtra, Mumbai 400 099 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **CAO, Jian** [CN/CN]; Unilever (China) Investing Company, 66 Lin Xin Road, Linkong Economic Development Zone, Shanghai, Changning District 200335 (CN). **VAN MALSEN, Kees Frederik** [NL/NL]; Unilever R&D Vlaardingen B.V., Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). **PELAN, Edward George** [GB/NL]; Unilever R&D Vlaardingen B.V., Olivier van Noortlaan 120, NL-3133

AT Vlaardingen (NL). **STOYANOV, Simeon Dobrev** [BG/NL]; Unilever R&D Vlaardingen B.V., Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). **TAO, Qingsheng** [CN/CN]; Unilever (China) Investing Company, 66 Lin Xin Road, Linkong Economic Development Zone, Shanghai, Changning District 200335 (CN). **WANG, Lin** [CN/CN]; Unilever (China) Investing Company, 66 Lin Xin Road, Linkong Economic Development Zone, Shanghai, Changning District 200335 (CN). **WANG, Xiaoli** [CN/CN]; Unilever (China) Investing Company, 66 Lin Xin Road, Linkong Economic Development Zone, Shanghai, Changning District 200335 (CN). **ZHOU, Weizheng** [CN/CN]; Unilever (China) Investing Company, 66 Lin Xin Road, Linkong Economic Development Zone, Shanghai, Changning District 200335 (CN).

(74) Agent: **VAN BENTHUM, Wim**; Unilever Patent Group, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(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, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:

— with international search report (Art. 21(3))

(54) Title: COMPOSITIONS IN THE FORM OF FIBRES

(57) Abstract: The present invention has as an objective to provide a fibrous material which can be used to structure non-aqueous liquids. These structured liquids can be used as ingredient in products such as oil-in-water emulsions or water-in-oil emulsions. This objective has been met by composite fibres comprising at least a lipophilic cellulose derivative. These fibres are very efficient structurants of non-aqueous liquids, such as vegetable oil in a food product, or lipid compounds in personal care products such as skin creams.



WO 2012/084441 A1

COMPOSITIONS IN THE FORM OF FIBRES

The present invention relates to a composition in the form of fibre, a method for production of these fibrous materials, and the use of these fibrous materials for structuring a non-
5 aqueous liquid phase.

BACKGROUND OF THE INVENTION

The structure and morphology of a consumer product is essential for the properties and the appreciation of the product. For example a food product like a margarine should not
10 be too soft and not be too hard, and should be spreadable under all normal household conditions and should melt at in body temperature when consumed. This can be achieved by using a correct ratio of saturated and unsaturated fats and oils in the formulation of the product. Similarly a deodorant stick should keep its consistency during storage, nevertheless should deliver its constituents when applied to the skin. These required
15 properties may lead to contradictory requirements in product development.

It is well known that thickeners and fibres can be used to create useful structures, both in foods as well as in cosmetic or personal care products. Numerous fibrous materials have been described, and several methods have been disclosed to produce fibrous materials.
20 The production of fibres out of vegetable or dairy proteins has been described, in order to use these fibres as meat replacers. Additionally fibres made by electrospinning are used in medical applications, especially as wound dressing materials.

WO 2007/068344 A1 discloses fibres like microcrystalline cellulose, that have been
25 modified to give them surface-active properties, and that are used as stabiliser for aerated food products and emulsions.

WO 89/10068 discloses microfragmented ionic polysaccharide/protein complex aqueous dispersions that are used for nutritious bulking, viscosity or texture control agents (also fat
30 replacer) in food products. These materials may be formed in the form of fibres, and the method may involve a fragmentation step by homogenisation.

WO 2008/100556 A2 discloses an electrospun composition comprising fibres of plant product derived biomaterials, e.g. carbohydrates such as polysaccharides (e.g. cellulose
35 and its derivatives), and materials derived from corn or soy, such as zein and soy protein.

The fibres may contain synthetic materials like polymers. These materials are used as scaffolds for wound healing.

WO 2009/042829 A1 discloses a method of making hydrogel fibres comprising
5 electrospinning an admixture of a carboxy-functionalized polymer (e.g. a polyacid such as polyacrylic acid) and a hydroxy-functionalized polymer (e.g. a polysaccharide such as dextran) to make fibres, optionally cross-linking the fibres to render them stable in aqueous solution; and fragmenting the cross-linked fibres step, by e.g. mechanical shearing, including sonication, into lengths less than 3mm, preferably less than 2 mm,
10 more preferably between about 100 nm and 1 mm. The resulting fibres can be used to form articles by attaching said fibres onto a surface, for use in medical or biological context (e.g. in wound healing or in stents). They are protein repellant.

WO 01/54667 relates to an electrospun pharmaceutical composition comprising an active
15 agent, and a polymeric carrier for use in therapy. The carrier may be water-soluble or water-insoluble.

WO 2006/136817 A1 discloses various polymers which may be used as source to create fibres by electrospinning.
20

US 4,287,219 discloses fibres made from proteins, with fat containing phase in the core of the fibrous materials. These are used as meat replacers.

Fernandez A. et al. (Food Hydrocolloids, vol. 23, 2009, 1427–1432) disclose
25 encapsulation of beta-carotene in electrospun fibres of zein prolamin, to protect the beta-carotene from oxidation.

Li Y. et al. (Journal of Food Science, vol. 74, 2009, C233-C240) discloses electrospun zein fibres as carriers to stabilise (-)-epigallocatechin gallate.
30

Kriegel C.-A. et al. (Critical Reviews in Food Science and Nutrition, vol. 48, 2008, 775-779) disclose the use of electrospun fibres in food products as ingredients.

Wongsasulak S. et al. (Journal of Food Engineering, vol. 98, 2010, p. 370–376) discloses
35 electrospinning of food-grade nanofibres from cellulose acetate and egg albumen blends.

These can be used for controlled delivery of nutraceuticals or pharmaceuticals to the gastro-intestinal tract.

Lee K.Y. et al. (Advanced Drug Delivery Reviews, vol. 61, 2009, p. 1020–1032) review
5 electrospinning of polysaccharides for regenerative medicine. Among the polysaccharides mentioned is ethylcellulose.

Wu X. et al. (Journal of Applied Polymer Science, vol. 97, 2005, p. 1292-1297) disclose
that the solvent from which ethylcellulose fibres are produced by electrospinning
10 influences the diameter and diameter distribution of these fibres. Similarly Park J.Y. et al. (Journal of Industrial and Engineering Chemistry., Vol. 13, 2007, p 1002-1008) disclose
that the solvent from which ethylcellulose fibres are produced by electrospinning
influences the surface properties of these fibres.

15 Schiffman J.D. et al. (Polymer Reviews, vol. 48, 2008, p. 317–352) disclose various combinations of cellulose materials and other polymers to create fibres by electrospinning. They also describe that proteins can be used to create fibres by means of electrospinning.

20 SUMMARY OF THE INVENTION

In spite of these disclosures, there still is a need to produce new fibrous materials, which can be used to structure non-aqueous liquid phases. The non-aqueous liquid phases may be oils or other lipophilic compounds. These non-aqueous liquid phases may be incorporated as ingredients of products such as oil-in-water emulsions or water-in-oil
25 emulsions.

We have now determined that this objective can be met by composite fibres comprising at least a lipophilic cellulose derivative, combined with a prolamin or a lipid material, or with a combination of a prolamin and a lipid compound. These fibres are very efficient
30 structurants of non-aqueous liquids, such as vegetable oil in a food product, or lipid compounds in personal care products such as skin creams.

Using these fibres has the advantage that in case of structuring food products, less saturated fats are required to structure the food product. Nevertheless similar sensory and
35 in-use physical properties can be achieved, like rheology, spreadability, storage stability, and chemical stability. Reducing the amounts of saturated fat in a product, makes a food

product healthier. When applied in personal care products, new structures can be made which are liked by consumers. Examples of this are a superior sensory feeling such as silky feel (like in skin care cream), or delivery of actives on the skin (like in skin cleansing product). Also improved temperature stability can be achieved.

5

Hence in a first aspect the present invention provides a composition in the form of a fibre, wherein the fibre comprises a lipophilic cellulose derivative, and at least one compound chosen from a prolamin and a lipid compound, wherein the fibre has a length from 1 micrometer to 10 millimeter,

10 wherein the fibre has a diameter from 30 nanometer to 50 micrometer, and wherein the aspect ratio of the fibre is larger than 10.

In a second aspect the present invention provides a method for preparation of composition in the form of a fibre according to the first aspect of the invention, wherein the
15 method comprises the spinning of a fibrous material from a solution comprising a lipophilic cellulose derivative, and at least one compound chosen from a prolamin and a lipid compound.

In a third aspect the present invention provides the use of a composition in the form of a
20 fibre according to the first aspect of the invention, as structurant of a non-aqueous liquid phase.

DETAILED DESCRIPTION

25 Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art.

All percentages, unless otherwise stated, refer to the percentage by weight. The abbreviation 'wt%' refers to percentage by weight.

30

In the context of the present invention, an average particle diameter is generally expressed as the $d_{3,2}$ value, which is the Sauter mean diameter, unless stated otherwise. The Sauter mean diameter is the diameter of a sphere that has the same volume/surface area ratio as a particle of interest. In case of fibrous material of which the cross-section
35 may not be completely circular, the diameter of the fibre as expressed herein, is the diameter of a circle having the same surface area as the cross-section of the fibre. Also

the $d_{4,3}$ value, which is the volume weighted mean diameter, may be used herein. The volume based particle size equals the diameter of the sphere that has same the same volume as a given particle.

5 In case a range is given, the given range includes the mentioned endpoints.

By the term 'fibre' or 'fibrous material', we mean any water-insoluble structure wherein the ratio between the length and the diameter ranges from about 10 to infinite. Here, the diameter means the largest distance of the cross-section. The materials of the "fibre"
10 substance can be organic, inorganic, polymeric and macromolecular. The cross-sectional area of the fibre may be not completely circular, and may be in the form of an oval or the like.

A 'non-aqueous liquid phase' as used in this context relates to a liquid at ambient
15 conditions (temperature about 20°C, atmospheric pressure), and where said liquid has a tendency to flow, as determined by having a loss modulus G'' larger than the storage modulus G' at shear rates $\dot{\gamma}$ (gamma) ranging from 1 per second to 500 per second. The non-aqueous character is defined as the material not being able to dissolve more than 10% by weight in water under ambient conditions, preferably less than 5% by weight,
20 preferably less than 1% by weight, preferably less than 0.5% by weight, preferably less than 0.2% by weight.

In the context of the present invention, a lipophilic fibre is considered to be a fibre which preferably has a three-phase contact angle between a drop of non-aqueous liquid, and a
25 film of the fibrous material, and air of less than 70° at 20°C. Here a non-aqueous liquid preferably comprises sunflower oil or silicon oil, or derivatives of silicon oil. Preferably the contact angle is less than 50°, more preferred less than 40°.

In the present context, the contact angle is measured as the angle in the droplet, as
30 schematically depicted in Figure 1.

Lipophilic cellulose derivatives

In order to achieve good structuring capacity, a fibre should have a good compatibility to a
35 continuous non-aqueous liquid phase. A poor compatibility causes agglomeration of the fibres and weak interaction with the continuous phase, which may induce a reduction of

mechanical properties. The preferential route is to use fibres that are compatible with the continuous phase, which are either made from appropriate starting materials or modified chemically or physically during the process of their production.

- 5 The compatibility between fibre and non-aqueous liquid can be estimated by measuring the fibre wetting by the non-aqueous liquid. Measure for this is the three phase contact angle of non-aqueous liquid or water droplet in air placed on the substrate made from the same material the fibres are made from. Alternatively the contact angle of non-aqueous liquid droplet in water (or other way around) on the substrate can be measured as well.
- 10 Here the implicit assumption is that both fibre and substrate have the comparable surface roughness and that line tension effects can be neglected. A better non-aqueous liquid wetting (or poorer water wetting) are indicative of better compatibility between the fibre and the non-aqueous liquid phase. Therefore one can convert the problem of compatibility between the fibre and non-aqueous liquid phase to a problem of preparing
- 15 fibres with optimal lipophilicity measured via the contact angle.

