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(54) Title: IN SITU FUNCTIONALIZATION OF POLYSACCHARIDES AND COMPOSITIONS THEREOF

(57) Abstract: A process is disclosed herein comprising the step of contacting an esterifying agent and a polysaccharide in the presence of a solvent and suitable reaction conditions for a reaction time sufficient to form a product comprising a polysaccharide ester composition, wherein the polysaccharide ester composition comprises a polysaccharide ester having a degree of substitution of about 0.001 to about 3; wherein the esterifying agent comprises an acyl halide, a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester; and the ratio of esterifying agent to polysaccharide is in the range of about 0.001:1 to about 3:1 on a molar equivalent basis. In one embodiment, the polysaccharide comprises poly alpha-1,3-glucan.



TITLE

In Situ Functionalization of Polysaccharides and Compositions Thereof

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims priority to and the benefit of U.S. provisional application number 62/425313, titled "In Situ Functionalization of Polysaccharides and Compositions Thereof," filed November 22, 2016, the disclosure of which is incorporated by reference herein in its entirety.

FIELD OF THE DISCLOSURE

10 The field relates to processes for preparing functionalized polysaccharide compositions by in situ derivatization of polysaccharides generated in enzymatic polymerization processes. The functionalized polysaccharide compositions can be used with minimal additional processing steps in applications such as coatings, films, adhesives,
15 personal care products, and as a moisture management component of a composite or blend.

BACKGROUND

 Polysaccharides are an important class of polymers and can be used in many industries as structural water insoluble materials and as
20 water soluble polymers. Polysaccharide derivatives can be extracted through nature in low quantities such as xanthan and guar gums. The process and low quantity limits the applications into specialty applications, such as in rheology modifiers and personal care products. More abundant non-derivative polysaccharides such as cellulose and starch can be used
25 as starting material for derivatization but require extensive processing and high degrees of purification. Once the starting material is extracted, the polysaccharide typically requires an activation step that can include solution, alteration of crystalline state, reagent complexation prior to derivatization. The chemical derivatization often uses co-solvents and
30 salts to modify the solubility of the starting material and product such as in the typical acetylation processes.

Driven by a desire to find new structural polysaccharides using enzymatic syntheses or genetic engineering of microorganisms or plant hosts, researchers have discovered polysaccharides that are biodegradable, and that can be made economically from renewable resource-based feedstocks. An example of such a polysaccharide is poly alpha-1,3-glucan, a glucan polymer characterized by having alpha-1,3-glycosidic linkages. This polymer has been isolated by contacting an aqueous solution of sucrose with a glucosyltransferase enzyme isolated from *Streptococcus salivarius* (Simpson et al., *Microbiology* 141:1451-1460, 1995). Furthermore, polysaccharides of different linkages, content of primary and secondary hydroxyl, tuned molecular weight, branched and linear architecture, crystallinity, and solubility can be isolated and functionalized.

US Patent No. 9278,988 discloses poly alpha-1,3-glucan ester compounds and methods of making them. Published patent application WO 2017/003808 discloses poly alpha-1,3-glucan esters and methods of their preparation using cyclic organic acid anhydrides.

More convenient and more economical processes for functionalization of polysaccharides such as poly alpha-1,3-glucan continue to be sought.

SUMMARY

Disclosed herein are processes for the in situ preparation of polysaccharide ester compositions. In one embodiment a process is disclosed, the process comprising the step:

a) contacting an esterifying agent and a polysaccharide in the presence of a solvent and suitable reaction conditions for a reaction time sufficient to form a product comprising a polysaccharide ester composition, the polysaccharide ester composition comprising a polysaccharide ester compound having a degree of substitution of about 0.001 to about 3;

wherein the esterifying agent comprises an acyl halide, a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester; and

the ratio of esterifying agent to polysaccharide is in the range of
5 about 0.001:1 to about 3:1 on a molar equivalent basis.

In one embodiment, the esterifying agent comprises an acyl halide. In some embodiments, the acyl halide comprises acetyl chloride, benzoyl chloride, propanoyl chloride, hexanoyl chloride, acetyl bromide, benzoyl bromide, propanoyl bromide, acetyl iodide, benzoyl iodide, or propanoyl
10 iodide. In another embodiment, the esterifying agent comprises a phosphoryl halide. In yet another embodiment, the esterifying agent comprises a carboxylic acid anhydride. In another embodiment, the esterifying agent comprises a haloformic acid ester. In yet another embodiment, the esterifying agent comprises a carbonic acid ester. In a
15 further embodiment, the esterifying agent comprises a vinyl ester.

In some embodiments, the solvent comprises dimethylacetamide, dimethylformamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof. In one embodiment, the esterifying agent comprises an acyl halide, and the solvent is selected from
20 dimethylacetamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof. In another embodiment, the esterifying agent is a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester, and the solvent is selected from dimethylacetamide, dimethylformamide, tetrahydrofuran, acetonitrile,
25 acetone, methyl ethyl ketone, or a mixture thereof. In some embodiments, the suitable reaction conditions include a reaction temperature in the range of about 30 °C to about 175 °C. In some embodiments, the suitable reaction conditions include a reaction pressure of about atmospheric pressure, less than atmospheric pressure, or greater than atmospheric
30 pressure.

In one embodiment, the polysaccharide comprises poly alpha-1,3-glucan. In another embodiment, the polysaccharide comprises poly alpha-1,3-1,6-glucan. In still another embodiment, the polysaccharide comprises water insoluble alpha-(1,3-glucan) polymer having 90% or greater alpha-1,3-glycosidic linkages, less than 1% by weight of alpha-1,3,6-glycosidic branch points, and a number average degree of polymerization in the range of from 55 to 10,000. In one embodiment, the polysaccharide comprises dextran.

In some embodiments, the polysaccharide ester composition comprises a polysaccharide ester compound wherein at least one ester group comprises a C₂-C₂₀ acyl group. In some embodiments, the polysaccharide ester composition comprises a polysaccharide ester compound having a degree of substitution of about 0.1 to about 1.5, or about 0.3 to about 1.5.

In one embodiment, the step a) contacting an esterifying agent with a polysaccharide in the presence of a solvent further comprises the steps of:

- i) contacting the polysaccharide and the solvent to form an initial mixture comprising water;
- ii) heating the initial mixture;
- iii) removing at least a portion of the water from the initial mixture under reduced pressure to obtain a mixture comprising a reduced water content; and
- iv) adding the esterifying agent to the mixture comprising a reduced water content.

In another embodiment, the process further comprises a step of removing at least a portion of the byproduct acid halide formed in the contacting step a).

In another embodiment, the process further comprises a step of combining the product comprising a polysaccharide ester composition with a polymer dispersed in or dissolved in a second solvent to form a blend of

the polysaccharide ester composition and the polymer. In some
embodiments, the process further comprises a step of casting a film from
the blend. In other embodiments, the process further comprises a step of
coating a substrate with the blend. In another embodiment, the process
5 further comprises a step of spinning fibers from the blend.

Another embodiment relates to a polysaccharide ester composition
obtained by the processes disclosed herein.

DETAILED DESCRIPTION

All patents, patent applications, and publications cited herein are
10 incorporated herein by reference in their entirety.

As used herein, the term “embodiment” or “disclosure” is not meant
to be limiting, but applies generally to any of the embodiments defined in
the claims or described herein. These terms are used interchangeably
herein.

15 In this disclosure, a number of terms and abbreviations are used.
The following definitions apply unless specifically stated otherwise.

The articles “a”, “an”, and “the” preceding an element or component
are intended to be nonrestrictive regarding the number of instances (i.e.,
occurrences) of the element or component. Therefore “a”, “an”, and “the”
20 should be read to include one or at least one, and the singular word form
of the element or component also includes the plural unless the number is
obviously meant to be singular.

The term “comprising” means the presence of the stated features,
integers, steps, or components as referred to in the claims, but that it does
25 not preclude the presence or addition of one or more other features,
integers, steps, components or groups thereof. The term “comprising” is
intended to include embodiments encompassed by the terms “consisting
essentially of” and “consisting of”. Similarly, the term “consisting
essentially of” is intended to include embodiments encompassed by the
30 term “consisting of”.

Where present, all ranges are inclusive and combinable. For example, when a range of "1 to 5" is recited, the recited range should be construed as including ranges "1 to 4", "1 to 3", "1-2", "1-2 & 4-5", "1-3 & 5", and the like.

5 As used herein in connection with a numerical value, the term "about" refers to a range of +/- 0.5 of the numerical value, unless the term is otherwise specifically defined in context. For instance, the phrase a "pH value of about 6" refers to pH values of from 5.5 to 6.5, unless the pH value is specifically defined otherwise.

10 It is intended that every maximum numerical limitation given throughout this Specification includes every lower numerical limitation, as if such lower numerical limitations were expressly written herein. Every minimum numerical limitation given throughout this Specification will include every higher numerical limitation, as if such higher numerical
15 limitations were expressly written herein. Every numerical range given throughout this Specification will include every narrower numerical range that falls within such broader numerical range, as if such narrower numerical ranges were all expressly written herein.

 The features and advantages of the present disclosure will be more
20 readily understood, by those of ordinary skill in the art from reading the following detailed description. It is to be appreciated that certain features of the disclosure, which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single element. Conversely, various features of the disclosure that are,
25 for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination.

 The use of numerical values in the various ranges specified in this application, unless expressly indicated otherwise, are stated as approximations as though the minimum and maximum values within the
30 stated ranges were both preceded by the word "about". In this manner, slight variations above and below the stated ranges can be used to

achieve substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including each and every value between the minimum and maximum values.

As used herein:

5 The terms “percent by volume”, “volume percent”, “vol%” and “v/v %” are used interchangeably herein. The percent by volume of a solute in a solution can be determined using the formula: $[(\text{volume of solute})/(\text{volume of solution})] \times 100\%$.

10 The terms “percent by weight”, “weight percentage (wt%)” and “weight-weight percentage (% w/w)” are used interchangeably herein. Percent by weight refers to the percentage of a material on a mass basis as it is comprised in a composition, mixture or solution.

The term “esterifying agent” refers to any compound that can react with another compound to form an ester as the reaction product.

15 Esterification is the general name for a chemical reaction in which two reactants, typically an alcohol and an acid, form an ester as the reaction product.

20 As used herein, the term “polysaccharide” means a polymeric carbohydrate molecule composed of long chains of monosaccharide units bound together by glycosidic linkages and on hydrolysis give the constituent monosaccharides or oligosaccharides.

25 The terms “increased”, “enhanced” and “improved” are used interchangeably herein. These terms may refer to, for example, a quantity or activity that is at least 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%, 125%, 150%, 175%, or 200% (or any integer between 1% and 200%) more than the quantity or activity for which the increased quantity or activity is being compared.

30 The phrase “water insoluble” means that less than 5 grams of the substance, for example, the alpha-(1,3-glucan) polymer, dissolves in 100 milliliters of water at 23°C. In other embodiments, water insoluble means

that less than 4 grams or 3 grams or 2 grams or 1 grams of the substance is dissolved in water at 23°C.

As used herein, “weight average molecular weight” or “ M_w ” is calculated as

- 5 $M_w = \sum N_i M_i^2 / \sum N_i M_i$; where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. The weight average molecular weight can be determined by techniques such as static light scattering, gas chromatography (GC), high pressure liquid chromatography (HPLC), gel permeation chromatography (GPC), small
10 angle neutron scattering, X-ray scattering, and sedimentation velocity.

- As used herein, “number average molecular weight” or “ M_n ” refers to the statistical average molecular weight of all the polymer chains in a sample. The number average molecular weight is calculated as $M_n = \sum N_i M_i / \sum N_i$ where M_i is the molecular weight of a chain and N_i is the number of
15 chains of that molecular weight. The number average molecular weight of a polymer can be determined by techniques such as gel permeation chromatography, viscometry via the (Mark-Houwink equation), and colligative methods such as vapor pressure osmometry, end-group determination, or proton NMR.

- 20 The term “fabric”, as used herein, refers to a multilayer construction of fibers or yarns.

- The term “fiber” as used herein refers to an elongate body the length dimension of which is much greater than the transverse dimensions of width and thickness. Accordingly, the term fiber includes monofilament
25 fiber, multifilament fiber, ribbon, strip, a plurality of any one or combinations thereof and the like having regular or irregular cross-section.

The term “yarn” as used herein refers to a continuous strand of fibers.