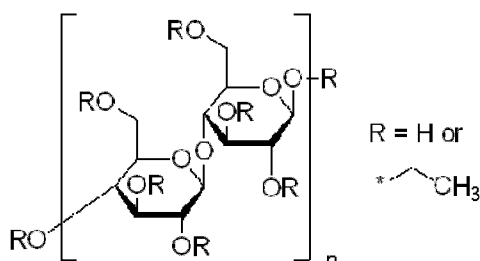
The lipophilic cellulose derivative is defined as a cellulose derivative which preferably has a three-phase contact angle between sunflower oil, and a film of the lipophilic cellulose derivative, and air is less than 70° at 20°C. Preferably the angle is less than 50°, most

20 preferred less than 40°.

The contact angle can be measured using standard equipment like the Drop shape analysis DSA100 (Krüss GmbH, Neunkirchen am Brand, Germany). This technique is common in the art.

25

- Preferably the lipophilic cellulose derivative comprises an alkylated cellulose. Examples of such alkylated celluloses are methyl-ethylcellulose, ethylcellulose, propylcellulose or butylcellulose. Another preferred lipophilic cellulose derivative is cellulose diacetate. Also combinations of these compounds are within the scope of the present invention. Most
- 30 preferred the lipophilic cellulose derivative comprises ethylcellulose. The general structural formula of ethylcellulose is:



The degree of substitution of the ethylcellulose preferably used in the present invention is preferably from 2 to 3, more preferably about 2.5. The average number of hydroxyl groups substituted per anhydroglucose unit (the 'monomer') is known as the 'degree of substitution' (DS). If all three hydroxyls are replaced, the maximum theoretical DS of 3 results.

Suitable sources and types of the ethylcellulose preferably used in the present invention are supplied by for example Ashland (formerly Hercules), Aldrich, and Dow Chemicals.

10 Suitable ethylcellulose preferably has a viscosity ranging from 5 to 300 cP at a concentration of 5 % in toluene/ethanol 80:20, more preferably from 100 to 300 cP at these conditions.

Prolamins

15 Prolamins are a group of plant storage proteins having a high proline content and are found in the seeds of cereal grains. Examples of these grains are wheat (protein gliadin), barley (protein hordein), rye (protein secalin), corn (protein zein) and as a minor protein, avenin in oats. The prolamins are characterised by a high glutamine and proline content and are generally soluble only in strong alcohol solutions.

20

Preferably the prolamin is chosen from the group of zein, gliadin, hordein, secalin, and avenin. Also combinations of these compounds are within the scope of the present invention.

25 Zein is the alcohol-soluble protein of corn and is classified as a prolamin. Biologically, zein is a mixture of proteins varying in molecular size and solubility. These proteins can be separated by differential solubilities and their related structures into four distinct types: alpha, beta, gamma, and delta. Alpha-zein is by far the most abundant, accounting for about 70% of the total. The next most abundant zein is gamma-zein, contributing to about

30 20% of the total.

Gluten is a storage protein from wheat and comprises two major protein groups, namely the gliadins (molecular weight 30,000–80,000) and glutenin polymers (molecular weight higher than 100,000). It is classified as prolamins due to the presence of aqueous alcohol

35 soluble gliadin groups.

Gliadin is a glycoprotein present in wheat and several other cereals within the grass genus *Triticum*. Gliadins are prolamins and are separated on the basis of electrophoretic mobility and isoelectric focusing. Together with glutenin it forms an important component of wheat gluten. Hordein is a major storage protein from barley. It is a glycoprotein also
5 classified as prolamins based on its solubility characteristics. Secalin, a storage protein found in rye, with high glutamine and proline content and low lysine content is also classified as prolamins.

10 *Lipids*

Lipid compounds in the context of the present invention are lipophilic materials which often are from natural origin, but they may also be synthetic compounds. Preferably the lipid compound comprises lecithin, fatty acid, monoglyceride, diglyceride, triglyceride, phytosterol, phytostanol, phytosteryl-fatty acid ester, phytostanyl-fatty acid ester, wax,
15 fatty alcohol, carotenoid, oil-soluble colourant, oil-soluble vitamin, oil soluble flavour, or oil soluble fragrance. Also combinations of these compounds are within the scope of the present invention.

Oils and fats such as dairy fats, or vegetable oils are a common source for
20 monoglycerides, diglycerides, and triglycerides. Examples of fat-soluble vitamins are vitamin A, vitamin D2, vitamin D3, vitamin E, and vitamin K. These vitamins include all compounds which function as the respective vitamin. The carotenoids include alpha-carotene, beta-carotene, lycopene, lutein, zeaxanthin.

25 Also materials like mineral oils, petrolatum, and silicon oils, and derivatives of these compounds are examples of compounds which could be used in the fibres of the invention as the lipid compound in the context of the present invention.

Lecithin: is a general term for a mixture which may originate from plant origin (e.g. soy
30 bean) or animal origin (e.g. egg yolk), and is used as emulsifier. The most important compounds in lecithin are phosphatidylcholine, phosphatidylethanolamine, and phosphatidylinositol. In commercially available lecithins also free fatty acids, triglycerides and mono- and diglycerides can be present. The nature of the phosphoric group and said fatty acids determine the emulsification properties of lecithin.

35 Fatty acid: fatty acids suitable in the present invention are C3 fatty acids and longer chains, preferably at least C12, up to preferably C26. The aliphatic tail may be saturated

or unsaturated. The chain can be unbranched or have branches like a hydroxy, methyl- or ethyl group. The fatty acid suitable in the present invention consists of minimum 3 carbon atoms and a maximum of 26.

Monoglyceride: an ester of glycerol and one fatty acid, wherein the fatty acid may be as
5 described above.

Diglyceride: an ester of glycerol and two fatty acids, wherein the fatty acids may be as described above.

Triglyceride: a glycerol which is esterified with three fatty acids, as described above. The fatty acids may be saturated, or monounsaturated or polyunsaturated. In the context of the
10 present invention, triglycerides are understood to be edible oils and fats. As used herein the term 'oil' is used as a generic term for oils and fats either pure or containing compounds in solution. Oils can also contain particles in suspension.

As used herein the term 'fats' is used as a generic term for compounds containing more than 80% triglycerides. They can also contain diglycerides, monoglycerides and free fatty
15 acids. In common language, liquid fats are often referred to as oils but herein the term fats is also used as a generic term for such liquid fats. Fats include: plant oils (for example: allanblackia oil, apricot kernel oil, arachis oil, arnica oil, argan oil, avocado oil, babassu oil, baobab oil, black seed oil, blackberry seed oil, blackcurrant seed oil, blueberry seed oil, borage oil, calendula oil, camelina oil, camellia seed oil, castor oil, cherry kernel oil, cocoa
20 butter, coconut oil, corn oil, cottonseed oil, evening primrose oil, grapefruit oil, grape seed oil, hazelnut oil, hempseed oil, illipe butter, jojoba oil, lemon seed oil, lime seed oil, linseed oil, kukui nut oil, macadamia oil, maize oil, mango butter, meadowfoam oil, melon seed oil, moringa oil, mowrah butter, mustard seed oil, olive oil, orange seed oil, palm oil, palm kernel oil, papaya seed oil, passion seed oil, peach kernel oil, plum oil, pomegranate seed
25 oil, poppy seed oil, pumpkins seed oil, rapeseed (or canola) oil, red raspberry seed oil, rice bran oil, rosehip oil, safflower oil, seabuckthorn oil, sesame oil, shea butter, soy bean oil, strawberry seed oil, sunflower oil, sweet almond oil, walnut oil, wheat germ oil); fish oils (for example: sardine oil, mackerel oil, herring oil, cod-liver oil, oyster oil); animal oils (for example: butter or conjugated linoleic acid, lard or tallow); or any mixture or fraction
30 thereof. The oils and fats may also have been modified by hardening, fractionation, chemical or enzymatical interesterification or by a combination of these steps.

Phytosterol: a group of steroid alcohols, phytochemicals naturally occurring in plants. At room temperature they are white powders with mild, characteristic odor, insoluble in water and soluble in alcohols. They can be used to decrease the LDL-cholesterol level in
35 plasma in humans.

Phytostanol: similar to the phytosterol, a group of steroid alcohols, phytochemicals naturally occurring in plants. They may also be obtained by hardening a phytosterol.

Phytosteryl-fatty acid ester: a phytosterol which has been modified by esterifying it with a fatty acid.

- 5 Phytostanyl-fatty acid ester: a phytostanol which has been modified by esterifying it with a fatty acid.

Waxes: a wax is a non-glyceride lipid substance having the following characteristic properties: plastic (malleable) at normal ambient temperatures; a melting point above approximately 45°C; a relatively low viscosity when melted (unlike many plastics);

- 10 insoluble in water but soluble in some organic solvents; hydrophobic. Waxes may be natural or artificial, but natural waxes, are preferred. Beeswax, carnauba (a vegetable wax) and paraffin (a mineral wax) are commonly encountered waxes which occur naturally. Some artificial materials that exhibit similar properties are also described as wax or waxy. Chemically speaking, a wax may be an ester of ethylene glycol (ethane-1,2-diol) and two fatty acids, as opposed to fats which are esters of glycerol (propane-1,2,3-triol) and three fatty acids. It may also be a combination of fatty alcohols with fatty acids, alkanes, ethers or esters. Preferred waxes are one or more waxes chosen from carnauba wax, shellac wax or beeswax or their synthetic equivalents. Also paraffin-based synthetic waxes are within the scope of the present invention.

20

Composite Fibres

In a first aspect the present invention provides A composition in the form of a fibre, wherein the fibre comprises a lipophilic cellulose derivative,

- 25 and at least one compound chosen from a prolamin and a lipid compound, wherein the fibre has a length from 1 micrometer to 10 millimeter, wherein the fibre has a diameter from 30 nanometer to 50 micrometer, and wherein the aspect ratio of the fibre is larger than 10.

- 30 In one preferred embodiment the fibrous material according to the invention comprises a lipophilic cellulose derivative, and a prolamin. In that case preferably the fibre comprises from 1% by weight to 99% by weight of a lipophilic cellulose derivative and from 1% by weight to 99% by weight of a prolamin. Preferably the fibre comprises from 10% by weight to 90% by weight of a lipophilic cellulose derivative and from 10% by weight to 90% by weight of a prolamin. Preferably the fibre comprises from 20% by weight to 80% by weight of a lipophilic cellulose derivative and from 20% by weight to 80% by weight of a prolamin.
- 35

In another preferred embodiment the fibrous material according to the invention comprises a lipophilic cellulose derivative, and a lipid material. In that case preferably the fibre comprises from 10% by weight to 99.9% by weight of lipophilic cellulose derivative and from 0.7% by weight to 90% by weight of a lipid compound. Preferably the fibre comprises from 70% by weight to 99% by weight of lipophilic cellulose derivative and from 1% by weight to 30% by weight of a lipid compound. Preferably the fibre comprises from 90% by weight to 98% by weight of lipophilic cellulose derivative and from 2% by weight to 10% by weight of a lipid compound.

10

Preferably the fibrous material according to the invention comprises the three mentioned classes of compounds. In that case the fibre preferably comprises 1% by weight to 98.9% by weight of a lipophilic cellulose derivative and from 1% by weight to 98.9% by weight of a prolamin, and from 0.1% by weight to 90% by weight of a lipid compound. Preferably the fibre comprises from 10% by weight to 89% by weight of a lipophilic cellulose derivative and from 10% by weight to 89% by weight of a prolamin, and from 1% by weight to 30% by weight of a lipid compound. Preferably the fibre comprises from 10% by weight to 88% by weight of a lipophilic cellulose derivative and from 10% by weight to 88% by weight of a prolamin, and from 2% by weight to 10% by weight of a lipid compound.

20

Examples of composite fibres are the following: ethylcellulose-zein composite, ethylcellulose-lecithin composite, ethylcellulose-triglyceride composite, ethylcellulose-hardstocks composite (hardstocks are fats solid at room temperature), ethylcellulose - phytosterol composite, ethylcellulose -phytosterol ester composite.

25

Preferably the fibre has a length from 1 micrometer to 10 millimeter, wherein the fibre has a diameter from 30 nanometer to 50 micrometer, and wherein the aspect ratio of the fibre is larger than 10.

30 Preferably the fibre has a length from 1 micrometer to 1,000 micrometer, preferably from 2 micrometer to 500 micrometer. Preferably the fibre has a length from 5 micrometer to 300 micrometer.

Preferably the fibre has a diameter from 50 nanometer to 40 micrometer, preferably from 100 nanometer to 25 micrometer, preferably from 300 nanometer to 10 micrometer, more preferably from 500 nanometer to 5 micrometer.

35

Preferably the fibre has an aspect ratio of larger than 50, preferably larger than 100, or preferably even larger than 200 or 500. The aspect ratio is defined as the ratio between the length and the diameter of an individual fibre.

5

The cross-sectional area of the fibres may be not completely circular, and may be in the form of an oval or the like. This may mean that for instance the cross-section of a fibre according to the invention may have a longest dimension of 2 to 5 microns, while the shortest dimension may be less than 1 micrometer. In that case the diameter of the fibre as expressed herein, is the diameter of a circle having the same surface area as the cross-section of the fibre.

The functions of lipid or other lipophilic materials in the fibres can be used to tune the lipophilicity of fibres for oil structuring; and/or to tune the meltdown property of fibre structured oil; and/or to tune the mechanical strength of fibres; and/or to tune the mechanical strength of the fibre network. This behaviour makes it possible to modify the properties of a product containing such structured non-aqueous liquids, for example to create a nice melting emulsion, or a skin cream with favourable properties to apply to the skin.

20

In principle long fibre lengths lead to good structuring properties when used to structure a non-aqueous liquid phase. On the other hand long hairy structures are often not desired in food products or personal care products. By using fibres having a relatively short length for structuring as compared to longer fibres, the lengths as defined in the claims lead to shear alignment. This means that under shear forces the fibres can align, and therewith give the impression to the consumer that a solid-liquid transition is obtained. This can be perceived to be analogous to a melting curve of a solid fat which melts upon chewing in the mouth or applying to the skin, and gives a positive impression to the consumer.

30 Preferably the fibre is obtained by a spinning process, preferably by an electrospinning process.

Spinning is a process that can be used to create fibres of polymeric materials. A preferred way of performing a spinning process, is by pressing a polymer in a liquid form through for example one or more nozzles or other orifices, to form continuous filaments. Usually the pressing through the nozzle may be done using an extruder, and there may be multiple

35

nozzles to create parallel filaments, like in a spinneret to form multiple continuous filaments. The polymer may be brought in liquid form by melting, or by dissolving in a suitable solvent. By pressing the molten polymer through the nozzle it may solidify by cooling (melt spinning). If the polymer is dissolved in a solvent, it may solidify by
5 precipitation in a liquid bath (wet spinning), or may solidify by evaporation of the solvent (dry spinning). Examples of the spinning process are shear-driven spinning, centrifugation spinning, jet spinning, and electrospinning.

In an electrospinning process (as described by Schiffman J.D. et al., Polymer Reviews,
10 vol. 48, 2008, p. 317–352) a molten or dissolved polymer is pressed through for example a capillary, to be collected on a collector. An electric field is applied between the capillary and the collector. Both the spinning and electrospinning methods are known in the art. Alternatively a system may be used that does not utilise nozzles or capillaries to create cones or jets of polymeric material. An example of such a system is the Nanospider™
15 technology from Elmarco (Liberec, Czech Republic). A cylinder is partly submerged in a bath of liquid polymer (solution). When the cylinder rotates, a thin layer of polymer is carried on the cylinder surface and exposed to a high voltage electric field. If the voltage exceeds a critical value, a number of electrospinning jets are generated from the polymer bath towards a collector. The jets are distributed over the electrode surface with
20 periodicity.

Method for production of fibrous materials

In a second aspect the present invention provides a method for preparation of
25 composition in the form of a fibre according to the first aspect of the invention, wherein the method comprises the spinning of a fibrous material from a solution comprising a lipophilic cellulose derivative, and at least one compound chosen from a prolamin and a lipid compound.

30 The general principles of a spinning process has been described herein before. Especially preferred the spinning method according to the second aspect of the invention involves electrospinning. Also electrospinning has been described herein before.

Preferably the electrospinning process which uses a capillary uses the following settings
35 and parameters. The nozzle from which the solution of the compounds is pressed preferably has an internal diameter of at least 0.1 millimeter. The upper diameter is

preferably less than 2 millimeter. During the electrospinning process cone is formed at the bottom and fibers are formed from the tip of this cone. The cone diameter usually is much smaller than the nozzle diameter. The nozzle play an indirect role as it is used as electrode as well that it influences electric field gradients. The flow rate from the nozzle

5 preferably is from 0.1 to 1,000 milliliter per hour, preferably from 1 to 100 milliliter per hour. These flow rates are per nozzle; multiple nozzles can be applied to create parallel flows. Preferably the metal collector is placed from 1 to 100 centimeter from the tip of the nozzle, preferably from 10 to 18 centimeter. The collector preferably is a copper mesh covering on a stainless steel mandrel, for example having about 12 cm internal diameter

10 and a length of about 30 cm. The positive lead from a high DC voltage supply is attached to the nozzle metal portion, and the collector is grounded. The voltage between the nozzle and the collector preferably is from 1 kV to 100 kV, preferably from 12 kV to 25 kV. The mandrel may rotate to create an evenly distributed mat during the spinning process, preferably at a rotational speed from 10 to 200 rpm, preferably from 70 to 130 rpm. The

15 temperature and pressure that are applied during the process preferably is from 5°C to 60°C, preferably from 20°C to 40°, preferably from 20°C to 25°C. The pressure may be at atmospheric pressure, but may also be reduced to facilitate the evaporation of the solvent. A mat of electrospun fibres is formed on the grounded copper mesh during the process.

20 The compounds used for making the fibres may be dissolved in a suitable solvent separately, and after dissolving the separate solutions may be combined, before being pressed through the nozzle to be collected on the collector. Alternatively the various compounds may be dissolved in the solvent simultaneously in order to make a mixture of compounds to be pressed through the nozzle. This way fibres are made with a fixed

25 composition.

Alternatively multiple parallel solutions can be made, which are mixed in a micro chamber or junction formed between different channels in line, just before its being pressed through a nozzle. Each solution may have its own pump and consequently its own flow rate. For

30 example one solution contains the lipophilic cellulose derivative, while another solution contains a prolamin. Both solutions are pumped to a three way valve where they mix, and subsequently they are pressed through the nozzle, and a fibrous material is collected on the collector. This has the advantage that the composition of the fibre can be varied during the preparation process, by adjusting the flow rate of one of the pumps relative to the

35 other. Additionally one of the solutions may contain a second compound (e.g. a lipid compound), or a third solution may be coupled in line, parallel to the other two solutions.

The solvent in the method according to the invention is a solvent in which the lipophilic cellulose derivative, the prolamin and the lipid compound can be dissolved. Examples of these solvents are alcohols, preferably ethanol, ethyl acetate, acetic acid, acetone, *N,N*-dimethylformamide (DMF), or any suitable combination of these solvents. The concentration of the compounds in the solvent is preferably from 5% by weight to 50% by weight, preferably between 10% by weight to 30% by weight. When the solution is released from the nozzle, the solvent evaporates.

- 10 In one preferred embodiment the fibrous material according to the invention comprises a lipophilic cellulose derivative and a prolamin. In that case the solution in the spinning step preferably comprises in addition to the solvent from 1% by weight to 99% by weight of a lipophilic cellulose derivative and from 1% by weight to 99% by weight of a prolamin. Preferably the solution comprises from 10% by weight to 90% by weight of a lipophilic
- 15 cellulose derivative and from 10% by weight to 90% by weight of a prolamin. Preferably the solution comprises from 20% by weight to 80% by weight of a lipophilic cellulose derivative and from 20% by weight to 80% by weight of a prolamin. Here this is all based on the weight of the compounds in the solvent.
- 20 In another preferred embodiment the fibrous material according to the invention comprises a lipophilic cellulose derivative and a lipid material. In that case the solution in the spinning step preferably comprises in addition to the solvent from 10% by weight to 99.9% by weight of lipophilic cellulose derivative and from 0.7% by weight to 90% by weight of a lipid compound. Preferably the solution comprises from 70% by weight to 99% by weight
- 25 of lipophilic cellulose derivative and from 1% by weight to 30% by weight of a lipid compound. Preferably the solution comprises from 90% by weight to 98% by weight of lipophilic cellulose derivative and from 2% by weight to 10% by weight of a lipid compound.
- 30 Preferably the fibrous material according to the invention comprises the three mentioned classes of compounds. In that case the solution in the spinning step preferably comprises in addition to the solvent from 1% by weight to 98.9% by weight of a lipophilic cellulose derivative and from 1% by weight to 98.9% by weight of a prolamin, and from 0.1% by weight to 90% by weight of a lipid compound. Preferably the solution comprises from 10%
- 35 by weight to 89% by weight of a lipophilic cellulose derivative and from 10% by weight to 89% by weight of a prolamin, and from 1% by weight to 30% by weight of a lipid

compound. Preferably the solution comprises from 10% by weight to 88% by weight of a lipophilic cellulose derivative and from 10% by weight to 88% by weight of a prolamin, and from 2% by weight to 10% by weight of a lipid compound.

- 5 In further preferred steps the method according to the invention additionally comprises the steps:
- a) dispersing the fibrous material obtained from the spinning step in a non-aqueous liquid; and
 - b) homogenising the mixture from step a), to fragment the fibrous material to an
- 10 average length from 1 micrometer to 10 millimeter.

This way the correct length of fibrous material is obtained. Preferably the length of the fibre that is obtained is from 1 micrometer to 1,000 micrometer, preferably from 2 micrometer to 500 micrometer. Preferably the fibre has a length from 5 micrometer to

15 300 micrometer.

Preferably in step a) the non-aqueous liquid comprises a vegetable oil, for example sunflower oil, palm oil, olive oil, rapeseed oil, or any other suitable oil or combinations of oils. The oil may be liquid at room temperature, or alternatively may be solid at room

20 temperature, in which case the oil should be melted first by increasing the temperature. A fat or oil from animal origin, such as fish oil, dairy fat, lard, or tallow, may be used as well. Such a vegetable or animal oil obtained from step b) may be used as an ingredient of food products.

25 The non-aqueous liquid in step a) may also be chosen from materials like mineral oils, petrolatum, and silicon oils, and derivatives of these compounds, and combinations of these. In that case the structured non-aqueous liquid obtained from step b) may be used as an ingredient of home care or personal care products.

30 In step b) the homogenisation preferably is carried out by subjecting the mixture of fibrous material and non-aqueous liquid to high shear. This high shear can be created by methods common in the art. These methods include rotor-stator systems, e.g. the Ultra-Turrax® (IKA Werke GmbH & Co. KG, Staufen, Germany), or a Silverson mixer (Silverson Machines Ltd., Chesham, Bucks, UK). Another method is high pressure homogenisation.

35 An example of such a high pressure homogeniser is the Microfluidizer® (Microfluidics

International Corporation, MA-Newton, USA). Also sonication, a colloid mill, and a ball mill may be used to homogenise the mixture.

In case of a rotor-stator system, e.g. the Ultra-Turrax[®], the rotational speed preferably
5 ranges from 1,000 to 30,000 rpm. The system is preferably homogenised during a period from 15 seconds to 60 minutes. This way a homogeneous mixture of cut fibres in oil can be achieved.

The amount of fibre to be added to the non-aqueous liquid in step a) of the preferred
10 method ranges from 0.05% by weight to 50% by weight, preferably from 1% by weight to 40% by weight. The mixture of homogenised non-aqueous liquid and fibrous material may be used as an ingredient of a food product or a personal care product, as applicable. In that case it may be brought into contact with other ingredients of such product.

Alternatively the homogenised non-aqueous liquid from step b) is diluted first with a non
15 aqueous liquid, before being brought into contact with the other ingredients of the product.

After the homogenisation step the material obtained in step b) may need to be cooled, as the temperature may have risen due to the homogenisation operation.

20 By the homogenisation step two possible fragmenting operations take place. First, if the fibrous material has been obtained from a spinning process and a mat of fibrous material has been formed, then the homogenisation first leads to break up of the mat. Individual fibres are obtained. Second the long fibres which are formed are broken into smaller pieces, leading to reduction of the length of the fibre. These two steps may take place
25 simultaneously, such that while the fibrous mat is broken into pieces, also long individual fibres are broken into shorter fibres.