- The term “textile” as used herein refers to garments and other
30 articles fabricated from fibers, yarns, or fabrics when the products retain the characteristic flexibility and drape of the original fabrics.

The present disclosure is directed to a process for preparing in situ a polysaccharide ester composition comprising a polysaccharide ester compound having a degree of substitution of about 0.001 to about 3. The
5 process comprises the step:

a) contacting an esterifying agent and a polysaccharide in the presence of a solvent and suitable reaction conditions for a reaction time sufficient to form a product comprising a polysaccharide ester composition, the polysaccharide ester composition comprising a polysaccharide ester
10 compound having a degree of substitution of about 0.001 to about 3;

wherein the esterifying agent comprises an acyl halide, a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester; and

the ratio of esterifying agent to polysaccharide is in the range of
15 about 0.001:1 to about 3:1 molar equivalents.

An advantage of the in situ preparation of polysaccharide ester compositions is the ability to use the material in a further processing step without the need to isolate the esterified polysaccharide from the reaction mixture, or from the solvent. In this way, polysaccharide ester
20 compositions can be combined with other polymers to form a blend, and the blend can be used for various applications, including forming films, coating substrates, spinning fibers comprising the blend of polymer and esterified polysaccharide, and other applications. Additionally, the in situ prepared polysaccharide ester compositions can be used as rheology
25 modifiers, as water absorbents, or as a moisture management component of a composite or blend.

The process comprises contacting an esterifying agent and a polysaccharide in the presence of a solvent and suitable reaction conditions to form a product comprising a polysaccharide ester
30 composition, the polysaccharide ester composition comprising a polysaccharide ester compound having a degree of substitution of about

0.001 to about 3. The degree of substitution of about 0.001 to about 3.0 also encompasses 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8 and 2.9, as well as 0.001 and 3 and any value in
5 between 0.001 and 3..

In one embodiment, the esterifying agent comprises an acyl halide, a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester; or a vinyl ester. Mixtures of these may also be used. The ratio of the esterifying agent to the polysaccharide determines the
10 degree of substitution (DoS) of the polysaccharide ester composition, with higher ratios providing higher DoS of the product, as described herein below.

In one embodiment, the esterifying agent comprises an acyl halide. Suitable acyl halides include acyl chlorides, acyl bromides, acyl iodides,
15 and mixtures thereof. Useful acyl chlorides include acetyl chloride, benzoyl chloride, propanoyl chloride, butanoyl chloride, pentanoyl chloride, hexanoyl chloride, heptanoyl chloride, octanoyl chloride, nonanoyl chloride, decanoyl chloride, undecanoyl chloride, dodecanoyl chloride, lauryl chloride, and branched isomers thereof. In one embodiment, the
20 acyl halide comprises acetyl chloride, benzoyl chloride, propanoyl chloride, hexanoyl chloride, acetyl bromide, benzoyl bromide, propanoyl bromide, acetyl iodide, benzoyl iodide, or propanoyl iodide. In one embodiment, the acyl halide comprises acetyl chloride. In one embodiment, the acyl halide comprises benzoyl chloride. In one embodiment, the acyl halide
25 comprises propanoyl halide. In one embodiment, the acyl halide comprises lauryl chloride. Acyl halides can be obtained commercially or prepared by known methods.

In one embodiment, the esterifying agent comprises a phosphoryl halide. Useful phosphoryl halides include phosphoryl chlorides and
30 phosphoryl bromides. Suitable phosphoryl halides include those having the structural formula $P(O)(OR)(OR')X$, wherein R and R' can be the same

or different from each other and are independently selected from C₁-C₈ alkyl or C₆-C₁₀ aryl radical, and X is Cl, Br, or I. In one embodiment, the phosphoryl halide comprises diphenyl phosphoryl chloride, diethyl phosphoryl chloride, or diisopropyl phosphoryl chloride. Phosphoryl

5 halides can be obtained commercially or prepared by known methods.

In one embodiment, the esterifying agent comprises a carboxylic acid anhydride. Suitable anhydrides include alkyl anhydrides, cyclic anhydrides, and aromatic anhydrides. The anhydrides can comprise from three to twelve carbon atoms and may be optionally substituted with alkyl

10 substituents. Examples of suitable carboxylic acid anhydrides include acetic anhydride, propionic anhydride, benzoic anhydride, maleic anhydride, succinic anhydride, and glutaric anhydride. In one embodiment, the carboxylic acid anhydride comprises maleic anhydride.

In one embodiment, the carboxylic acid anhydride comprises acetic

15 anhydride. In one embodiment, the carboxylic acid anhydride comprises propionic anhydride. In one embodiment, the carboxylic acid anhydride comprises benzoic anhydride. Carboxylic acid anhydrides can be obtained commercially or prepared using known methods.

In one embodiment, the esterifying agent comprises a haloformic acid ester. Suitable haloformic acid esters include phenyl fluoroformate, phenyl chloroformate, and p-NO₂-phenyl chloroformate. Haloformic acid esters can be obtained commercially or prepared using known methods.

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In one embodiment, the esterifying agent comprises a carbonic acid ester. Suitable carbonic acid esters include chlorocarbonic acid ethyl ester, chlorocarbonic acid methyl ester, and chlorocarbonic acid propyl ester. Carbonic acid esters can be obtained commercially or prepared using known methods.

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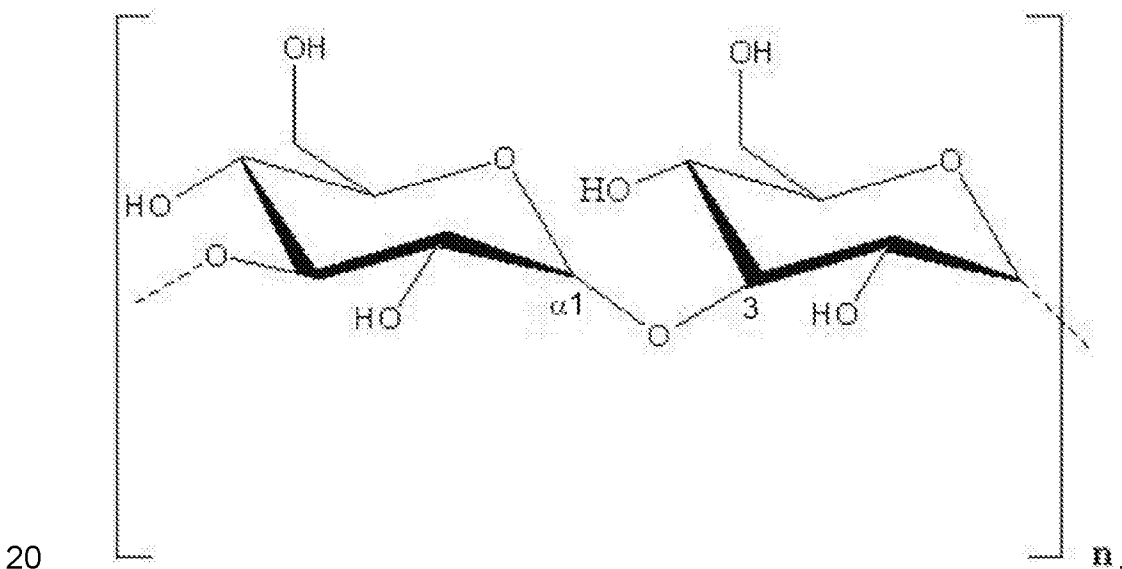
In another embodiment, the esterifying agent comprises a vinyl ester. Suitable vinyl esters include, for example, vinyl acetate, vinyl benzoate, vinyl 4-tert-butylbenzoate, vinyl chloroformate, vinyl cinnamate,

30 vinyl decanoate, vinyl neodecanoate, vinyl neononanoate, vinyl pivalate,

vinyl propionate, vinyl stearate, vinyl trifluoroacetate, and vinyl valerate. In one embodiment, the vinyl ester comprises vinyl acetate. In another embodiment, the vinyl ester comprises vinyl benzoate. Vinyl esters can be obtained commercially or prepared using known methods.

5 In the processes discloses herein, polysaccharides including poly alpha-1,3-glucan; poly alpha-1,3-1,6-glucan; water insoluble alpha-(1,3-glucan) polymer having 90% or greater alpha-1,3-glycosidic linkages, less than 1% by weight of alpha-1,3,6-glycosidic branch points, and a number average degree of polymerization in the range of from 55 to 10,000; and
10 dextran can be used. Mixtures of these polysaccharides can also be used.

In one embodiment, the polysaccharide comprises poly alpha-1,3-glucan. The terms "poly alpha-1,3-glucan", "alpha-1,3-glucan polymer" and "glucan polymer" are used interchangeably herein. The term "glucan" herein refers to a polysaccharide of D-glucose monomers that are linked
15 by glycosidic linkages. Poly alpha-1,3-glucan is a polymer comprising glucose monomeric units linked together by glycosidic linkages, wherein at least 50% of the glycosidic linkages are alpha-1,3-glycosidic linkages. Poly alpha-1,3-glucan is a type of polysaccharide. The structure of poly alpha-1,3-glucan can be illustrated as follows:



The poly alpha-1,3-glucan can be prepared using chemical methods, or it can be prepared by extracting it from various organisms, such as fungi, that produce poly alpha-1,3-glucan. Alternatively, poly alpha-1,3-glucan can be enzymatically produced from sucrose using one or more glucosyltransferase (gtf) enzymes, as described in U.S. Patent Nos. 7,000,000; 8,642,757; and 9,080,195, for example. Using the procedures given therein, the polymer is made directly in a one-step enzymatic reaction using a recombinant glucosyltransferase enzyme, for example the gtfJ enzyme, as the catalyst and sucrose as the substrate.

10 The poly alpha-1,3-glucan is produced with fructose as the by-product. As the reaction progresses, the poly alpha-1,3-glucan precipitates from solution.

The process to produce poly alpha-1,3-glucan from sucrose using, for example, a glucosyl transferase enzyme, can result in a slurry of the poly alpha-1,3-glucan in water. The slurry can be filtered to remove some of the water, giving the solid poly alpha-1,3-glucan as a wet cake containing in the range of from 30 to 50 percent by weight of poly alpha-1,3-glucan, with the remainder being water. In some embodiments, the wet cake comprises in the range of from 35 to 45 percent by weight of the poly alpha-1,3-glucan. The wet cake can be washed with water to remove any water soluble impurities, for example, sucrose, fructose, or phosphate buffers. In some embodiments, the wet cake comprising the poly alpha-1,3-glucan can be used as is. In other embodiments, the wet cake can be further dried, for example under atmospheric or reduced pressure, at elevated temperature, by freeze drying, or a combination thereof, to give a powder comprising greater than or equal to 50 percent by weight of the poly alpha-1,3-glucan. In some embodiments, the poly alpha-1,3-glucan can be a powder, comprising less than or equal to 20 percent by weight water. In other embodiments, the poly alpha-1,3-glucan can be a dry powder comprising less than or equal to 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, or 1 percent by weight water.

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In some embodiments, the percentage of glycosidic linkages between the glucose monomer units of the poly alpha-1,3-glucan that are alpha-1,3 is greater than or equal to 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, or 100% (or any integer value between 50% and 100%). In such embodiments, accordingly, poly alpha-1,3-glucan has less than or equal to 50%, 40%, 30%, 20%, 10%, 5%, 4%, 3%, 2%, 1%, or 0% (or any integer value between 0% and 50%) of glycosidic linkages that are not alpha-1,3.

The terms “glycosidic linkage” and “glycosidic bond” are used interchangeably herein and refer to the type of covalent bond that joins a carbohydrate (sugar) molecule to another group such as another carbohydrate. The term “alpha-1,3-glycosidic linkage” as used herein refers to the type of covalent bond that joins alpha-D-glucose molecules to each other through carbons 1 and 3 on adjacent alpha-D-glucose rings. This linkage is illustrated in the poly alpha-1,3-glucan structure provided above. Herein, “alpha-D-glucose” will be referred to as “glucose”. All glycosidic linkages disclosed herein are alpha-glycosidic linkages, except where otherwise noted.

The “molecular weight” of poly alpha-1,3-glucan can be represented as number-average molecular weight (M_n) or as weight-average molecular weight (M_w). Alternatively, molecular weight can be represented as Daltons, grams/mole, DP_w (weight average degree of polymerization), or DP_n (number average degree of polymerization). Various means are known in the art for calculating these molecular weight measurements, such as high-pressure liquid chromatography (HPLC), size exclusion chromatography (SEC), or gel permeation chromatography (GPC).

The poly alpha-1,3-glucan may have a weight average degree of polymerisation (DP_w) of at least about 400. In some embodiments, the poly alpha-1,3-glucan has a DP_w of from about 400 to about 1400, or from about 400 to about 1000, or from about 500 to about 900.

The poly alpha-1,3-glucan used to produce poly alpha-1,3-glucan ester compositions as described herein is preferably linear/unbranched. In certain embodiments, poly alpha-1,3-glucan has no branch points or less than about 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, or 1% branch points as a percent of the glycosidic linkages in the polymer. Examples of branch points include alpha-1,6 branch points, such as those present in mutan polymer.

The M_n or M_w of poly alpha-1,3-glucan used to prepare poly alpha-1,3-glucan ester compositions as described herein may be at least about 500 to about 300000. Alternatively, M_n or M_w can be at least about 10000, 25000, 50000, 75000, 100000, 125000, 150000, 175000, 200000, 225000, 250000, 275000, or 300000 (or any integer between 10000 and 300000), for example.

The poly alpha-1,3-glucan can be used as a dry powder, for example, containing less than 5% by weight of water, or in other embodiments, the poly alpha-1,3-glucan can be used a wet cake, containing greater than 5% by weight of water. Depending on the amount of water contained in the glucan, sufficient esterifying agent in excess of that required for the desired degree of substitution in the product polysaccharide ester composition can be used in the contacting step, or the water can be removed before the esterifying agent is added. Water content of the glucan can be determined by methods known in the art, for example by using an automatic moisture analyzer by weight difference.

In one embodiment, the polysaccharide comprises water insoluble alpha-(1,3-glucan) polymer having 90% or greater α -1,3-glycosidic linkages, less than 1% by weight of alpha-1,3,6-glycosidic branch points, and a number average degree of polymerization in the range of from 55 to 10,000.

The phrase "alpha-(1,3-glucan) polymer" means a polysaccharide comprising glucose monomer units linked together by glycosidic linkages wherein at least 50% of the glycosidic linkages are α -1,3-glycosidic

linkages. In other embodiments, the percentage of α -1,3-glycosidic linkages can be greater than or equal to 90%, 95%, 96%, 97%, 98%, 99% or 100% (or any integer value between 50% and 100%). Accordingly, the α -(1,3 $\rightarrow$ glucan) polymer comprises less than or equal to 10%, 5%, 4%,
5 3%, 2%, 1% or 0% of glycosidic linkages that are not α -1,3-glycosidic linkages. The α -(1,3 $\rightarrow$ glucan) polymer also has a number average degree of polymerization in the range of from 55 to 10,000.

In one embodiment, the polysaccharide is poly alpha-1,3-1,6-glucan. In one embodiment, the polysaccharide comprises poly alpha-1,3-
10 1,6-glucan wherein (i) at least 30% of the glycosidic linkages of the poly alpha-1,3-1,6-glucan are alpha-1,3 linkages, (ii) at least 30% of the glycosidic linkages of the poly alpha-1,3-1,6-glucan are alpha-1,6 linkages, (iii) the poly alpha-1,3-1,6-glucan has a weight average degree of polymerization (DP_w) of at least 1000; and (iv) the alpha-1,3 linkages and
15 alpha-1,6 linkages of the poly alpha-1,3-1,6-glucan do not consecutively alternate with each other. In another embodiment, at least 60% of the glycosidic linkages of the poly alpha-1,3-1,6-glucan are alpha-1,6 linkages. The term "alpha-1,6-glycosidic linkage" as used herein refers to the covalent bond that joins alpha-D-glucose molecules to each other through
20 carbons 1 and 6 on adjacent alpha-D-glucose rings.

Poly alpha-1,3-1,6-glucan is a product of a glucosyltransferase enzyme, as disclosed in United States Patent Application Publication 2015/0232785 A1.

The glycosidic linkage profile of a poly alpha-1,3-1,6-glucan herein
25 can be determined using any method known in the art. For example, a linkage profile can be determined using methods that use nuclear magnetic resonance (NMR) spectroscopy (e.g., ^{13}C NMR or ^1H NMR). These and other methods that can be used are disclosed in Food Carbohydrates: Chemistry, Physical Properties, and Applications (S. W. Cui, Ed., Chapter 3, S. W. Cui, Structural Analysis of Polysaccharides,
30

Taylor & Francis Group LLC, Boca Raton, FL, 2005), which is incorporated herein by reference.

The terms "poly alpha-1,3-1,6-glucan" and "alpha-1,3-1,6-glucan polymer" are used interchangeably herein (note that the order of the linkage denotations "1,3" and "1,6" in these terms is of no moment). Poly alpha-1,3-1,6-glucan herein is a polymer comprising glucose monomeric units linked together by glycosidic linkages (i.e., glucosidic linkages), wherein at least about 30% of the glycosidic linkages are alpha-1,3-glycosidic linkages, and at least about 30% of the glycosidic linkages are alpha-1,6-glycosidic linkages. Poly alpha-1,3-1,6-glucan is a type of polysaccharide containing a mixed glycosidic linkage content. The meaning of the term poly alpha-1,3-1,6-glucan in certain embodiments herein excludes "alternan," which is a glucan containing alpha-1,3 linkages and alpha-1,6 linkages that consecutively alternate with each other (U.S. Pat. No. 5702942, U.S. Pat. Appl. Publ. No. 2006/0127328). Alpha-1,3 and alpha-1,6 linkages that "consecutively alternate" with each other can be visually represented by ...G-1,3-G-1,6-G-1,3-G-1,6-G-1,3-G-1,6-G-1,3-G-..., for example, where G represents glucose.

The "molecular weight" of a poly alpha-1,3-1,6-glucan herein can be represented as number-average molecular weight (M_n) or as weight-average molecular weight (M_w). Alternatively, molecular weight can be represented as Daltons, grams/mole, DP_w (weight average degree of polymerization), or DP_n (number average degree of polymerization). Various means are known in the art for calculating these molecular weight measurements such as with high-pressure liquid chromatography (HPLC), size exclusion chromatography (SEC), or gel permeation chromatography (GPC).

The term "poly alpha-1,3-1,6-glucan wet cake" herein refers to poly alpha-1,3-1,6-glucan that has been separated from a slurry and washed with water or an aqueous solution. Poly alpha-1,3-1,6-glucan is not completely dried when preparing a wet cake. Depending on the amount of

water contained in the glucan, sufficient esterifying agent in excess of that required for the desired degree of substitution in the product polysaccharide ester composition can be used in the contacting step, or the water can be removed before the esterifying agent is added.

5 An "aqueous composition" herein refers to a solution or mixture in which the solvent is at least about 20 wt% water, for example, and which comprises poly alpha-1,3-1,6-glucan. Examples of aqueous compositions herein are aqueous solutions and hydrocolloids.

In some embodiments:

- 10 (i) at least 30% of the glycosidic linkages of the poly alpha-1,3-1,6-glucan are alpha-1,3 linkages,
- (ii) at least 30% of the glycosidic linkages of the poly alpha-1,3-1,6-glucan are alpha-1,6 linkages,
- (iii) the poly alpha-1,3-1,6-glucan has a weight average degree of
- 15 polymerization (DP_w) of at least 1000; and
- (iv) the alpha-1,3 linkages and alpha-1,6 linkages of the poly alpha-1,3-1,6-glucan do not consecutively alternate with each other.

At least 30% of the glycosidic linkages of poly alpha-1,3-1,6-glucan are alpha-1,3 linkages, and at least 30% of the glycosidic linkages of the

20 poly alpha-1,3-1,6-glucan are alpha-1,6 linkages. Alternatively, the percentage of alpha-1,3 linkages in poly alpha-1,3-1,6-glucan herein can be at least 31%, 32%, 33%, 34%, 35%, 36%, 37%, 38%, 39%, 40%, 41%, 42%, 43%, 44%, 45%, 46%, 47%, 48%, 49%, 50%, 51%, 52%, 53%, 54%, 55%, 56%, 57%, 58%, 59%, 60%, 61%, 62%, 63%, or 64%. Alternatively

25 still, the percentage of alpha-1,6 linkages in poly alpha-1,3-1,6-glucan herein can be at least 31%, 32%, 33%, 34%, 35%, 36%, 37%, 38%, 39%, 40%, 41%, 42%, 43%, 44%, 45%, 46%, 47%, 48%, 49%, 50%, 51%, 52%, 53%, 54%, 55%, 56%, 57%, 58%, 59%, 60%, 61%, 62%, 63%, 64%, 65%, 66%, 67%, 68%, or 69%.

30 A poly alpha-1,3-1,6-glucan can have any one the aforementioned percentages of alpha-1,3 linkages and any one of the aforementioned

percentages of alpha-1,6 linkages, just so long that the total of the percentages is not greater than 100%. For example, poly alpha-1,3-1,6-glucan herein can have (i) any one of 30%, 31%, 32%, 33%, 34%, 35%, 36%, 37%, 38%, 39%, or 40% (30%-40%) alpha-1,3 linkages and (ii) any
 5 one of 60%, 61%, 62%, 63%, 64%, 65%, 66%, 67%, 68%, or 69% (60%-69%) alpha-1,6 linkages, just so long that the total of the percentages is not greater than 100%. Non-limiting examples include poly alpha-1,3-1,6-glucan with 31% alpha-1,3 linkages and 67% alpha-1,6 linkages. In certain embodiments, at least 60% of the glycosidic linkages of the poly
 10 alpha-1,3-1,6-glucan are alpha-1,6 linkages.

A poly alpha-1,3-1,6-glucan can have, for example, less than 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, or 1% of glycosidic linkages other than alpha-1,3 and alpha-1,6. In another embodiment, a poly alpha-1,3-1,6-glucan only has alpha-1,3 and alpha-1,6 linkages.

15 Other examples of alpha-1,3 and alpha-1,6 linkage profiles and methods for their product are disclosed in published United States patent application 2015/0232785. The linkages and DP_w of Glucan produced by various Gtf Enzymes, as disclosed in US 2015/0232785, are listed in Table 1.

20

Table 1
Linkages and DP_w of Glucan Produced by Various Gtf Enzymes

Gtf	Glucan Alpha Linkages		DP _w
	% 1,3	% 1,6	
4297	31	67	10540
3298	50	50	1235
0544	62	36	3815
5618	34	66	3810
2379	37	63	1640

The backbone of a poly alpha-1,3-1,6-glucan disclosed herein can be linear/unbranched. Alternatively, there can be branches in the poly alpha-1,3-1,6-glucan. A poly alpha-1,3-1,6-glucan in certain embodiments can thus have no branch points or less than about 30%, 29%, 28%, 27%,
5 26%, 25%, 24%, 23%, 22%, 21%, 20%, 19%, 18%, 17%, 16%, 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, or 1% branch points as a percent of the glycosidic linkages in the polymer.

The alpha-1,3 linkages and alpha-1,6 linkages of a poly alpha-1,3-1,6-glucan do not consecutively alternate with each other. For the
10 following discussion, consider that ...G-1,3-G-1,6-G-1,3-G-1,6-G-1,3-G-... (where G represents glucose) represents a stretch of six glucose monomeric units linked by consecutively alternating alpha-1,3 linkages and alpha-1,6 linkages. Poly alpha-1,3-1,6-glucan in certain embodiments herein comprises less than 2, 3, 4, 5, 6, 7, 8, 9, 10, or more glucose
15 monomeric units that are linked consecutively with alternating alpha-1,3 and alpha-1,6 linkages.

The molecular weight of a poly alpha-1,3-1,6-glucan can be measured as DP_w (weight average degree of polymerization) or DP_n (number average degree of polymerization). Alternatively, molecular
20 weight can be measured in Daltons or grams/mole. It may also be useful to refer to the number-average molecular weight (M_n) or weight-average molecular weight (M_w) of the poly alpha-1,3-1,6-glucan.

A poly alpha-1,3-1,6-glucan can have a DP_w of at least about 1000. For example, the DP_w of the poly alpha-1,3-1,6-glucan can be at least
25 about 10000. Alternatively, the DP_w can be at least about 1000 to about 15000. Alternatively still, the DP_w can be at least about 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, 10000, 11000, 12000, 13000, 14000, or 15000 (or any integer between 1000 and 15000), for example. Given that a poly alpha-1,3-1,6-glucan herein can have a DP_w of at least
30 about 1000, such a glucan polymer is typically water-insoluble.