The present invention also provides a composition in the form of a fibre obtainable by the method according to the second aspect of the invention,
30 wherein the fibre has a length from 1 micrometer to 10 millimeter,
wherein the fibre has a diameter from 30 nanometer to 50 micrometer,
and wherein the aspect ratio of the fibre is larger than 10. Preferably the fibre has a length from 1 micrometer to 1,000 micrometer, preferably from 2 micrometer to 500 micrometer. Preferably the fibre has a length from 5 micrometer to 300 micrometer. Preferably the fibre
35 has a diameter from 50 nanometer to 40 micrometer, preferably from 100 nanometer to 25 micrometer, preferably from 200 nanometer to 25 micrometer, preferably from 300

nanometer to 10 micrometer, more preferably from 500 nanometer to 5 micrometer. The aspect ratio of the fibre preferably is larger than 50, preferably larger than 100, or preferably even larger than 200 or 500.

5

Use of the composition in the form of a fibre

In a third aspect the present invention provides the use of a composition in the form of a fibre according to the first aspect of the invention, as structurant of a non-aqueous liquid phase. Possible products that may be structured by the composition in the form of fibre
10 according to the invention are food products such as water-in-oil emulsions or oil-in-water emulsions, or personal care products, such as skin creams. These personal care products may be oil-in-water emulsions. Also double emulsions and multiple emulsions (like oil-in-water-in-oil and water-in-oil-in-water emulsions) are emulsions of which the non-aqueous liquid phase can be structured by the fibres of the invention.

15

In the case of food products, the non-aqueous liquid phase can be a lipid phase, for example droplets of a dairy fat or sunflower oil dispersed in an aqueous phase to form an oil-in-water emulsion. Examples of oil-in-water emulsions are dressings and mayonnaise-type products, dairy spreads, and body lotions and skin creams. In case of water-in-oil
20 emulsion such as margarines, butter, and other spreads, the lipid phase can be considered to be the continuous vegetable oil phase or butter fat phase, as applicable.

In case of personal care products, the non-aqueous liquid phase may be chosen from materials like mineral oils, petrolatum, and silicon oils, and derivatives of these
25 compounds, and combinations of these.

The amount of non-aqueous liquid phase in such products may range from 1% by weight to 99% by weight of the product, depending on the product. For example a shortening may contain 99% by weight of edible oil or fat. A margarine contains about 80% edible oils
30 and fats. A water-in-oil spread may contain from 20 to 70% by weight of edible oils and fats. A dressing or mayonnaise may contain from about 5% by weight up to 80% by weight of non-aqueous lipid phase. A dairy spread may contain about 20 to 30% by weight of edible oils and fats. A skin cream may contain about 5 to 20% by weight of lipid compounds.

35

The amount of fibre in the non-aqueous liquid phase preferably ranges from 0.01% by weight of the lipid phase to 50% by weight of the non-aqueous liquid phase, preferably from 0.2% by weight to 25% by weight, more preferred from 0.5% by weight to 10% by weight, more preferred maximally 5% by weight.

5

Hence preferably the present invention provides a food product comprising a non-aqueous liquid phase, wherein the non-aqueous liquid phase comprises a composition in the form of a fibre according to the first aspect of the invention.

- 10 The fibrous material leads to structuring of the non-aqueous liquid phase. By rheology measurements it can be shown that the physical behaviour of the structured lipids is such that it resembles lipid phases that are structured by solid triglycerides (for example like in butter and margarine), for example in meltdown behaviour upon increase of temperature. Also extended temperature stability can be obtained.

15

- By rheology measurements is meant that storage modulus G' (in Pa) and loss modulus G'' (in Pa) are determined. The elasticity of the system is determined by these rheology measurements. G' and G'' can be determined as function of the strain γ (gamma, in %) at a fixed temperature, and as function of temperature at a fixed strain. When measured as
20 function of temperature, the meltdown behaviour is determined. This determines how structured non-aqueous liquid behaves under the influence of temperature.

- In general, the storage modulus (G') describe how a material behave like solid, and the loss modulus (G'') describes how a material behave like liquid. If G' is larger than G'' , it
25 means that the oil behaves like a solid or semi-solid, and otherwise, like a liquid. The point where G' equals G'' is a characteristic one: beyond this point the material starts to flow.

- Temperature-dependent behaviour can characterize the meltdown process of sample. Meltdown is an important property for margarine, but also for other products an
30 appropriate temperature dependency is important. 5°C is to mimic temperature in a refrigerator, and higher value indicates good stability of margarine in the fridge. 25°C is to mimic temperature when margarine is taken out of fridge and in use. A value at 25°C should be slightly lower than that at 5°C, but not too much. 37°C is to mimic mouth temperature. A lower value indicates more thorough meltdown in the mouth. An ideal
35 temperature curve should be high enough from 5° C to 25° C, then decrease gradually with temperature increasing, finally reach a very low level.

The meltdown index is introduced to determine how much structured non-aqueous liquid loses its structure upon temperature increase. The meltdown index is calculated by:

$$\text{meltdown index} = \log_{10} (G'_{5^{\circ}\text{C}} / G'_{37^{\circ}\text{C}})$$

5

A meltdown index of more than 1 is considered to be good, and the higher the meltdown index, the better the structuring behaviour connected with acceptable properties of the structured non-aqueous liquid for the consumer. For example a food emulsion structured by the fibrous network shows similar behaviour as a standard margarine wherein the oil is structured by solid fat crystals. These crystals melt upon consumption and/or use, leading to favourable properties.

Also the viscosity (in Pa.s) of a structured non-aqueous liquid can be determined as function of the shear rate (in 1/s) can be determined in order to compare for example a margarine (structured by solid (saturated) fat crystals) and structured non-aqueous liquid.

Here the temperature influences the interaction within the fibrous network, by increase of temperature the interactions between fibres becomes less, generally leading to softer non-aqueous liquids at increased temperature. The relatively short fibres that structure the non-aqueous liquid may align, to soften the structured non-aqueous liquid. This way the meltdown behaviour of vegetable edible oils that are structured by saturated fat crystals can be mimicked, while not using the saturated fats.

The advantage of using the fibrous materials according to the invention is that the amount of saturated triglycerides that is required to structure triglycerides can be reduced, which leads to a healthier triglyceride profile of foods containing such structured lipid phase.

Preferably the food product according to the invention is a water-in-oil emulsion or an oil-in-water emulsion.

30

The food products of the invention may be all kinds of food products, for instance marinades, sauces, seasonings, butter, spray products, spreads, liquid shallow frying products, seasonings, dressings, mayonnaise, low-fat mayonnaise, and ice cream.

Preferably, food products according to the invention are spreads (water-in-oil emulsions or oil-in-water emulsions), margarines (water-in-oil emulsions), dairy products such as butter

(water-in-oil emulsion), or liquid water-in-oil emulsions or liquid oil-in-water emulsions designed for shallow frying.

Many food emulsions are stabilised by solid fat particles, especially margarine-type of emulsions and spreads. These are water-in-oil emulsions. The solid fat usually is mainly a saturated fat, which is considered to be unhealthy when consumed in large amounts. Therefore replacing saturated fats by the fibrous materials has the advantage that the amount of saturated fat can be reduced, and has a beneficial health effect for the consumer. Nevertheless similar sensory and in-use physical property can be achieved, like rheology, spreadability, storage stability, and chemical stability.

In another preferred embodiment, the present invention provides a personal care product comprising a non-aqueous liquid phase, wherein the non-aqueous liquid phase comprises a composition in the form of a fibre according to the first aspect of the invention. In this case the personal care product is for example a skin cream, a body lotion, bodywash, handwash, facial foam, shampoo, or hair conditioner. When applied in personal care products, new structures can be made which are liked by consumers. Examples of this are a superior sensory feeling such as silky feel (like in skin care cream), or deliver actives on the skin (like in skin cleansing product).

20

The non-aqueous liquid phase in personal care products as described in here is preferably chosen from materials like mineral oils, petrolatum, and silicon oils, and derivatives of these compounds, and combinations of these.

25

DESCRIPTION OF FIGURES

Figure 1: Schematic representation of the contact angle as defined herein. Droplet is dark, on the surface of a film. The contact angle as indicated is the angle in the droplet between the surface and the tangential line hitting the droplet.

Figure 2: Three scanning electron microscope pictures of fibrous mat produced by electrospinning ethylcellulose, as described in example 2. From top to bottom: A magnification 80× (scale width 500 micrometer); B magnification 1,000× (scale width 50 micrometer); C magnification 10,000× (scale width 5 micrometer).

Figure 3: Optical microscopy image of ethylcellulose fibre after homogenising. Bar width is 100 micrometer.

Figure 4: Image of the dispersion of ethylcellulose fibre in oil by means of phase contrast microscopy, bar width 100 micrometer; from example 2.

Figure 5: Rheology profile (G' (black triangles) and G'' (white triangles) (in Pa) as function of temperature (in °C), at fixed strain of 0.1% and frequency of 1 Hz) of ethylcellulose fibre structured oil; from example 2.

Figure 6: Photograph of ethylcellulose fibre structured oil; from example 2.

Figure 7: Scanning electron microscope picture of fibres obtained by electrospinning ethylcellulose-zein mixture; as described in Example 3; magnification 5,000× (scale width 5 micrometer).

Figure 8: Rheology profile (G' (squares) and G'' (triangles) (in Pa) as function of temperature (in °C), at fixed strain of 0.1% and frequency of 1 Hz) of ethylcellulose-zein composite fibre structured oil; from example 3.

Figure 9: Scanning electron microscope picture of fibres obtained by electrospinning ethylcellulose-zein mixture; as described in example 4; scale width 10 micrometer.

Figure 10: Rheology profile of oil structured with ethylcellulose-zein fibre (G' (closed squares and triangles) and G'' (open squares and triangles) (in Pa) as function of strain γ (gamma, in %), at 25°C; from example 4. Squares: margarine; triangle: ethylcellulose-zein structured oil.

Figure 11: Two scanning electron microscope pictures of fibrous mat produced by electrospinning ethylcellulose-inES48 triglyceride mixture, as described in example 5. From top to bottom: A magnification 100× (scale width 500 micrometer); B magnification 10,000× (scale width 5 micrometer).

Figure 12: The rheology profile (G' (closed squares and triangles) and G'' (open squares and triangles) (in Pa) as function of temperature (in °C), at fixed strain of 0.1% and frequency of 1 Hz) of ethylcellulose fibre structured oil (triangles) and ethylcellulose-inES48 triglyceride fibre structured oil (squares); from example 5.

Figure 13: Photograph of ethylcellulose-inES48 triglyceride fibre structured oil; from example 5.

30

EXAMPLES

The following non-limiting examples illustrate the present invention.

Raw materials:

Ethylcellulose: Aqualon® Ethylcellulose (type N 100) was purchased from Hercules (Widnes, UK). Ethoxyl content was 48.0-49.5%, and degree of substitution was 2.46-2.57. Viscosity was 80-105 mPa.s (at 5% and 25°C in 80/20 toluene/ethanol).

- 5 Ethanol (95%) supplied by Shanghai Dongfeng reagent (China)

Sunflower oil, (100%), brand: Duoli, supplied by Shanghai Jia Ge Food Co., Ltd (China).

Dimethicone: Polydimethylsiloxanem, trademark & product name: PMX-200 Fluid, 50 cPs, molecular weight: 3,200; refractive index: 1.402, specific gravity: 0.960, manufacturer: Dow Corning (Midland MI, USA).

- 10 Demineralised water was obtained from a Millipore filter system.

Zein from corn was obtained from Sigma-Aldrich (Schnelldorf, Germany).

inES48 triglyceride: inES48 is an interesterified mixture of 65% dry fractionated palm oil stearin with an iodine value of 14 and 35% palm kernel oil. inES48 contains about 86.2% saturated fatty acids, about 11.5% mono-unsaturated fatty acids, and about 2.3% poly-

- 15 unsaturated fatty acids, and is free from trans fatty acids. Obtained from Unimills (Zwijndrecht, Netherlands).

Rheology analysis

Rheological analysis was performed in a controlled stress rheometer (Anton Paar,

- 20 Physica MCR501, Austria) with a parallel-plate (PP 25) measuring system. This configuration has been chosen because of some particles contained in the each sample. Prior to each experiment, samples were left to equilibrate for the same time after loading PP25.

25 *Determination of fibre size distribution*

The process of sample preparation can be described as following: 1g sample dispersed in 50 ml hexane under stirring; filtrate under vacuum, and collect the cake left; redisperse cake in 50 ml hexane under stirring; take a drop of dispersion onto glass slide; count and calculate fibre length after hexane evaporating using a Leica DM LB 2 (Leica

- 30 Microsystems Ltd, Germany) light microscope and image analysis software (Software: Leica QWin Standard V3.5.1). The collected fibres are distributed in equal classes of 10 micrometer length.