A poly alpha-1,3-1,6-glucan can have an M_w of at least about 50000, 100000, 200000, 300000, 400000, 500000, 600000, 700000, 800000, 900000, 1000000, 1100000, 1200000, 1300000, 1400000, 1500000, or 1600000 (or any integer between 50000 and 1600000), for example. The M_w in certain embodiments is at least about 1000000. Alternatively, poly alpha-1,3-1,6-glucan can have an M_w of at least about 4000, 5000, 10000, 20000, 30000, or 40000, for example.

A poly alpha-1,3-1,6-glucan herein can comprise at least 20 glucose monomeric units, for example. Alternatively, the number of glucose monomeric units can be at least 25, 50, 100, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, or 9000 (or any integer between 10 and 9000), for example.

Poly alpha-1,3-1,6-glucan can be used as a dry powder or as a wet cake containing greater than 5% by weight of water.

In some embodiments, the polysaccharide comprises dextran. In one embodiment, the dextran comprises:

- (i) 87-93% alpha-1,6 glycosidic linkages;
- (ii) 0.1-1.2% alpha-1,3-glycosidic linkages;
- (iii) 0.1-0.7% alpha-1,4-glycosidic linkages;
- (iv) 7.7-8.6% alpha-1,3,6-glycosidic linkages;
- (v) 0.4-1.7% alpha-1,2,6-glycosidic or alpha-1,4,6-glycosidic linkages

wherein the weight-average molecular weight (M_w) of the dextran is about 50-200 million Daltons, the z-average radius of gyration of the dextran is about 200-280 nm. Optionally, the dextran is not a product of *Leuconostoc mesenteroides* glucosyltransferase enzyme. In other embodiments, the coating composition consists essentially of the dextran polymer having (i) about 89.5-90.5 wt% glucose linked at positions 1 and 6; (ii) about 0.4-0.9 wt% glucose linked at positions 1 and 3; (iii) about 0.3-0.5 wt% glucose linked at positions 1 and 4; (iv) about 8.0-8.3 wt%

glucose linked at positions 1, 3 and 6; and (v) about 0.7-1.4 wt% glucose linked at: (a) positions 1, 2 and 6, or (b) positions 1, 4 and 6.

The terms “dextran”, “dextran polymer” and “dextran compound” are used interchangeably herein and refer to complex, branched alpha-
5 glucans generally comprising chains of substantially (mostly) alpha-1,6-linked glucose monomers, with side chains (branches) linked mainly by alpha-1,3-linkage. The term “gelling dextran” herein refers to the ability of one or more dextrans disclosed herein to form a viscous solution or gel-like composition (i) during enzymatic dextran synthesis and, optionally, (ii)
10 when such synthesized dextran is isolated (e.g., >90% pure) and then placed in an aqueous composition.

Dextran “long chains” herein can comprise “substantially [or mostly] alpha-1,6-glycosidic linkages”, meaning that they can have at least about 98.0% alpha-1,6-glycosidic linkages in some aspects. Dextran herein can
15 comprise a “branching structure” (branched structure) in some aspects. It is contemplated that in this structure, long chains branch from other long chains, likely in an iterative manner (e.g., a long chain can be a branch from another long chain, which in turn can itself be a branch from another long chain, and so on). It is contemplated that long chains in this structure
20 can be “similar in length”, meaning that the length (DP [degree of polymerization]) of at least 70% of all the long chains in a branching structure is within plus/minus 30% of the mean length of all the long chains of the branching structure.

Dextran in some embodiments can also comprise “short chains”
25 branching from the long chains, typically being one to three glucose monomers in length, and comprising less than about 10% of all the glucose monomers of a dextran polymer. Such short chains typically comprise alpha-1,2-, alpha-1,3-, and/or alpha-1,4-glycosidic linkages (it is believed that there can also be a small percentage of such non-alpha-1,6
30 linkages in long chains in some aspects).

The “molecular weight” of dextran herein can be represented as number-average molecular weight (Mn) or as weight-average molecular weight (Mw), the units of which are in Daltons or grams/mole.

Alternatively, molecular weight can be represented as DPw (weight
5 average degree of polymerization) or DPn (number average degree of polymerization). Various means are known in the art for calculating these molecular weight measurements such as with high-pressure liquid chromatography (HPLC), size exclusion chromatography (SEC), or gel permeation chromatography (GPC).

10 The term “radius of gyration” (Rg) herein refers to the mean radius of dextran, and is calculated as the root-mean-square distance of a dextran molecule’s components (atoms) from the molecule’s center of gravity. Rg can be provided in Angstrom or nanometer (nm) units, for example. The “z-average radius of gyration” of dextran herein refers to the
15 Rg of dextran as measured using light scattering (e.g., MALS). Methods for measuring z-average Rg are known and can be used herein, accordingly. For example, z-average Rg can be measured as disclosed in U.S. Patent No. 7531073, U.S. Patent Appl. Publ. Nos. 2010/0003515 and 2009/0046274, Wyatt (*Anal. Chim. Acta* 272:1-40), and Mori and Barth
20 (Size Exclusion Chromatography, Springer-Verlag, Berlin, 1999), all of which are incorporated herein by reference.

The dextran polymer can be produced via an enzymatic process using glucosyltransferase enzyme comprising an amino acid sequence that is described in United States Patent Application Publication

25 2016/0122445 A1. In some embodiments, the dextran can comprise (i) about 87-93 wt% glucose linked only at positions 1 and 6; (ii) about 0.1-1.2 wt% glucose linked only at positions 1 and 3; (iii) about 0.1-0.7 wt% glucose linked only at positions 1 and 4; (iv) about 7.7-8.6 wt% glucose linked only at positions 1, 3 and 6; and (v) about 0.4-1.7 wt% glucose
30 linked only at: (a) positions 1, 2 and 6, or (b) positions 1, 4 and 6. In certain embodiments, a dextran can comprise (i) about 89.5-90.5 wt%

glucose linked only at positions 1 and 6; (ii) about 0.4-0.9 wt% glucose linked only at positions 1 and 3; (iii) about 0.3-0.5 wt% glucose linked only at positions 1 and 4; (iv) about 8.0-8.3 wt% glucose linked only at positions 1, 3 and 6; and (v) about 0.7-1.4 wt% glucose linked only at: (a) positions 1, 2 and 6, or (b) positions 1, 4 and 6.

In other embodiments, the dextran polymer can comprise about 87, 87.5, 88, 88.5, 89, 89.5, 90, 90.5, 91, 91.5, 92, 92.5, or 93 wt% glucose linked only at positions 1 and 6. There can be about 87-92.5, 87-92, 87-91.5, 87-91, 87-90.5, 87-90, 87.5-92.5, 87.5-92, 87.5-91.5, 87.5-91, 87.5-90.5, 87.5-90, 88-92.5, 88-92, 88-91.5, 88-91, 88-90.5, 88-90, 88.5-92.5, 88.5-92, 88.5-91.5, 88.5-91, 88.5-90.5, 88.5-90, 89-92.5, 89-92, 89-91.5, 89-91, 89-90.5, 89-90, 89.5-92.5, 89.5-92, 89.5-91.5, 89.5-91, or 89.5-90.5 wt% glucose linked only at positions 1 and 6, in some instances.

In other embodiments, the dextran polymer can comprise about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, or 1.2 wt% glucose linked only at positions 1 and 3. There can be about 0.1-1.2, 0.1-1.0, 0.1-0.8, 0.3-1.2, 0.3-1.0, 0.3-0.8, 0.4-1.2, 0.4-1.0, 0.4-0.8, 0.5-1.2, 0.5-1.0, 0.5-0.8, 0.6-1.2, 0.6-1.0, or 0.6-0.8 wt% glucose linked only at positions 1 and 3, in some instances.

In other embodiments, the dextran polymer can comprise about 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, or 0.7 wt% glucose linked only at positions 1 and 4. There can be about 0.1-0.7, 0.1-0.6, 0.1-0.5, 0.1-0.4, 0.2-0.7, 0.2-0.6, 0.2-0.5, 0.2-0.4, 0.3-0.7, 0.3-0.6, 0.3-0.5, or 0.3-0.4 wt% glucose linked only at positions 1 and 4, in some instances.

In other embodiments, the dextran polymer can comprise about 7.7, 7.8, 7.9, 8.0, 8.1, 8.2, 8.3, 8.4, 8.5, or 8.6 wt% glucose linked only at positions 1, 3 and 6. There can be about 7.7-8.6, 7.7-8.5, 7.7-8.4, 7.7-8.3, 7.7-8.2, 7.8-8.6, 7.8-8.5, 7.8-8.4, 7.8-8.3, 7.8-8.2, 7.9-8.6, 7.9-8.5, 7.9-8.4, 7.9-8.3, 7.9-8.2, 8.0-8.6, 8.0-8.5, 8.0-8.4, 8.0-8.3, 8.0-8.2, 8.1-8.6, 8.1-8.5, 8.1-8.1, 8.1-8.3, or 8.1-8.2 wt% glucose linked only at positions 1, 3 and 6, in some instances.

In other embodiments, the dextran polymer can comprise about 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, or 1.7 wt% glucose linked only at (a) positions 1, 2 and 6, or (b) positions 1, 4 and 6. There can be about 0.4-1.7, 0.4-1.6, 0.4-1.5, 0.4-1.4, 0.4-1.3, 0.5-1.7, 0.5-1.6, 5 0.5-1.5, 0.5-1.4, 0.5-1.3, 0.6-1.7, 0.6-1.6, 0.6-1.5, 0.6-1.4, 0.6-1.3, 0.7-1.7, 0.7-1.6, 0.7-1.5, 0.7-1.4, 0.7-1.3, 0.8-1.7, 0.8-1.6, 0.8-1.5, 0.8-1.4, 0.8-1.3 wt% glucose linked only at (a) positions 1, 2 and 6, or (b) positions 1, 4 and 6, in some instances.

It is believed that dextran herein may be a branched structure in 10 which there are long chains (containing mostly or all alpha-1,6-linkages) that iteratively branch from each other (e.g., a long chain can be a branch from another long chain, which in turn can itself be a branch from another long chain, and so on). The branched structure may also comprise short branches from the long chains; these short chains are believed to mostly 15 comprise alpha-1,3 and -1,4 linkages, for example. Branch points in the dextran, whether from a long chain branching from another long chain, or a short chain branching from a long chain, appear to comprise alpha-1,3, -1,4, or -1,2 linkages off of a glucose involved in alpha-1,6 linkage. On average, about 20%, 21%, 22%, 23%, 24%, 25%, 26%, 27%, 28%, 29%, 20 30%, 15-35%, 15-30%, 15-25%, 15-20%, 20-35%, 20-30%, 20-25%, 25-35%, or 25-30% of all branch points of dextran in some embodiments branch into long chains. Most (>98% or 99%) or all the other branch points branch into short chains.

The long chains of a dextran branching structure can be similar in 25 length in some aspects. By being similar in length, it is meant that the length (DP) of at least 70%, 75%, 80%, 85%, or 90% of all the long chains in a branching structure is within plus/minus 15% (or 10%, 5%) of the mean length of all the long chains of the branching structure. In some aspects, the mean length (average length) of the long chains is about 10- 30 50 DP (i.e., 10-50 glucose monomers). For example, the mean individual length of the long chains can be about 10, 15, 16, 17, 18, 19, 20, 21, 22,

23, 24, 25, 30, 35, 40, 45, 50, 10-50, 10-40, 10-30, 10-25, 10-20, 15-50, 15-40, 15-30, 15-25, 15-20, 20-50, 20-40, 20-30, or 20-25 DP.

Dextran long chains in certain embodiments can comprise substantially alpha-1,6-glycosidic linkages and a small amount (less than 2.0%) of alpha-1,3- and/or alpha-1,4-glycosidic linkages. For example, dextran long chains can comprise about, or at least about, 98%, 98.25%, 98.5%, 98.75%, 99%, 99.25%, 99.5%, 99.75%, or 99.9% alpha-1,6-glycosidic linkages. A dextran long chain in certain embodiments does not comprise alpha-1,4-glycosidic linkages (i.e., such a long chain has mostly alpha-1,6 linkages and a small amount of alpha-1,3 linkages). Conversely, a dextran long chain in some embodiments does not comprise alpha-1,3-glycosidic linkages (i.e., such a long chain has mostly alpha-1,6 linkages and a small amount of alpha-1,4 linkages). Any dextran long chain of the above embodiments may further not comprise alpha-1,2-glycosidic linkages, for example. Still in some aspects, a dextran long chain can comprise 100% alpha-1,6-glycosidic linkages (excepting the linkage used by such long chain to branch from another chain).

Short chains of a dextran molecule in some aspects are one to three glucose monomers in length and comprise less than about 5-10% of all the glucose monomers of the dextran polymer. At least about 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, or all of, short chains herein are 1-3 glucose monomers in length. The short chains of a dextran molecule can comprise less than about 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, or 1% of all the glucose monomers of the dextran molecule, for example.

Short chains of a dextran molecule in some aspects can comprise alpha-1,2-, alpha-1,3-, and/or alpha-1,4-glycosidic linkages. Short chains, when considered all together (not individually) may comprise (i) all three of these linkages, or (ii) alpha-1,3- and alpha-1,4-glycosidic linkages, for example. It is believed that short chains of a dextran molecule herein can be heterogeneous (i.e., showing some variation in linkage profile) or

homogeneous (i.e., sharing similar or same linkage profile) with respect to the other short chains of the dextran.

Dextran in certain embodiments can have a weight average molecular weight (Mw) of about, or at least about, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 105, 110, 115, 120, 125, 130, 135, 140, 145, 150, 155, 160, 165, 170, 175, 180, 185, 190, 195, or 200 million (or any integer between 50 and 200 million) (or any range between two of these values).. The Mw of dextran can be about 50-200, 60-200, 70-200, 80-200, 90-200, 100-200, 110-200, 120-200, 50-180, 60-180, 70-180, 80-180, 90-180, 100-180, 110-180, 120-180, 50-160, 60-160, 70-160, 80-160, 90-160, 100-160, 110-160, 120-160, 50-140, 60-140, 70-140, 80-140, 90-140, 100-140, 110-140, 120-140, 50-120, 60-120, 70-120, 80-120, 90-120, 100-120, 110-120, 50-110, 60-110, 70-110, 80-110, 90-110, 100-110, 50-100, 60-100, 70-100, 80-100, 90-100, or 95-105 million, for example. Any of these Mw's can be represented in weight average degree of polymerization(DPw), if desired, by dividing Mw by 162.14.

The z-average radius of gyration of a dextran herein can be about 200-280 nm. For example, the z-average Rg can be about 200, 205, 210, 215, 220, 225, 230, 235, 240, 245, 250, 255, 260, 265, 270, 275, or 280 nm (or any integer between 200-280 nm). As other examples, the z-average Rg can be about 200-280, 200-270, 200-260, 200-250, 200-240, 200-230, 220-280, 220-270, 220-260, 220-250, 220-240, 220-230, 230-280, 230-270, 230-260, 230-250, 230-240, 240-280, 240-270, 240-260, 240-250, 250-280, 250-270, or 250-260 nm.

Contacting an esterifying agent and a polysaccharide in the in situ processes disclosed herein provides a product comprising a polysaccharide ester composition. The polysaccharide ester composition comprises a polysaccharide ester compound having a degree of substitution of about 0.001. to about 3, depending on the amount of water present during the contacting step and the molar ratio of esterifying agent and polysaccharide. In one embodiment, the polysaccharide ester

composition comprises a polysaccharide ester having a degree of substitution of about 0.1 to about 1.5, or about 0.3 to about 1.5. In another embodiment, the polysaccharide ester composition comprises a polysaccharide ester having a degree of substitution of 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3, or any value between 0.001 and 3. The polysaccharide ester composition comprises a polysaccharide ester compound wherein at least one ester group comprises a C₂–C₂₀ acyl group, for example acetyl ester, propionate ester, butyrate ester, pentanoate ester, hexanoate ester, heptanoate ester, octanoate ester, nonoate ester, decyl ester, undecyl ester, dodecyl, laurate, or benzoate ester. Mixtures of different esters can also be obtained by appropriate selection of two or more esterifying agents.

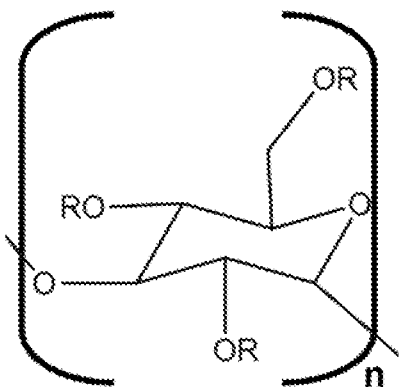
The polysaccharide ester compositions disclosed herein comprise synthetic, man-made compounds in which at least a portion of the hydroxyl groups contained in the polysaccharide starting material are converted to esters. The polysaccharides typically form a slurry in the solvent used in the contacting step, and as the reaction with the esterifying agent proceeds, the polysaccharide ester can solubilize and form a solution. As used herein, the phrase “a product comprising a polysaccharide ester composition” also includes at least a portion of the solvent from the contacting step of the process disclosed herein. As used herein, the phrase “product comprising a polysaccharide ester composition” also includes reaction by-products, such as salts, and can optionally comprise excess esterifying agent. Polysaccharide ester compositions disclosed herein encompass polysaccharide ester compositions comprising poly alpha-1,3-glucan ester compounds, polysaccharide ester compositions comprising poly alpha-1,3-1,6-glucan ester compounds, polysaccharide ester compositions comprising ester compounds of water insoluble alpha-(1,3-glucan) polymer having 90% or greater alpha-1,3-glycosidic linkages, less than 1% by weight of alpha-1,3,6-glycosidic branch points, and a

number average degree of polymerization in the range of from 55 to 10,000, and polysaccharide ester compositions comprising dextran ester compounds. Mixtures of polysaccharides can also be used.

Polysaccharide ester compositions disclosed herein comprise a

- 5 polysaccharide ester having a degree of substitution of about 0.001 to about 3 and wherein at least one ester group comprises a C₂-C₂₀ acyl group. In another embodiment, polysaccharide ester compositions disclosed herein comprise a polysaccharide ester having a degree of substitution of about 0.1 to about 3 and wherein at least one ester group
- 10 comprises a C₂-C₂₀ acyl group.

The terms “poly alpha-1,3-glucan ester compound”, “poly alpha-1,3-glucan ester”, and “poly alpha-1,3-glucan ester derivative” are used interchangeably herein. A poly alpha-1,3-glucan ester compound herein can be represented by the structure:



15 Regarding the formula of this structure, n can be at least 6, and each R can independently be a hydrogen atom (H) or a C₂-C₂₀ acyl group. A poly alpha-1,3-glucan ester compound herein has a degree of substitution of about 0.001 to about 3.0.

- 20 A poly alpha-1,3-glucan ester compound, or an ester compound of the polysaccharide ester compositions disclosed herein, is termed an “ester” herein by virtue of comprising the substructure -C_G-O-CO-C-, where “-C_G-” represents carbon 2, 4, or 6 of a glucose monomeric unit of a poly alpha-1,3-glucan ester compound, for example, and where “-CO-C-”
- 25 is comprised in the acyl group. The carbonyl group (-CO-) of the acyl

group is ester-linked to carbon 2, 4, or 6 of a glucose monomeric unit of a poly alpha-1,3-glucan ester compound.

Examples of a C₂-C₂₀ acyl group include the following:

an ethanoyl group (COCH_3),

- 5 a propanoyl group (COCH_2CH_3),
a butanoyl group ($\text{COCH}_2\text{CH}_2\text{CH}_3$),
a pentanoyl group ($\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a hexanoyl group ($\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a heptanoyl group ($\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
10 an octanoyl group ($\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a nonanoyl group ($\text{CO-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a decanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a undecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a dodecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
15 a tridecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_3$),
a tetradecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-CH}_2\text{CH}_2\text{CH}_3$),
a pentadecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
20 a hexadecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a heptadecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
25 an octadecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
a nonadecanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
an eicosanoyl group ($\text{CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$),
30

[illegible][illegible][illegible][illegible][illegible][illegible]

Common names for the above are acetyl (ethanoyl group),

15 propionyl (propanoyl group), butyryl (butanoyl group), valeryl (pentanoyl group), caproyl (hexanoyl group); enanthyl (heptanoyl group), caprylyl (octanoyl group), pelargonyl (nonanoyl group), capryl (decanoyl group), lauroyl (dodecanoyl group), myristyl (tetradecanoyl group), palmityl (hexadecanoyl group), stearyl (octadecanoyl group), arachidyl (eicosanoyl group), behenyl (docosanoyl group), lignoceryl (tetracosanoyl group), and cerotyl (hexacosanoyl group).

Regarding nomenclature, a poly alpha-1,3-glucan ester compound can be referenced herein by referring to the organic acid(s) corresponding with the acyl group(s) in the compound. For example, an ester compound

comprising acetyl groups can be referred to as a poly alpha-1,3-glucan acetate, an ester compound comprising propionyl groups can be referred to as a poly alpha-1,3-glucan propionate, and an ester compound comprising butyryl groups can be referred to as a poly alpha-1,3-glucan butyrate. However, this nomenclature is not meant to refer to the poly alpha-1,3-glucan ester compounds herein as acids *per se*. Corresponding nomenclature can be used and intended for ester compounds of poly

alpha-1,3-1,6-glucan, of water insoluble alpha-(1,3-glucan) polymer having 90% or greater alpha-1,3-glycosidic linkages, less than 1% by weight of alpha-1,3,6-glycosidic branch points, and a number average degree of polymerization in the range of from 55 to 10,000, and of dextran, which
5 can be present in the polysaccharide ester compositions obtained by the processes disclosed herein.

The terms "polysaccharide mixed ester" and "mixed ester" are used interchangeably herein. A polysaccharide mixed ester contains two or more types of an acyl group. Examples of such mixed esters are poly
10 alpha-1,3-glucan acetate propionate (comprises acetyl and propionyl groups) and poly alpha-1,3-glucan acetate butyrate (comprises acetyl and butyryl groups), wherein the polysaccharide is poly alpha-1,3-glucan.

The terms "organic acid" and "carboxylic acid" are used interchangeably herein. An organic acid has the formula $R-COOH$, where
15 R is an organic group and $COOH$ is a carboxylic group. The R group herein is typically a saturated linear carbon chain (up to seven carbon atoms). Examples of organic acids are acetic acid (CH_3-COOH), propionic acid (CH_3-CH_2-COOH) and butyric acid ($CH_3-CH_2-CH_2-COOH$).

The term "degree of substitution" (DoS) as used herein refers to the
20 average number of hydroxyl groups substituted in each monomeric unit (glucose) of a poly alpha-1,3-glucan ester compound or other polysaccharide ester compound disclosed herein. For example, since there are three hydroxyl groups in each monomeric unit in poly alpha-1,3-glucan, the DoS in a poly alpha-1,3-glucan ester compound herein can be
25 no higher than 3.

The "molecular weight" of poly alpha-1,3-glucan, poly alpha-1,3-glucan ester compounds, polysaccharide, and polysaccharide ester compounds disclosed herein can be represented as number-average molecular weight (M_n) or as weight-average molecular weight (M_w).
30 Alternatively, molecular weight can be represented as Daltons, grams/mole, DPw (weight average degree of polymerization), or DPn

(number average degree of polymerization). Various means are known in the art for calculating these molecular weight measurements, such as high-pressure liquid chromatography (HPLC), size exclusion chromatography (SEC), or gel permeation chromatography (GPC).

5 In one embodiment, the polysaccharide ester compositions disclosed herein comprise a polysaccharide ester compound containing one type of acyl group. In another embodiment, the polysaccharide ester compositions disclosed herein comprise a polysaccharide ester compound containing two or more different types of acyl groups.

10 The poly alpha-1,3-glucan ester compound or other polysaccharide ester compound of the polysaccharide ester compositions disclosed herein has a degree of substitution (DoS) of about 0.001 to about 3.0. Alternatively, the DoS of a poly alpha-1,3-glucan ester compound disclosed herein can be about 0.1 to about 1.5, or 0.3 to about 1.5.

15 Alternatively still, the DoS can be at least about 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, or 3, or any value between 0.001 and 3. It would be understood by those skilled in the art that since, for example, a poly alpha-1,3-glucan ester compound disclosed
20 herein has a degree of substitution between about 0.001 to about 3.0, the R groups of the compound cannot only be hydrogen.

 The percentage of glycosidic linkages between the glucose monomer units of the poly alpha-1,3-glucan ester compound that are alpha-1,3 is at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%,
25 98%, 99%, or 100% (or any integer between 50% and 100%). In such embodiments, accordingly, the compound has less than about 50%, 40%, 30%, 20%, 10%, 5%, 4%, 3%, 2%, 1%, or 0% (or any integer value between 0% and 50%) of glycosidic linkages that are not alpha-1,3.