Example 1 – Measurement of Contact Angle

The contact angle of ethylcellulose and zein was determined using a Drop shape analysis DSA100 (Krüss GmbH, Neunkirchen am Brand, Germany). In the present context, the contact angle is measured as the angle in the droplet, as schematically depicted in Figure

5 1. The method applied was the following:

- dissolve ethylcellulose or zein in a solvent to make homogenous solution;
- case a few drops of a solution onto a whole glass slide, under slowly spinning the glass slide to evenly spread the drops on the glass slide;
- dry, smooth and even film formed after solvent has evaporated;
- 10 - 5 microliter drop of demineralised sunflower oil or dimethicone is brought onto the surface, at ambient pressure, humidity and temperature;

Measured contact angles:

Sunflower oil - ethylcellulose film: 37°.

15 of Sunflower - zein film: 29°.

Dimethicone - ethylcellulose film 24°.

Dimethicone - zein film: 31°.

20 Example 2 – Standard Procedure for making Fibres and Structuring*Preparation of electrospun ethylcellulose fibre*

This example shows the basic procedure for making fibres by electrospinning. 1 gram ethylcellulose was dissolved in 9 gram aqueous ethanol solution (90 wt%). The solution was loaded onto a 10 mL syringe plunger. A blunt end stainless steel adapter with outer
25 diameter of 0.9 mm was then placed on the syringe to act as the electrospinning nozzle and charging point for the contained ethylcellulose solution. The filled syringe was placed in a cole-parmer syringe pump with flowing rate of 1.25 ml/hr. The positive lead from the high DC voltage supply was attached to the adapter metal portion. The voltage was set at 19 kV. The grounded collector was a copper mesh covering on a stainless steel mandrel
30 (12 cm internal diameter and 30 cm length) placed 10 cm from the tip of the adapter. The mandrel was rotated at 100 rpm during the spinning process. In the experiment, 10 ml of the ethylcellulose solution was electrospun to form a nice, white mat on the grounded copper mesh. After electrospinning, the ethylcellulose mat was removed from the copper mesh and process for scanning electron microscopy evaluation. The results of fibrous mat
35 can be seen in Figure 2 (magnification 80×, 1,000×, and 10,000×, respectively). The

average diameter of ethylcellulose fibre varied from 100 nanometer to 500 nanometer. The thickness of ethylcellulose mat was approximately 500 micrometer.

Preparation of ethylcellulose fibre structured oil

- 5 2 gram inES48 (triglyceride hardstock) was melted in 17.6 g sunflower oil used as lipid phase. 0.6 gram of ethylcellulose mat was torn into small pieces first, and then dispersed into oil phase under homogenization at the rate of $10,000 \text{ min}^{-1}$ for 5 min using an Ultra Turrax IKA T-25 digital (IKA Werke GmbH & Co. KG, Staufen, Germany). The concentration of fibre in the lipid phase was 3 % by weight. After totally dispersing the oil
- 10 phase containing ethylcellulose fibre continued homogenizing at the rate of $14,000 \text{ min}^{-1}$ for another 5 min. The resultant oil was put in the ethanol/water bath where temperature is -20°C , then fast stir using spatula to transfer heat as quick as possible. The cooling rate can vary from -15°C/min to -20°C/min . When temperature decreased to 5°C , the structured emulsion was stored at 5°C for 48 hr. Through this process ethylcellulose mat
- 15 was broken down into single and short ethylcellulose fibre dispersing evenly in oil (see Figure 3), and the fibre structured oil showed good rheological behavior and temperature response. Figure 4 shows the dispersion of ethylcellulose fibre in oil by means of phase contrast microscopy. Figure 5 shows rheological response (G' and G'' as function of temperature, at fixed strain of 0.1% and frequency of 1 Hz) profile of fibre structured oil.
- 20 Figure 6 is a photograph of ethylcellulose fibre structured oil.

G' and G'' both show a plateau first upon increase of temperature from 5°C to about 20°C , and upon reaching higher temperatures the structured oil starts to loose some of its structure (G' and G'' decrease). The meltdown index of ethylcellulose structured oil was

25 2.9.

Example 3 - Preparation of ethylcellulose-zein composite fibre

Preparation of ethylcellulose-zein composite fibre with one syringe

- 30 1. Ethylcellulose was dissolved in 90 wt% ethanol/water to prepare 10% ethylcellulose solution.
2. Zein was dissolved in 80 wt% ethanol/water to prepare 23% zein solution.
3. Ethylcellulose solution and zein solution were mixed at a volume ratio of 1 to 1.
4. The mixture was loaded into a 10 ml syringe.
- 35 5. The electrospinning parameters were: 1) voltage: 18-20 kV; 2) distance from the tip of needle to collector: 10 cm; 3) flowing rate: 1.25 ml/hr.

6. ethylcellulose/Zein composite fibres were collected on the rotary copper mesh.
7. The fibres were separated from the copper mesh and torn into small pieces. The result is shown in Figure 7. The diameter of ethylcellulose-zein composite fibre varied from 500 nanometer to 3 micrometer.

5

Preparation of ethylcellulose-zein composite fibre structured oil

Oil was structured in the same way as described in example 2 except for the electrospun fibre. In this case the electrospun fibre was ethylcellulose-zein composite fibre as prepared above. The concentration of ethylcellulose-zein composite fibre was 5% by weight, and the composition also contained 5% by weight of inES48 triglyceride, in addition to the fibre and the sunflower oil.

Figure 8 shows the rheological response (G' and G'' as function of temperature, at fixed strain of 0.1% and frequency of 1 Hz) profile of ethylcellulose-zein fibre structured oil. The meltdown index in the present case was 1.4.

Example 4 - Preparation of ethylcellulose-zein composite fibre

Preparation of ethylcellulose-zein composite fibres with two syringes

1. Ethylcellulose was dissolved in 90 wt% ethanol/water to prepare 10% ethylcellulose solution.
2. Zein was dissolved in 80 wt% ethanol/water to prepare 23% zein solution.
3. Ethylcellulose and zein solution were loaded into two 10 ml syringes, respectively.
4. The syringes were fixed onto one pump and the two solutions were mixed in a three valve connector at a volume ratio of 1 to 1, then the mixture was spun from one spinneret.
5. The electrospinning parameters were: 1) voltage: 18-20 kV; 2) distance from the tip of needle to collector: 10 cm; 3) flowing rate: 1.25 ml/hr.
6. Ethylcellulose/zein composite fibres were collected on the rotary copper mesh.
7. The fibres were separated from the copper mesh and torn into small pieces.

A SEM image of the composite fibre is shown in Figure 9. The diameter of ethylcellulose-zein composite fibre varied from 500 nanometer to 3 micrometer.

Preparation of ethylcellulose-zein composite fibre structured oil

The procedure applied for this example is the same as in example 3. The concentration of ethylcellulose-zein composite fibre was 5% by weight, and the composition also contained 5% by weight of inES48 triglyceride, in addition to the fibre and the sunflower oil.

5

Figure 10 shows the rheology profile of oil structured with the ethylcellulose-zein fibre (G' and G'' (in Pa) versus strain γ (gamma in %), at temperature 25°C. The rheology profile was compared to the rheology profile of margarine. The margarine was a commercially available Flora margarine (ex Unilever, bought in a local shop in Shanghai, China),
10 containing 70% fat, of which 25% is saturated fats. This graph shows that the rheology profile of oil structured with ethylcellulose-zein composite fibres is comparable with margarine. An oil phase structured by lipophilic fibres can be designed such that the viscosity profile of margarine is effectively mimicked.

15

Example 5 - Preparation of electrospun ethylcellulose-triglyceride composite fibre*Preparation of electrospun ethylcellulose-inES48 triglyceride composite fibre*

The method for this example is the same as example 2 except for the electrospun solution. In this case, the spinning solution consisted of 1 gram ethylcellulose, 0.05 gram
20 inES48 triglyceride dissolved in 9 g aqueous ethanol solution (90 wt%) at 53 °C. In this experiment, 10 ml of solution was spun to form a white mat. The results are shown in Figure 11 (magnification 100×, 10,000×, respectively). The diameter of ethylcellulose-inES48 composite fibre varied from 50 nanometer to 500 nanometer. The thickness of ethylcellulose-inES48 triglyceride composite fibre mat was approximately 200 micrometer.

25

Preparation of ethylcellulose-inES48 composite fibre structured oil

The process for this example is similar as in example 2 except for the composition of oil. In this case the structured oil consisted of 0.5 gram ethylcellulose-inES48 composite fibre, 0.475 gram inES48 and 9.025 gram sunflower oil. The concentration of fibre in the lipid
30 phase was 5% by weight. The rheology curves (G' and G'' as function of temperature) and photograph of structured oil are shown in Figure 12 and Figure 13.

Additionally a similar composition was made of sunflower oil containing 5 wt% inES48, and structured with 5% ethylcellulose fibre (as prepared in example 2). The rheology
35 profile (G' and G'' as function of temperature) of this composition is also shown in Figure 12.

The rheology parameters of ethylcellulose-inES48 composite fibre structured oil as compared to ethylcellulose fibre structured oil shows the following. First the meltdown behaviour can be tuned by the composite fibre, in the present case the oil structured with the ethylcellulose-inES48 composite fibre was a bit softer (G' and G'' lower) than the oil structured with the ethylcellulose fibre. The meltdown index of the ethylcellulose-inES48 composite fibre structured oil was 1.3, while it was 1.2 of the ethylcellulose fibre structured oil. A slight improvement in meltdown behaviour can be found by addition of triglyceride in the ethylcellulose fibre. Moreover the rheology profile of the ethylcellulose-inES48 composite fibre structured oil shows a little plateau at lower temperatures, while the ethylcellulose fibre has steeper curves. Such a plateau will lead to stability of the structured oil at room temperatures, the oil does not become too soft when the temperature of the structured oil is increased from fridge temperature to room temperature.

15

By addition of lipid (triglyceride in this case), the meltdown behaviour can be adjusted. This may lead to the creation of structured non-aqueous liquids with favourable properties for the consumers. Food products and personal care products can be designed which show good melting behaviour, meaning not too rapid and not too slow melting. This behaviour can be controlled by modification of the composition of the fibres.

20

CLAIMS

1. A composition in the form of a fibre,
wherein the fibre comprises a lipophilic cellulose derivative,
and at least one compound chosen from a prolamin and a lipid compound,
wherein the fibre has a length from 1 micrometer to 10 millimeter,
wherein the fibre has a diameter from 30 nanometer to 50 micrometer,
and wherein the aspect ratio of the fibre is larger than 10.
2. A composition according to claim 1, wherein the three-phase contact angle between sunflower oil, and a film of the lipophilic cellulose derivative, and air is less than 70° at 20°C.
3. A composition according to any of claims 1 to 2, wherein the lipophilic cellulose derivative comprises ethylcellulose.
4. A composition according to any of claims 1 to 3, wherein the prolamin is chosen from the group of zein, gliadin, hordein, secalin, and avenin.
5. A composition according to any of claims 1 to 4, wherein the lipid compound comprises lecithin, fatty acid, monoglyceride, diglyceride, triglyceride, phytosterol, phytostanol, phytosteryl-fatty acid ester, phytostanyl-fatty acid ester, wax, fatty alcohol, carotenoid, oil-soluble colourant, oil-soluble vitamin, oil soluble flavour, or oil soluble fragrance.
6. A composition according to any of claims 1 to 5, wherein the fibre has a length from 1 micrometer to 1,000 micrometer, preferably from 2 micrometer to 500 micrometer.
7. A composition according to any of claims 1 to 6, wherein the fibre has a diameter from 100 nanometer to 25 micrometer.
8. A composition according to any of claims 1 to 7, wherein the fibre is obtained by a spinning process, preferably by an electrospinning process.

9. A method for preparation of composition in the form of a fibre according to any of claims 1 to 8, wherein the method comprises the spinning of a fibrous material from a solution comprising a lipophilic cellulose derivative, and at least one compound chosen from a prolamin and a lipid compound.
10. A method according to claim 9, wherein the spinning involves electrospinning.
11. A method according to claim 9 or 10, additionally comprising the steps:
- a) dispersing the fibrous material obtained from the spinning step in a non-aqueous liquid; and
 - b) homogenising the mixture from step a), to fragment the fibrous material to an average length from 1 micrometer to 10 millimeter.
12. A composition in the form of a fibre obtainable by the method according to any of claims 9 to 11,
wherein the fibre has a length from 1 micrometer to 10 millimeter,
wherein the fibre has a diameter from 30 nanometer to 50 micrometer,
and wherein the aspect ratio of the fibre is larger than 10.
13. Use of a composition in the form of a fibre according to any of claims 1 to 8 or claim 12, as structurant of a non-aqueous liquid phase.
14. A food product comprising a non-aqueous liquid phase, wherein the non-aqueous liquid phase comprises a composition in the form of a fibre according to any of claims 1 to 8 or claim 12.
15. A personal care product comprising a non-aqueous liquid phase, wherein the non-aqueous liquid phase comprises a composition in the form of a fibre according to any of claims 1 to 8 or claim 12.