 The backbone of a poly alpha-1,3-glucan ester compound disclosed
30 herein is preferably linear/unbranched. In certain embodiments, the compound has no branch points or less than about 10%, 9%, 8%, 7%, 6%,

5%, 4%, 3%, 2%, or 1% branch points as a percent of the glycosidic linkages in the polymer. Examples of branch points include alpha-1,6 branch points.

The formula of a polysaccharide ester compound, for example a poly alpha-1,3-glucan ester compound, of the polysaccharide ester composition in certain embodiments can have an n value of at least 6. Alternatively, n can have a value of at least 10, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600, 1700, 1800, 1900, 2000, 2100, 2200, 2300, 2400, 2500, 2600, 2700, 2800, 2900, 3000, 3100, 3200, 3300, 3400, 3500, 3600, 3700, 3800, 3900, or 4000 (or any integer between 10 and 4000).

The molecular weight of a poly alpha-1,3-glucan ester compound or other polysaccharide ester compound can be measured as number-average molecular weight (M_n) or as weight-average molecular weight (M_w). Alternatively, molecular weight can be measured in Daltons or grams/mole.

The poly alpha-1,3-glucan ester may have a weight average degree of polymerization (DP_w) of at least about 20. In some embodiments, the poly alpha-1,3-glucan ester has a DP_w of from about 20 to about 1400, or from about 20 to about 1000, or from about 40 to about 900.

The M_n or M_w of poly alpha-1,3-glucan ester compounds or other polysaccharide ester compounds disclosed herein may be at least about 1000. Alternatively, the M_n or M_w can be at least about 1000 to about 600000. Alternatively still, the M_n or M_w can be at least about 10000, 25000, 50000, 75000, 100000, 125000, 150000, 175000, 200000, 225000, 250000, 275000, or 300000 (or any integer between 10000 and 300000), for example.

The esterifying agent and the polysaccharide are contacted in the presence of a solvent. Suitable solvents include those which are inert under the reaction conditions employed and which can optionally solubilize at least a portion of the polysaccharide ester composition produced.

Typically, the polysaccharide starting material is not soluble in the solvent and is used as a slurry. Suitable solvents are aprotic solvents. In one embodiment, the esterifying agent comprises an acyl halide and the solvent is selected from dimethylacetamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof. In another embodiment, the esterifying agent is a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester, and the solvent is selected from dimethylacetamide, dimethylformamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof. In one embodiment, the solvent comprises dimethylacetamide. In another embodiment, the solvent comprises dimethylformamide. In one embodiment, the solvent is anhydrous, for example containing less than about 0.1 wt% water, based on the total weight of water and solvent. Larger amounts of water in the solvent may necessitate use of excess esterifying agent beyond that required for the desired degree of substitution of the polysaccharide ester composition. Suitable solvents can be obtained commercially.

The product comprising a polysaccharide ester composition also includes the solvent used in the contacting step. Optionally, a portion of the solvent can be removed, for example by distillation, to increase the concentration of the polysaccharide ester composition of the product.

In the processes disclosed herein, the esterifying agent and the polysaccharide are contacted under suitable reaction conditions. Sufficient reaction time, in conjunction with selection of appropriate reaction temperature and reaction pressure, enables formation of a product comprising a polysaccharide ester composition as disclosed herein. Suitable reaction conditions include a reaction temperature in the range of about 30 °C to about 175 °C, for example in the range of about 30 °C to about 50 °C, or in the range of about 30 °C to about 75 °C, or in the range of about 50 °C to about 100 °C, or in the range of about 60 °C to about 150 °C, or in the range of about 80 °C to about 175 °C. The

particular esterifying agent and solvent selected for use will influence the choice of reaction temperature as well, as the reaction temperature should be below the boiling point of the esterifying agent and the solvent for ease of process operation. Suitable reaction conditions include a reaction

- 5 pressure of about atmospheric pressure, less than atmospheric pressure, or greater than atmospheric pressure. Choice of reaction pressure is also influenced by the particular esterifying agent and solvent selected, as lower reaction pressure can be used with higher boiling esterifying agents and solvents, while higher reaction pressure may be needed for use with
- 10 lower boiling esterifying agents and solvents.

In some embodiments, the step of contacting an esterifying agent with a polysaccharide in the presence of a solvent further comprises the steps of:

- i) contacting the polysaccharide and the solvent to form an initial
- 15 mixture comprising water;
- ii) heating the initial mixture;
- iii) removing at least a portion of the water from the initial mixture under reduced pressure to obtain a mixture comprising a reduced water content; and
- 20 iv) adding the esterifying agent to the mixture comprising a reduced water content.

These additional steps are useful to remove at least a portion of any water contained in the polysaccharide and/or the solvent. It is desirable to minimize the amount of water present in the contacting step in order to

25 avoid using excess esterifying agent, as any water present will react with the esterifying agent.

In one embodiment, anhydrous solvent and dried polysaccharide are used, and the contacting of the esterifying agent and the polysaccharide in the presence of the solvent and suitable reaction

30 conditions is performed in a manner minimizing moisture intrusion, for example under an atmosphere of dry nitrogen or argon.

As the esterifying agent reacts with the polysaccharide, byproduct acid halide is formed. For example, in the case where acetyl chloride is used as the esterifying agent, byproduct hydrogen chloride is generated as the polysaccharide is functionalized to a polysaccharide ester composition. Optionally, at least a portion of the byproduct acid halide may be removed during or after the contacting step, for example by heating the product comprising a polysaccharide ester composition under reduced pressure, or by contacting the product comprising a polysaccharide ester composition with an acid-exchange resin.

The polysaccharide ester composition prepared in situ can be used in further applications, for example structural to non-structural applications for films, coatings, adhesives, dispersions, rheology modifiers, foams, personal care products, water absorbents, formed objects or fibers as a major or minor component or as a component of a composite. In one embodiment, the polysaccharide ester composition can be used as a water retention value modifier. In one embodiment, the product comprising a polysaccharide ester composition can be used as a compatibilizer, for example in a styrene acrylonitrile resin (SAN), and in rubbers such as acrylonitrile butadiene styrene (ABS).

The product comprising a polysaccharide ester composition can be used directly in a variety of processes, for example to cast a film, coat a substrate, or spin fibers. In one embodiment, the process disclosed herein further comprises a step of casting a film from the product comprising a polysaccharide ester composition. Films can be cast by methods known in the art. In another embodiment, the process disclosed herein further comprises a step of coating a substrate with the product comprising a polysaccharide ester composition. Substrates can be as described herein below. In yet another embodiment, the process disclosed herein further comprises a step of spinning fibers from the product comprising a polysaccharide ester composition. Spinning fibers comprising a polysaccharide ester composition as disclosed herein can be performed as

described herein below, but without the addition of another polymer to form a blend of the polysaccharide ester composition and the polymer.

In some embodiments, the process further comprises a step of combining the product comprising a polysaccharide ester composition with
5 a polymer dispersed in or dissolved in a second solvent to form a blend of the polysaccharide ester composition and the polymer. In one embodiment, the second solvent is the same as the solvent present in the contacting step, which is also present in the product. In one embodiment, the second solvent is different from the solvent present in the contacting
10 step, and the second solvent is chosen to be compatible with the solvent of the contacting step to avoid formation of two solvent phases. Alternatively, the polymer can be added to the product comprising the polysaccharide ester composition and the solvent from the contacting step and the blend formed in this manner.

15 Suitable polymers for blending with the product comprising the polysaccharide ester composition can include, for example, polyacrylates, polyaramids, polyphenylene isophthalamide, poly-m-phenylene isophthalamide, polyphenylene terephthalamide, vinyl polymers, polyethylene, polypropylene, poly(vinyl chloride), polystyrene,
20 polytetrafluoroethylene, poly(alpha -methylstyrene), poly(acrylic acid), poly(isobutylene), poly(methacrylic acid), poly(methyl methacrylate), poly(1-pentene), poly(1,3-butadiene), poly(vinyl acetate), poly(2-vinyl pyridine), 1,4-polyisoprene, 3,4-polychloroprene, polyethers, poly(ethylene oxide), poly(propylene oxide), poly(trimethylene glycol),
25 poly(tetramethylene glycol), polyacetals, polyformaldehyde, polyacetaldehyde, polyesters, poly(3-propionate), poly(10-decanoate), poly(ethylene terephthalate), poly(m-phenylene terephthalate); polyamides, polycaprolactam, poly(11-undecanoamide), poly(hexamethylene sebacamide), poly(tetramethylene-m-
30 benzenesulfonamide), polyetheretherketone, polyetherimide, poly(phenylene oxide), polyamide (including polyureas), polyamideimide,

polyarylate, polybenzimidazole, polycarbonates, polyurethane, polyimide, polyhydrazide, phenolic resins, polysilane, polysiloxane, polycarbodiimide, polyimine, azo polymers, polysulfide, polysulfane, cellulose polymers, or starch polymers. In some embodiments, the polysaccharide ester

- 5 composition can be blended with starch, cellulose including various esters, ethers, and graft copolymers thereof, polyphenylene isophthalamide, or polyphenylene terephthalamide. The one or more polymers may be crosslinkable in the presence of a multifunctional crosslinking agent or crosslinkable upon exposure to actinic radiation or other type of radiation.
- 10 The one or more polymers may be homopolymers of any of the foregoing polymers, random copolymers, block copolymers, alternating copolymers, random tripolymers, block tripolymers, alternating tripolymers, or derivatives thereof (e.g., graft copolymers, esters, or ethers thereof).

- The blends can comprise the polysaccharide ester composition and
- 15 the one or more polymers in a weight ratio in the range of from 0.01:99.99 to 99.99:0.01, on a solvent-free basis. In other embodiments, the weight ratio can be in the range of from 1:99 to 99:1, or from 5:95 to 95:5, or from 10:90 to 90:10, or from 20:80 to 80:20, or from 30:70 to 70:30, or from 40:60 to 60:40, or from 45:55 to 55:45, on a solvent-free basis.

- 20 In some embodiments, the process further comprises a step of casting a film from the blend of the polysaccharide ester composition and the polymer. Films can be cast by methods known in the art.

- In some embodiments, the process can further comprise a step of coating a substrate with the blend of the polysaccharide ester composition
- 25 and the polymer. In some embodiments, the substrate can comprise metal, paper, or plastic. In some embodiments, the substrate can be a fibrous substrate such as fabrics, for example to provide clothing which has good water impermeability and improved comfort for the wearer. In one embodiment, a coated fibrous substrate comprises a fibrous substrate
- 30 having a surface, wherein the surface comprises a coating comprising a

blend of a polymer and a polysaccharide ester composition as disclosed herein on at least a portion of the surface.

Fibrous substrates can include fibers, yarns, fabrics, fabric blends, textiles, nonwovens, paper, leather, and carpets. In one embodiment, the
5 fibrous substrate is a fiber, a yarn, a fabric, a textile, or a nonwoven. The fibrous substrates can contain natural or synthetic fibers, including cotton, cellulose, wool, silk, rayon, nylon, aramid, acetate, polyurethaneurea, acrylic, jute, sisal, sea grass, coir, polyamide, polyester, polyolefin, polypropylene, polyaramid, or blends thereof. By "fabric blends" is meant
10 fabric made of two or more types of fibers. Typically, these blends are a combination of at least one natural fiber and at least one synthetic fiber, but also can include a blend of two or more natural fibers or of two or more synthetic fibers. Nonwoven substrates include, for example, spun-laced nonwovens such as SONTARA® available from DuPont and spun-
15 bonded-meltblown-spunbonded nonwovens.

In some embodiments, the process can further comprise a step of spinning fibers from the blend comprising a polymer and the product comprising a polysaccharide ester composition.

The fibers can be spun from organic solutions. The concentration
20 of the polysaccharide ester composition in the solvent should be in the range of from 5 to 30 percent by weight, for example 5 to 10, or 5 to 15, or 5 to 20, or 5 to 25, or 10 to 20, or 10 to 30, or 15 to 25, or 15 to 30, based on the total weight of the solution. Below 5 percent by weight, the fiber forming ability of the solution is degraded while concentrations above 30
25 percent by weight are problematic, requiring increasingly refined techniques in order to form the fibers.