Figure 1

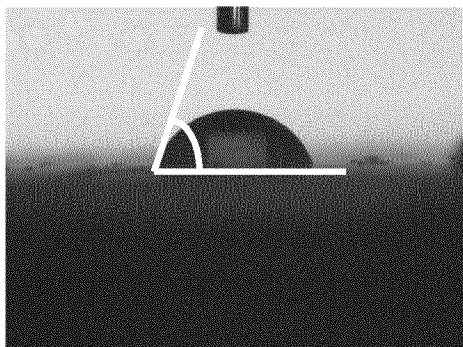


Figure 2

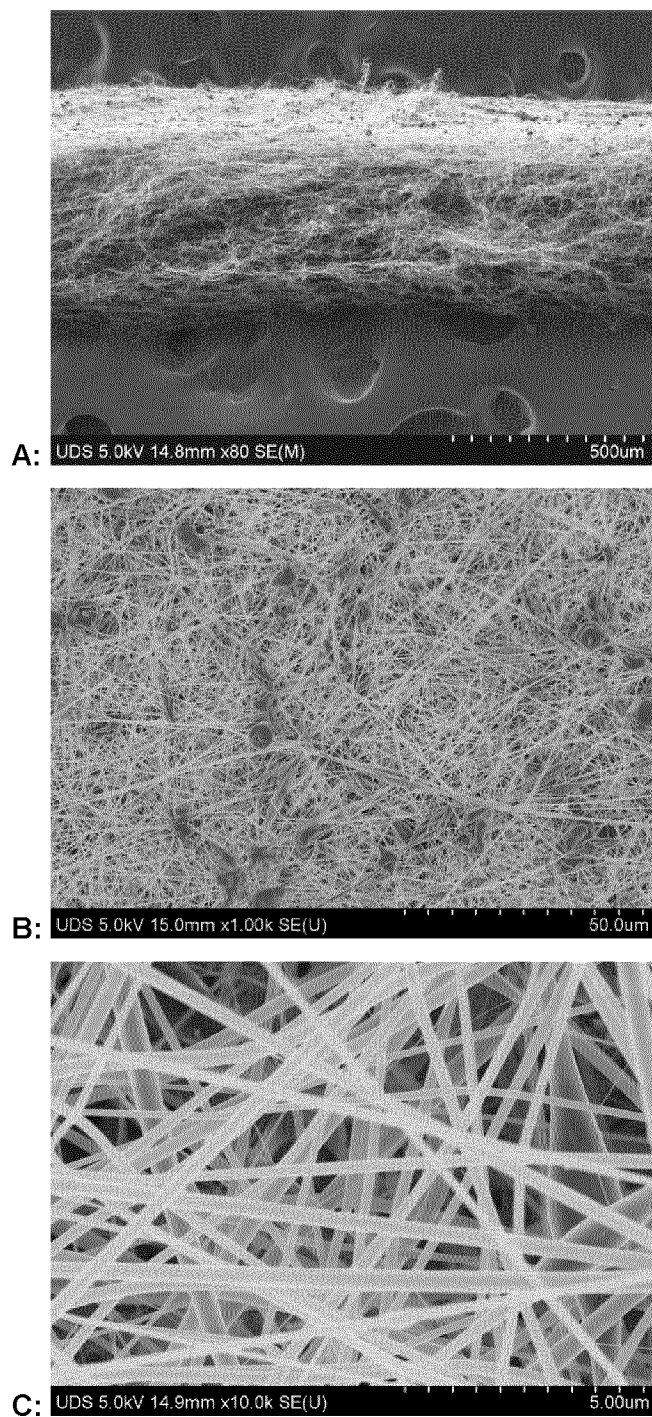


Figure 3

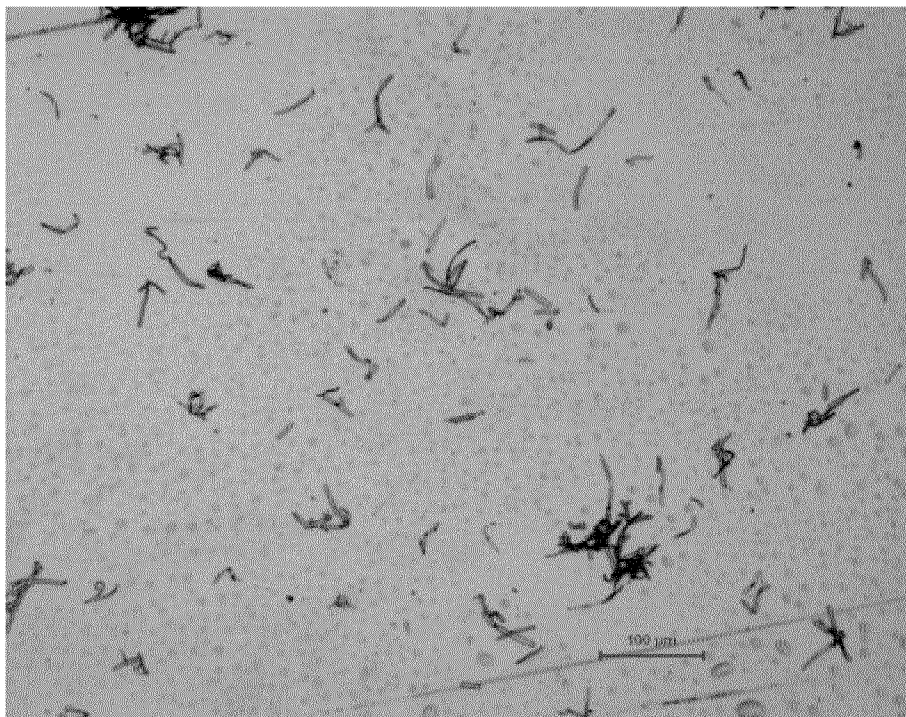


Figure 4

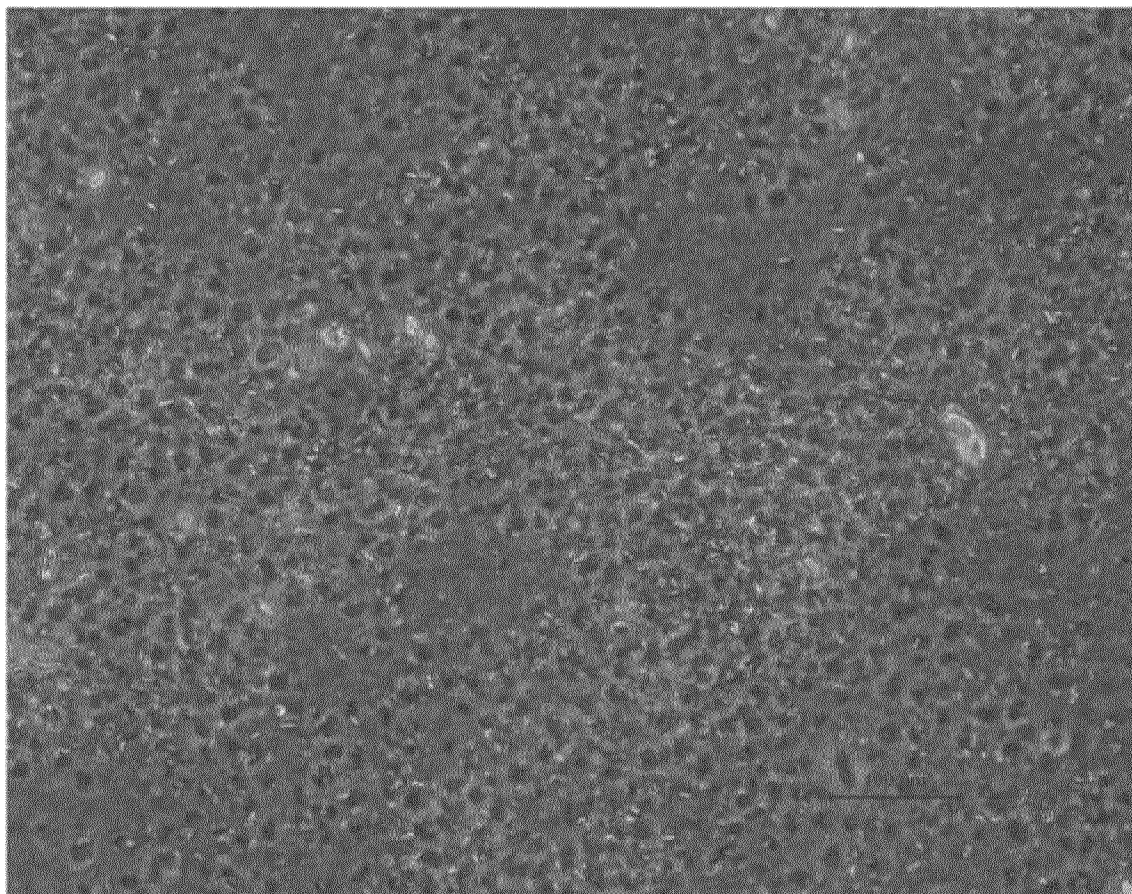


Figure 5

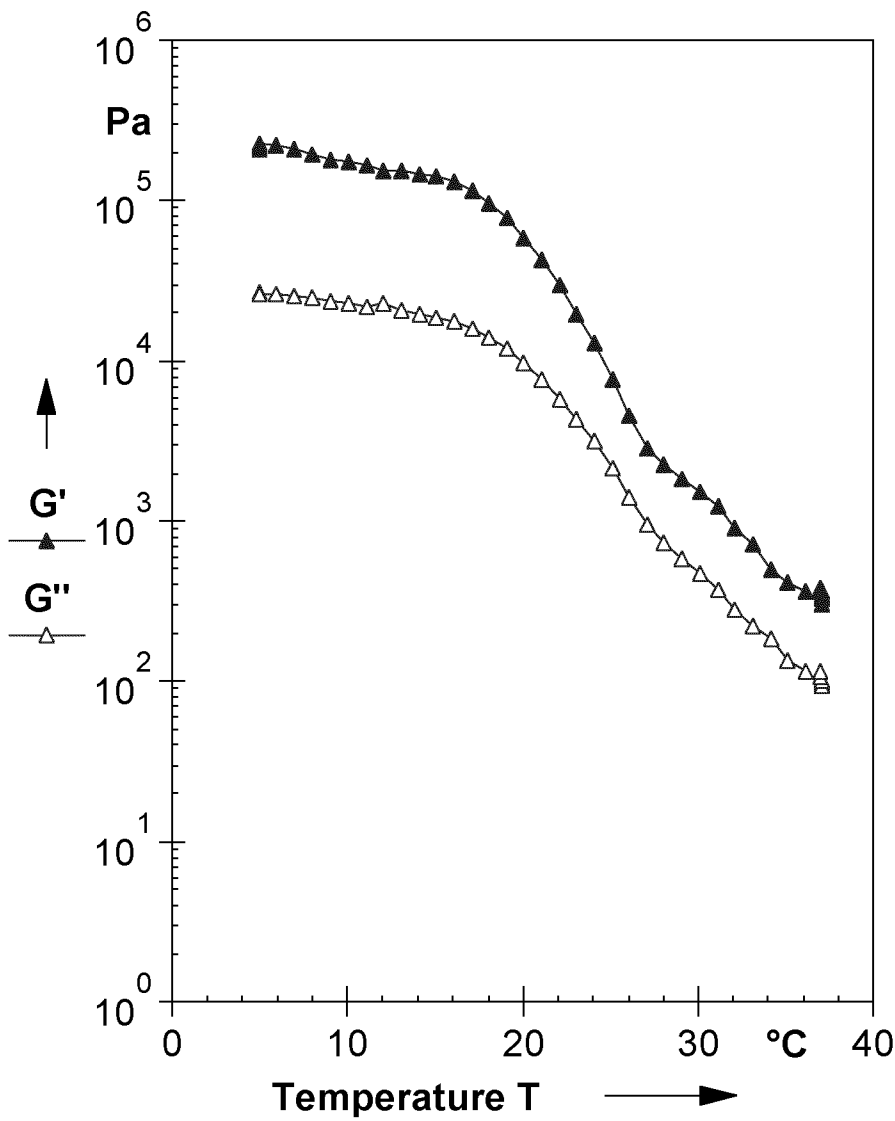


Figure 6

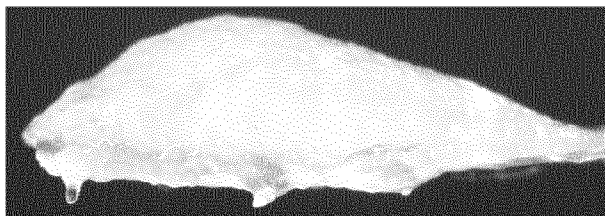


Figure 7

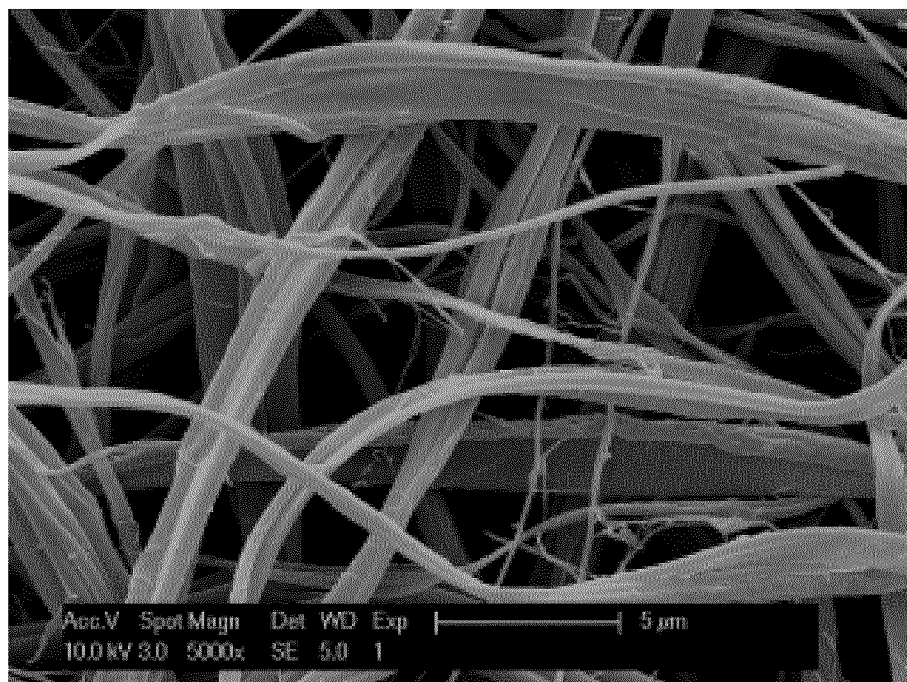


Figure 8

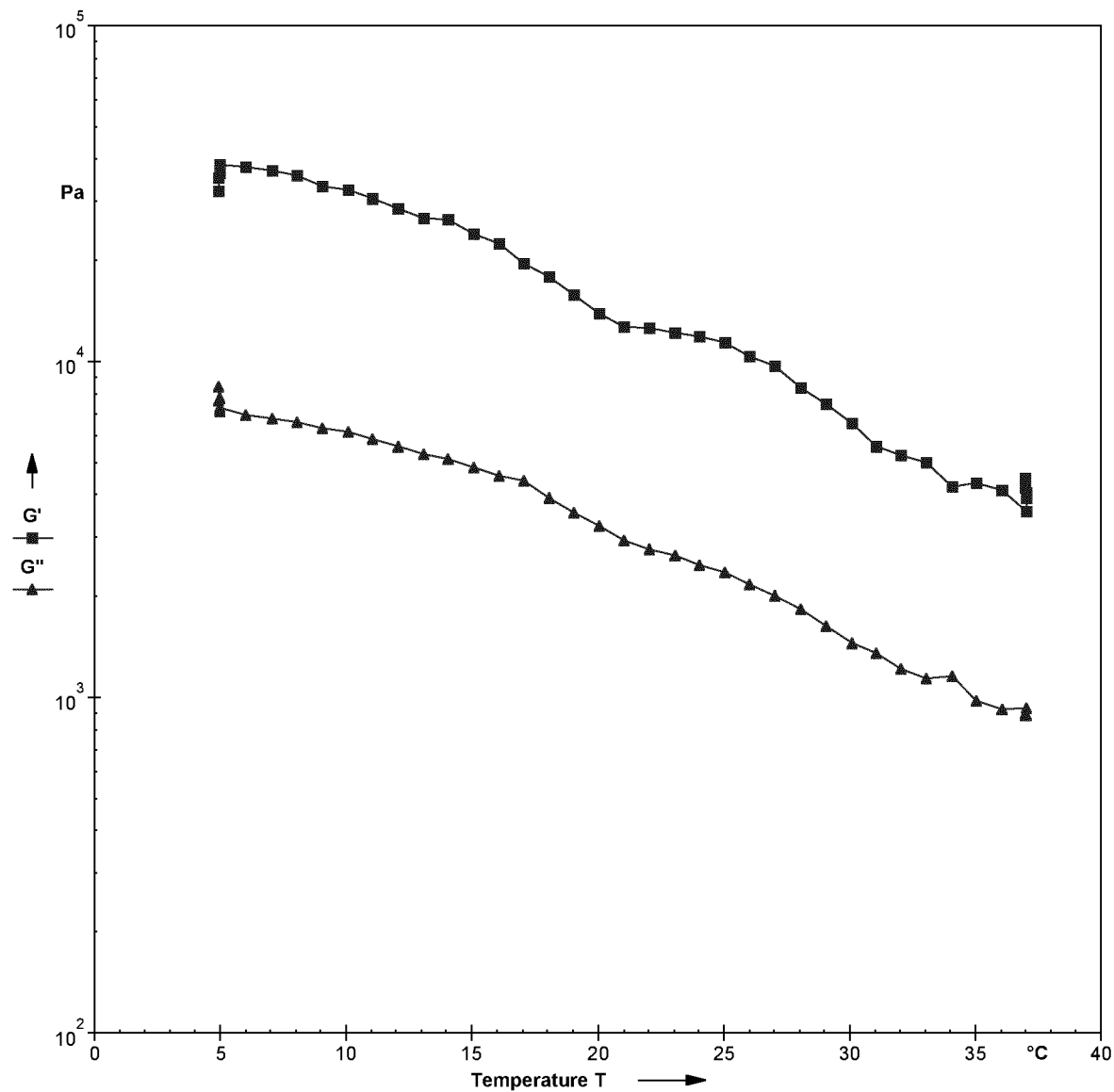


Figure 9

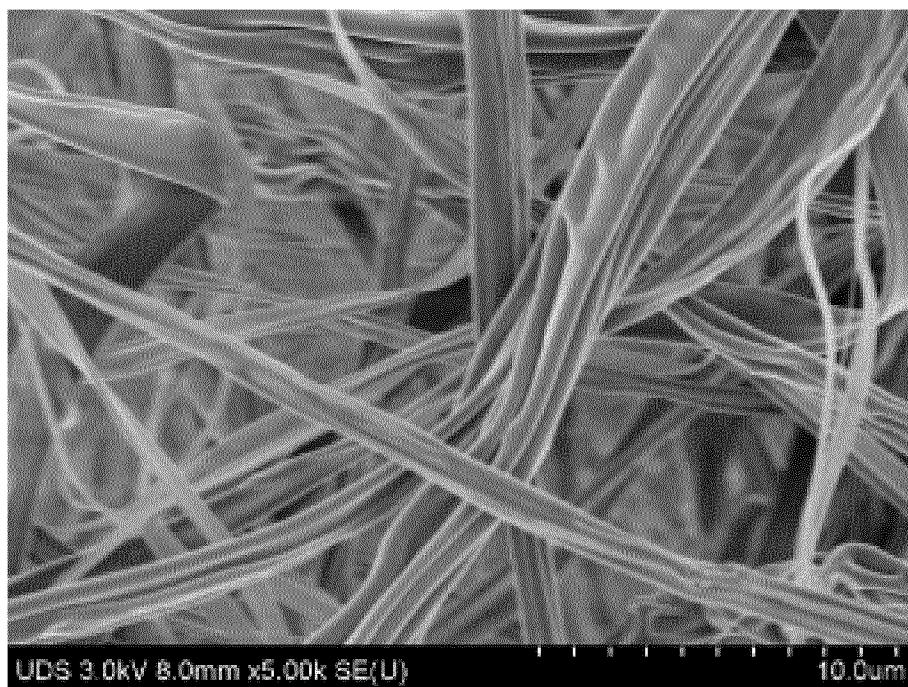


Figure 10

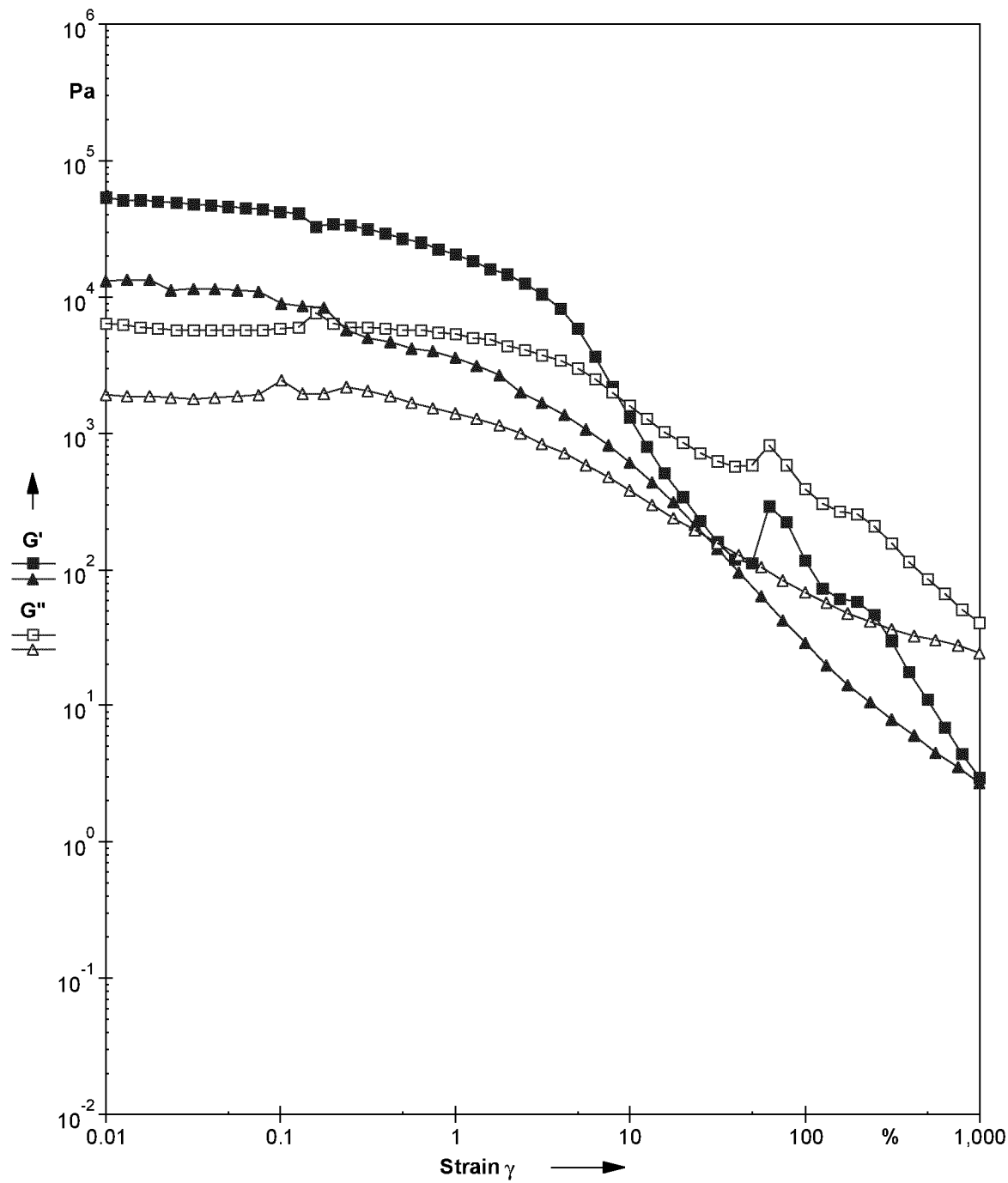


Figure 11

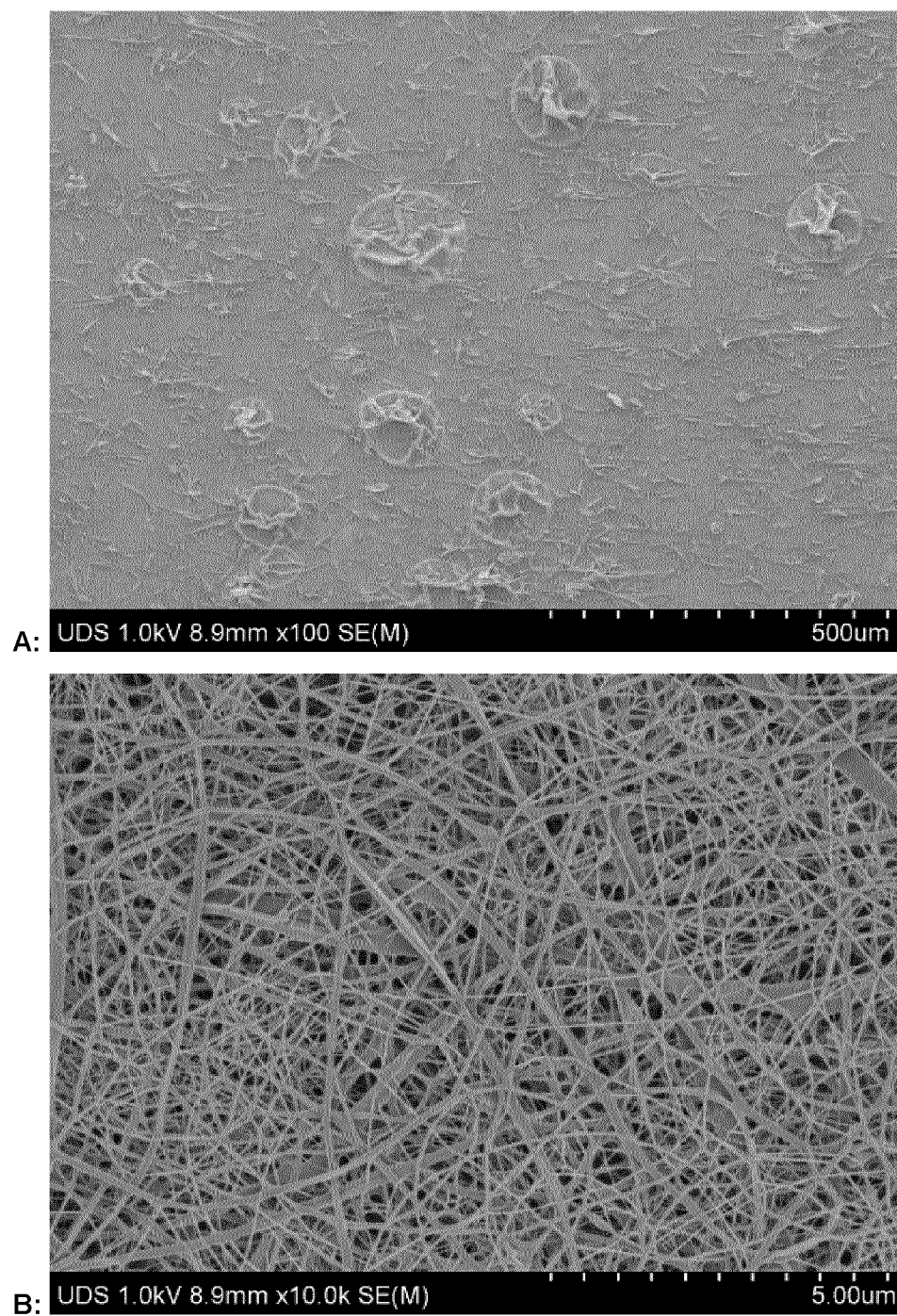


Figure 12

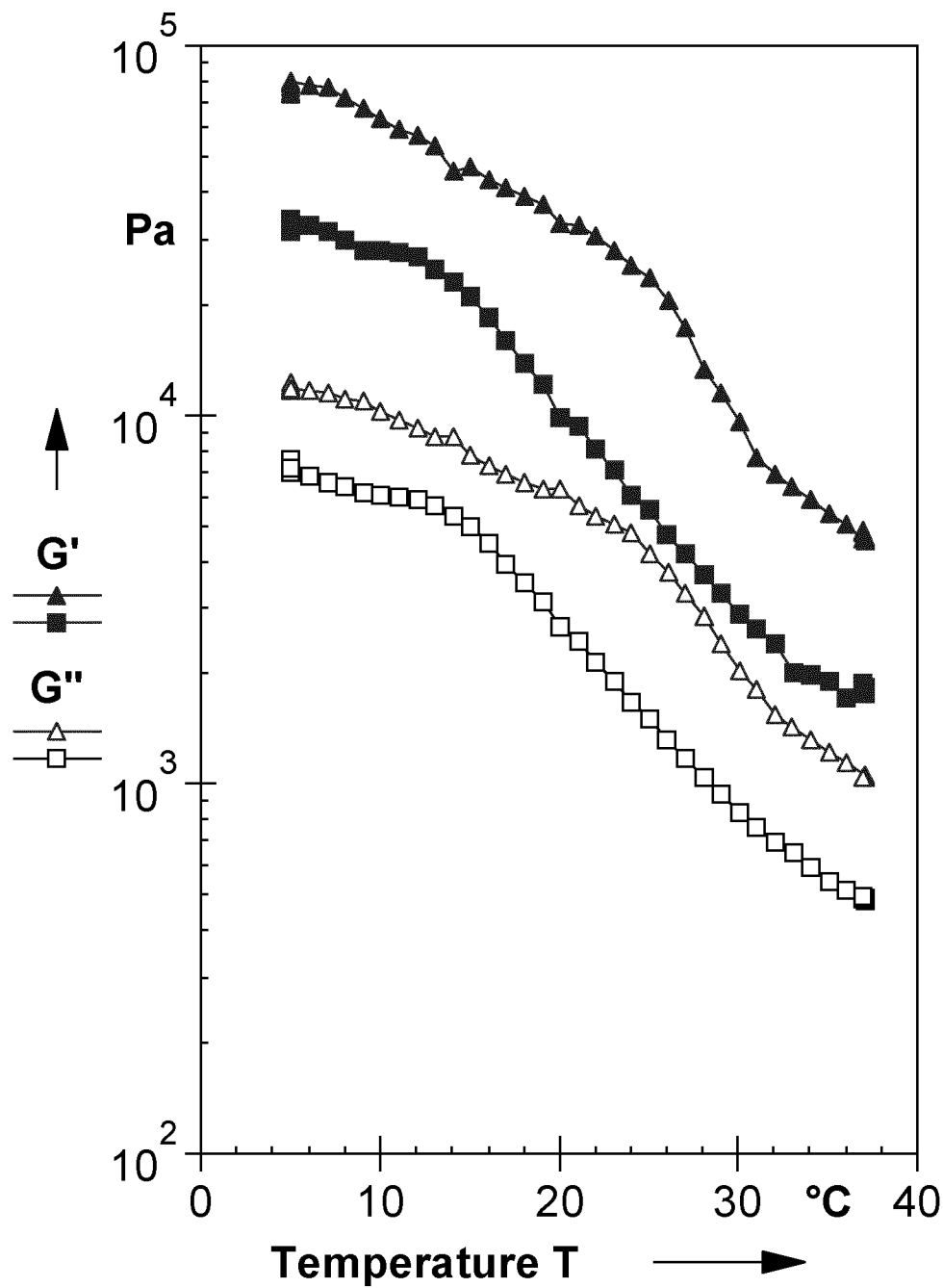
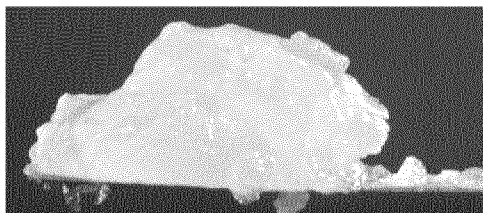


Figure 13



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/071409

A. CLASSIFICATION OF SUBJECT MATTER INV. A23L1/00 A23L1/0534 A23L1/10 A61K8/64 A61K8/73 A23D7/005 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 A61K 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 practical, search terms used) EPO-Internal, WPI Data																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>WO 2010/121492 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; UNILEVER HINDUSTAN [IN]; CAO JIAN) 28 October 2010 (2010-10-28)</td> <td>1,3,5-8, 12-15</td> </tr> <tr> <td>A</td> <td>page 6, line 25 - page 10, line 20; claims 1-15; examples 1-7</td> <td>9-11</td> </tr> <tr> <td>X</td> <td>EP 2 230 294 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 22 September 2010 (2010-09-22) cited in the application claims 1-15</td> <td>1,2,5</td> </tr> <tr> <td>X</td> <td>US 3 948 828 A (BECKER CARL ET AL) 6 April 1976 (1976-04-06) the whole document</td> <td>9</td> </tr> <tr> <td></td> <td style="text-align: center;">----- -/-</td> <td></td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	WO 2010/121492 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; UNILEVER HINDUSTAN [IN]; CAO JIAN) 28 October 2010 (2010-10-28)	1,3,5-8, 12-15	A	page 6, line 25 - page 10, line 20; claims 1-15; examples 1-7	9-11	X	EP 2 230 294 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 22 September 2010 (2010-09-22) cited in the application claims 1-15	1,2,5	X	US 3 948 828 A (BECKER CARL ET AL) 6 April 1976 (1976-04-06) the whole document	9		----- -/-	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
X	WO 2010/121492 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; UNILEVER HINDUSTAN [IN]; CAO JIAN) 28 October 2010 (2010-10-28)	1,3,5-8, 12-15																		
A	page 6, line 25 - page 10, line 20; claims 1-15; examples 1-7	9-11																		
X	EP 2 230 294 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 22 September 2010 (2010-09-22) cited in the application claims 1-15	1,2,5																		
X	US 3 948 828 A (BECKER CARL ET AL) 6 April 1976 (1976-04-06) the whole document	9																		
	----- -/-																			
☒ Further documents are listed in the continuation of Box C. ☒ 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 "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "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 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family																				
Date of the actual completion of the international search 16 March 2012		Date of mailing of the international search report 23/03/2012																		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Adechy, Miriam																		

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/071409

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/042829 A1 (MASSIA STEPHEN [US]; BOWEN BENJAMIN [US]; LOUIE KATHERINE [US]) 2 April 2009 (2009-04-02) cited in the application the whole document	1-14
A	----- US 2009/169682 A1 (OKUMURA FUMIO [JP] ET AL) 2 July 2009 (2009-07-02) the whole document -----	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/071409

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2010121492	A1	28-10-2010	NONE
EP 2230294	A1	22-09-2010	AT 542880 T 15-02-2012
		AT 544839 T 15-02-2012	
		AU 2006326717 A1 21-06-2007	
		AU 2010206086 A1 19-08-2010	
		BR PI0620521 A2 16-11-2011	
		CA 2632318 A1 21-06-2007	
		CN 101331218 A 24-12-2008	
		EP 1960501 A1 27-08-2008	
		EP 2230294 A1 22-09-2010	
		US 2009306223 A1 10-12-2009	
		WO 2007068344 A1 21-06-2007	
		ZA 200804379 A 30-09-2009	
US 3948828	A	06-04-1976	DE 2417921 A1 17-10-1974
			FR 2225488 A1 08-11-1974
			IT 1004219 B 10-07-1976
			JP 50009630 A 31-01-1975
			US 3948828 A 06-04-1976
WO 2009042829	A1	02-04-2009	NONE
US 2009169682	A1	02-07-2009	US 2009169682 A1 02-07-2009
			WO 2007043656 A1 19-04-2007