The soluble blend of polymer and polysaccharide ester composition can be fed directly to a spinneret and the resulting fiber quenched in a coagulation bath, for example, an acidic coagulation bath. Suitable acidic
30 coagulants include, for example, glacial acetic acid, aqueous acetic acid, sulfuric acid, combinations of sulfuric acid, sodium sulfate, and zinc

sulfate. In some embodiments, the liquid coagulant can be maintained at a temperature in the range of 0 to 100°C, and preferably in the range of 15 to 70°C. In some embodiments, extrusion is effected directly into the acidic coagulation bath. In such a circumstance, known in the art as “wet-spinning,” the spinneret is partially or fully immersed in the acidic coagulation bath. The spinnerets and associated fittings should be constructed of corrosion resistant alloys such as stainless steel or platinum/gold. The thus coagulated fiber can then be passed into a second bath provided to neutralize and/or dilute residual acid from the first coagulation bath. The secondary bath preferably contains H₂O, methanol, or aqueous NaHCO₃, or a mixture thereof. In some embodiments, the wound fiber package can be soaked in one or more neutralizing wash baths for a period of time. A sequence of baths comprising any combinations of water, methanol or aqueous NaHCO₃ can also be used.

Any of the known methods for spinning fibers from an organic solution can be used, for example, wet spinning, dry spinning and air gap spinning are all useful methods. In each of these methods, a solution of the blend of polymer and polysaccharide ester composition is forced through a single or multi-holed spinneret or other form of a die. The spinneret holes can be of any cross-sectional shape, for example, round, flat, square, rectangular, a polygon or multi-lobed. The material can then be passed into a coagulation bath wherein the coagulation bath comprises a liquid coagulant which dissolves the solvent but not the polymer in order to form the desired fiber. In some embodiments, the fiber strand is first passed through an inert, noncoagulating layer, for example, air in the form of an air gap, prior to introduction into the coagulating bath. In other embodiments, the material can be extruded directly into a coagulating bath. In general, the method comprises:

- 1) providing a solution of the blend comprising the polymer and the product comprising a polysaccharide ester composition;
- 2) causing the solution to flow through a spinneret; and

3) removing at least a portion of the solvent.

The fibers can be used to produce an article. In some embodiments, the article can be a carpet, a textile, fabric, yarn, or apparel.

In one embodiment, a process for in situ esterification of a polysaccharide can further comprise a step of combining the product comprising a polysaccharide ester composition with a polymer dispersed in or dissolved in a second solvent to form a blend of the polysaccharide ester composition and the polymer, and the process may optionally include a step of casting a film from the blend, coating a substrate with the blend, or spinning fibers from the blend.

Non-limiting embodiments of the disclosure herein include:

1. A process comprising the step:

a) contacting an esterifying agent and a polysaccharide in the presence of a solvent and suitable reaction conditions for a reaction time sufficient to form a product comprising a polysaccharide ester composition, the polysaccharide ester composition comprising a polysaccharide ester compound having a degree of substitution of about 0.001 to about 3;

wherein the esterifying agent comprises an acyl halide, a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester; and

the ratio of esterifying agent to polysaccharide is in the range of about 0.001:1 to about 3:1 on a molar equivalent basis.

2. The process of embodiment 1, wherein the esterifying agent comprises an acyl halide.

3. The process of embodiment 1 or 2, wherein the acyl halide comprises acetyl chloride, benzoyl chloride, propanoyl chloride, acetyl bromide, benzoyl bromide, propanoyl bromide, acetyl iodide, benzoyl iodide, or propanoyl iodide.

4. The process of embodiment 1, wherein the esterifying agent comprises a phosphoryl halide.

5. The process of embodiment 1, wherein the esterifying agent comprises a carboxylic acid anhydride.

6. The process of embodiment 1, wherein the esterifying agent comprises a haloformic acid ester.

5 7. The process of embodiment 1, wherein the esterifying agent comprises a carbonic acid ester.

8. The process of embodiment 1, wherein the esterifying agent comprises a vinyl ester.

9. The process of embodiment 1, 2, or 3, wherein the esterifying
10 agent comprises an acyl halide and the solvent is selected from dimethylacetamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof.

10. The process of embodiment 1, 4, 5, 6, 7, or 8, wherein the
15 esterifying agent is a phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester, and the solvent is selected from dimethylacetamide, dimethylformamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof.

11. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10,
20 wherein the suitable reaction conditions include a reaction temperature in the range of about 30 °C to about 175 °C.

12. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11,
wherein the suitable reaction conditions include a reaction pressure of
25 about atmospheric pressure, less than atmospheric pressure, or greater than atmospheric pressure.

13. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, or
12, wherein the polysaccharide comprises poly alpha-1,3-glucan, poly
alpha-1,3-1,6-glucan, or dextran.

14. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12,
30 or 13, wherein the polysaccharide comprises poly alpha-1,3-glucan.

15. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13, wherein the polysaccharide comprises poly alpha-1,3-1,6-glucan.

16. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13, wherein the polysaccharide comprises water insoluble alpha-(1,3-
5 glucan) polymer having 90% or greater alpha-1,3-glycosidic linkages, less than 1% by weight of alpha-1,3,6-glycosidic branch points, and a number average degree of polymerization in the range of from 55 to 10,000.

17. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, or 13 wherein the polysaccharide comprises dextran.

10 18. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, or 17, wherein the polysaccharide ester composition comprises a polysaccharide ester compound wherein at least one ester group comprises a C₂-C₂₀ acyl group.

15 19. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, or 18, wherein the polysaccharide ester composition has a degree of substitution of about 0.001 to about 1.5.

20 20. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, or 19, wherein the step a) contacting an esterifying agent with a polysaccharide in the presence of a solvent further comprises the steps of:

i) contacting the polysaccharide and the solvent to form an initial mixture comprising water;

ii) heating the initial mixture;

25 iii) removing at least a portion of the water from the initial mixture under reduced pressure to obtain a mixture comprising a reduced water content; and

iv) adding the esterifying agent to the mixture comprising a reduced water content.

30 21. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20, further comprising a step of removing at

least a portion of the byproduct acid halide formed in the contacting step a).

22. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, or 21, further comprising a step of
5 combining the product comprising a polysaccharide ester composition with a polymer dispersed in or dissolved in a second solvent to form a blend of the polysaccharide ester composition and the polymer.

23. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, or 22, further comprising a step of
10 casting a film from the blend, coating a substrate with the blend, or spinning fibers from the blend.

24. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, or 23, further comprising a step of casting a film from the blend.

15 25. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, or 23, further comprising a step of coating a substrate with the blend.

26. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, or 23, further comprising a step of
20 spinning fibers from the blend.

27. The process of embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, or 26, wherein the polymer comprises polyacrylates, polyaramids, polyphenylene isophthalamide, poly-m-phenylene isophthalamide, polyphenylene
25 terephthalamide, vinyl polymers, polyethylene, polypropylene, poly(vinyl chloride), polystyrene, polytetrafluoroethylene, poly(alpha -methylstyrene), poly(acrylic acid), poly(isobutylene), poly(methacrylic acid), poly(methyl methacrylate), poly(1-pentene), poly(1,3-butadiene), poly(vinyl acetate), poly(2-vinyl pyridine), 1,4-polyisoprene, 3,4-polychloroprene, polyethers,
30 poly(ethylene oxide), poly(propylene oxide), poly(trimethylene glycol), poly(tetramethylene glycol), polyacetals, polyformaldehyde,

polyacetaldehyde, polyesters, poly(3-propionate), poly(10-decanoate),
poly(ethylene terephthalate), poly(m-phenylene terephthalate);
polyamides, polycaprolactam, poly(11-undecanoamide),
poly(hexamethylene sebacamide), poly(tetramethylene-m-
5 benzenesulfonamide), polyetheretherketone, polyetherimide,
poly(phenylene oxide), polyamide (including polyureas), polyamideimide,
polyarylate, polybenzimidazole, polycarbonates, polyurethane, polyimide,
polyhydrazide, phenolic resins, polysilane, polysiloxane, polycarbodiimide,
polyimine, azo polymers, polysulfide, polysulfane, cellulose polymers, or
10 starch polymers.

28. A polysaccharide ester composition obtained by the process of
embodiment 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19,
20, 21, 22, or 27.

29. A film obtained by the process of embodiment 23, 24, or 27.

15 30. A coated substrate obtained by the process of embodiment
23, 25, or 27.

31. Fibers obtained by the process of embodiment 23, 26, or 27.

Unless otherwise defined, all technical and scientific terms used
herein have the same meaning as commonly understood by one of
20 ordinary skill in the art. Although methods and materials similar or
equivalent to those described herein can be used in the practice or testing
of embodiments of the disclosed compositions, suitable methods and
materials are described below. In addition, the materials, methods, and
examples are illustrative only and not intended to be limiting.

25 In the foregoing specification, the concepts have been disclosed
with reference to specific embodiments. However, one of ordinary skill in
the art appreciates that various modifications and changes can be made
without departing from the scope of the invention as set forth in the claims
below.

30 Benefits, other advantages, and solutions to problems have been
described above with regard to specific embodiments. However, the

benefits, advantages, solutions to problems, and any feature(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature of any or all embodiments.

5

EXAMPLES

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

10 The disclosure is further defined in the following Examples. It should be understood that the Examples, while indicating certain embodiments, is given by way of illustration only. From the above discussion and the Examples, one skilled in the art can ascertain essential characteristics of this disclosure, and without departing from the spirit and
15 scope thereof, can make various changes and modifications to adapt to various uses and conditions.

 All materials other than polysaccharides were used as received from Aldrich, unless otherwise indicated. Dimethylacetamide (DMAc) was obtained as anhydrous or as reagent grade and distilled in the presence of
20 glucan before reactions.

 Dissolved solids of a solution is the weight of polymer dissolved divided by the weight of polymer dissolved plus solvent. For example, a 10wt% solution would be composed of 10g polymer / (10g polymer plus 90g DMAc).

25 As the molecular weight of the glucan polymer is increased by functionalization (in situ esterification), the mass of the functional polymer increases. "Functional solids" refers to the solids in the product composition and is based on [mass functional polymer / (solvent + mass functional polymer)]. Gravimetric analysis can be used to determine %
30 functional solids.

Dissolved solids was determined by isolating a known mass of solution by precipitating the solution into a non-solvent for the derivative polymer such as water or methanol, washing the solid polymer that precipitates and drying the polymer. The solids are determined as weight
5 of the polymer divided by weight of the solution.

Representative Preparation of Poly Alpha-1,3-Glucan

Poly alpha-1,3-glucan can be prepared using a gtfJ enzyme preparation as described in U.S. Patent No. 7,000,000; U.S. Patent Appl.
10 Publ. No. 2013/0244288, now U.S. Patent No. 9,080,195; and U.S. Patent Appl. Publ. No. 2013/0244287, now U.S. Patent No. 8,642,757 (all of which are incorporated herein by reference in their entirety).

Poly alpha-1,3-glucan polymer can be synthesized, and wet cake thereof prepared, following the procedures disclosed in U.S. Appl. Publ.
15 No. 2014/0179913, now U.S. Patent No. 9,139,718 (see Example 12 therein, for example), both of which are incorporated herein by reference in their entirety.

Two samples of poly alpha-1,3-glucan were used. Glucan #1 was ground dry powder. Glucan #1 was dried for a minimum of 24 hours at 60
20 °C under vacuum and low nitrogen purge. Glucan #2 was wet cake.

In Situ Preparation of Glucan Acetate

The set-up included a reaction kettle, nitrogen, vacuum, stirring, an optional scrubber. The final solution can be used in a process without
25 isolating the glucan acetate.

Example 1

This example targeted 1 DoS with approximately 10% functional solids.

30 Glucan #1 powder was weighed (260 g with 90% solids, 1.44 moles) charged with DMAc (2810 g) into a 2L jacketed reaction kettle

equipped with U-shaped Teflon coated motor driven stir, react-IR probe, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour.

- 5 Vacuum was slowly applied to 27-29 inches Hg and the temperature equilibrated to 80-85 °C. DMAc and water were distilled over until the FTIR probe OH peak was flat and water was removed from the vessel over an hour of distillation. The volume of the liquor overhead was 275 mL. The vessel was cooled to 40 °C in 1 hour and purged with nitrogen.
- 10 Acetyl chloride (103 mL, 113 g, 1.44 moles) was drawn into a calibrated glass syringe in 2 portions. One portion of 50 mL acetyl chloride was added quickly. The mixture gelled quickly and was agitated for half an hour to a homogenous solution. The N₂ purge was acidic at pH 1 from HCl generation. The second portion of 53 mL acetyl chloride was added
- 15 and stirring was maintained with the temperature at 45 °C for 30 additional minutes. The N₂ purge was monitored to reach DMAc pH of 3-4. The reaction mixture was a homogenous clear solution.

A portion of the reaction mixture was isolated into methanol, washed, and dried for analysis. The ¹H NMR spectra was obtained in

20 DMSO/LiCl and showed conversion to 0.97 DoS.

Example 2

This example targeted a 0.5 DoS with approximate 10% functional solids. Example 2 was run similarly to Example 1 but without the IR probe

25 and with additions as specified here. Glucan #1 powder was weighed (158 g with 99.8% solids, 0.98 moles) charged with DMAc (1894 g) into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to

30 change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29 inches Hg and the temperature

equilibrated to 80-85 °C. DMAc and water were distilled. The volume of the liquor overhead was 185 mL. The vessel was cooled to 45 °C in 1 hour and purged with nitrogen. Acetyl chloride (37 mL, 41 g, 0.52 moles) was drawn into a calibrated glass syringe. The acetyl chloride was added over 4 minutes. An exotherm was observed over 7 minutes with an increase in temperature to 51 °C. The mixture gelled quickly and was agitated for 25 minutes. The N₂ purge was monitored to reach DMAc pH of 3-4. The reaction mixture cleared after stirring at 45 °C for 30 minutes and was cooled after an additional hour of stirring.

Example 3

This example targeted a 1.5 DoS with approximate 10% functional solids. This example was run similarly to Example 1 but without the IR probe and with additions as specified here. Glucan #1 powder was weighed (253 g with 99.8% solids, 1.56 moles) charged with DMAc (2810 g) into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29 inches Hg and the temperature equilibrated to 80-85 °C. DMAc and water were distilled. The volume of the liquor overhead was 275 mL. The vessel was cooled to 45 °C in 2 hours and purged with nitrogen. In portions acetyl chloride was drawn into a calibrated glass syringe. The first 50 mL portion of acetyl chloride was added over 2 minutes. An exotherm was observed over the 2 minutes with an increase in temperature to 48 °C. Further addition of acyl chloride resumed with addition of 26 mL, 20 mL and 15 mL over 8 minutes with a temperature rise of 6 °C. Further addition of acyl chloride resumed with 56 mL over 5 minutes. The N₂ purge was monitored to reach DMAc pH of 3-4. The reaction mixture cleared and was cooled after an additional hour of stirring.

Example 4

This example targeted a DoS of 1 with approximate 10% functional solids. This example was run similarly to Example 2, using a rotor stator to disperse the powder in DMAc, and additions as specified here. In a beaker Glucan #1 powder was weighed (185 g with 99.8% solids, 1.14 moles), mixed with DMAc (2000 g) and rotor-statured to a dispersion. The dispersion was charged into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29 inches Hg and the temperature equilibrated to 80-85 °C. DMAc and water were distilled. The volume of the liquor overhead was 200 mL. The vessel was cooled to 45 °C in 1 hour and purged with nitrogen. Acetyl chloride (40.5 mL, 45 g, 0.56 moles) was drawn into a calibrated glass syringe. The acetyl chloride was added quickly under a minute. A second portion of acetyl chloride (40.5 mL, 45 g, 0.56 moles) was drawn into a calibrated glass syringe and added under a minute. The mixture gelled and an exotherm was observed over 2 minutes with an increase in temperature to 56 °C. The N₂ purge was monitored to reach DMAc pH of 3-4. The reaction mixture was mixed at 45 °C for 30 minutes to a homogenous clear solution.

Example 5

This example targeted a DoS of 1 with approximate 10% functional solids. This example was run using Glucan #2 wet-cake washed with three half liter aliquots of acetone. The washed Glucan #2 (70 g dry basis, 0.43 moles) was then mixed with 900 g DMAc and was rotor-statured in a beaker for a minute. The Glucan #2 mixture was added to the 2L jacketed reactor and assembly of the reactor was completed with U-shaped Teflon

coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The dispersion was heated to 86 °C. Vacuum of 28 inches Hg was applied and dropped the temperature to 5 80 °C. Distillation of DMAc and acetone was completed in 10 minutes. The volume of the liquor overhead was 90 mL. The vessel was cooled to 45 °C in 1 hour and purged with nitrogen. Acetyl chloride (20 mL, 0.28 moles) was added by syringe in under a minute. The exotherm was monitored and temperature increased by 5 °C. The viscosity increased 10 instantly. Heating was maintained and set to 50 °C. Some gels remained after 20 minutes of stirring. A second portion of acetyl chloride (20 mL, 0.28 moles) was added by syringe in under a minute. The exotherm was monitored and temperature increased by 5 °C. After 3 minutes, the viscosity dropped and the appearance of the solution was clear. The N₂ 15 purge was monitored to reach DMAc pH of 3-4 over 2 hours from the first acetyl chloride addition. The solution was stirred under reduced pressure to degas the solution.

A portion of the solution was isolated and solids were found to be 11.6 wt%.

20

In Situ Preparation of Glucan Benzoate

The set-up included a reaction kettle, nitrogen, vacuum, stirring, an optional scrubber. The final solution can be used in a process without isolating the glucan benzoate.

25

Example 6

This example targeted a DoS of 1 with approximate 10% functional solids. This example was run similarly to Example 4, using a rotor stator to disperse the powder in DMAc, and additions as specified here. In a 30 beaker Glucan #1 powder was weighed (73.4 g with 99.8% solids, 0.45 moles), mixed with DMAc (939 g) and rotor statored to a dispersion. The

dispersion was charged into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29 inches Hg and the temperature equilibrated to 78 °C. DMAc and water were distilled. The volume of the liquor overhead was 100 mL. The vessel was cooled for 18 hours and purged with nitrogen. The vessel was reheated to 88 °C. Benzoyl chloride (52.6 mL, 63.7 g, 0.45 moles) was drawn into a calibrated glass syringe. The benzoyl chloride was added quickly under a minute. The mixture gelled after 20 minutes of reaction time and an exotherm was not readily observed. After 5 additional minutes the gelling resulted in the whole mass to stop stirring. After an additional 2 minutes the reaction appeared to lower in viscosity and clear. For a total time of 1 hour, the reaction was complete. The N₂ purge was monitored to reach DMAc pH of 3-4. Vacuum was applied to the reaction but nothing distilled over.

A portion of the solution was isolated and solids were found to be 9.9 wt%. By mass balance the DoS was observed to be 0.74 DoS.

Example 7

This example targeted a DoS of 1 with approximate 10% functional solids. This example was run similarly to Example 6, using a rotor stator to disperse the powder in DMAc, and additions as specified here. In a beaker Glucan #1 powder was weighed (73.4 g with 99.8% solids, 0.45 moles), mixed with DMAc (939 g) and rotor stator to a dispersion. The dispersion was charged into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29

inches Hg and the temperature equilibrated to 93 °C. DMAc and water were distilled. The volume of the liquor overhead was 100 mL. The vessel was cooled for 20 minutes to 95 °C and purged with nitrogen. Benzoyl chloride (52.6 mL, 63.7 g, 0.45 moles) was drawn into a calibrated glass syringe. The benzoyl chloride was added quickly under a minute. The mixture gelled after 20 minutes of reaction time and an exotherm was not readily observed. After 30 additional minutes, the reaction appeared to lower in viscosity and clear. The N₂ purge was monitored to reach DMAc pH of 3-4. Vacuum was applied to the reaction but nothing distilled over. A 55 mL sample of solution was isolated and sampled for solids. Solids were found to be 9.3 wt%. The remaining solution was stirred at 55 °C for 18 hours and solids were found to be 9.9 wt%.

Example 8

This example targeted DoS 0.5 with approximate 20% functional solids. This example was run similarly to Example 6 but with no rotor stator, and additions as specified here. The Glucan #1 powder was weighed (72 g with 99.8% solids, 0.44 moles) and mixed with DMAc (460 g) into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29 inches Hg and the temperature equilibrated to 76 °C. DMAc and water were distilled. The volume of the liquor overhead was 50 mL. The vessel was equilibrated for 20 minutes to 95 °C and purged with nitrogen. Benzoyl chloride (26 mL, 31.2 g, 0.22 moles) was drawn into a calibrated glass syringe. The benzoyl chloride was added quickly under a minute. The mixture gelled after 6 minutes of reaction time and an exotherm was not readily observed. After 10 additional minutes, the reaction remained highly viscous. After a total of an hour of mixing, the reaction appeared to

decrease in viscosity and clear with time. The N₂ purge was monitored to reach DMAc pH of 3-4. The solution was clear and was poured from the reactor.

5

Example 9

This example targeted DoS 0.5 with approximate 10% functional solids. This example was run similarly to Example 8 but with no rotor stator, and additions as specified here. The Glucan #1 powder was weighed (36 g with 99.8% solids, 0.22 moles) and mixed with DMAc (460 g) into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 28-29 inches Hg and the temperature equilibrated to 84 °C. DMAc and water were distilled. The volume of the liquor overhead was 65 mL. The vessel was equilibrated for 30 minutes to 90 °C and purged with nitrogen. Benzoyl chloride (15 mL, 18 g, 0.13 moles) was drawn into a calibrated glass syringe. The benzoyl chloride was added quickly under a minute. The mixture gelled after an hour of mixing and an exotherm was not readily observed. After an additional hour of mixing, the reaction appeared to decrease in viscosity and clear with time. The N₂ purge was monitored to reach DMAc pH of 3-4. The solution was clear and poured from the reactor.

25

Example 10

This example targeted DoS 0.75 with approximate 8% functional solids. This example was run similarly to Example 9 but with no rotor stator, and additions as specified here. The Glucan #1 powder was weighed (73.4 g with 99.8% solids, 0.44 moles) and mixed with DMAc (937 g) into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser

connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 28-29 inches Hg and the temperature equilibrated to 82 °C. DMAc and water were distilled. The volume of the liquor overhead was 100 mL. The vessel was equilibrated for 45 minutes to 90 °C and purged with nitrogen. Benzoyl chloride (26.3 mL, 31.6 g, 0.22 moles) was drawn into a calibrated glass syringe. The benzoyl chloride was added quickly under a minute. The mixture gelled after 40 minutes of mixing and an exotherm was not readily observed. After an additional 30 minutes of mixing, the reaction mixture appeared to decrease in viscosity and remained slightly cloudy. An additional charge of benzoyl chloride (13 mL, 16 g, 0.11 moles) was added. The N₂ purge was monitored to reach DMAc pH of 3-4. The solution was clear and poured from the reactor. A portion was isolated and solids were found to be 6.1 wt%.

In Situ Preparation of Glucan Propionate

Example 11

This example targeted DoS 1 with approximate 10% functional solids. This example was run similarly to Example 7, using a rotor stator to disperse the powder in DMAc, and additions as specified here. In a beaker Glucan #1 powder was weighed (73.4 g with 99.8% solids, 0.45 moles), mixed with DMAc (939 g) and rotor stator to a dispersion. The dispersion was charged into a 2L jacketed reaction kettle equipped with U-shaped Teflon coated motor driven stir, nitrogen inlet, thermocouple, vigreux condenser connected to second condenser with collection funnel and vacuum with valves to change vacuum/nitrogen flow. The vessel was heated to 100 °C over an hour. Vacuum was slowly applied to 27-29 inches Hg and the temperature equilibrated to 88 °C. DMAc and water were distilled. The volume of the liquor overhead was 105 mL. The vessel was cooled for 36 minutes to 65 °C and purged with nitrogen.

Propionyl chloride (40.3 mL, 42.7 g, 0.46 moles) was drawn into a calibrated glass syringe. The propionyl chloride was added quickly under a minute. The mixture showed an increase in viscosity in 4 minutes and exotherm of 8 °C. The reaction mixture cleared with an additional 2 minutes of stirring. The N₂ purge was monitored to reach DMAc pH of 3-4. Vacuum was applied to the reaction but nothing distilled over. A 35 g sample of solution was isolated into methanol and washed. Solids were found to be 10.2% solids.

10

In Situ Preparation of Glucan Laurate

Example 12

This example reached a DoS of 1.2 and approximately 15% functional solids. In a 250 mL 3 neck flask with stir bar, nitrogen purge, condenser, glucan (5 g, 99.8% solids, 0.030 moles) was added, then DMAc was added. The glucan/DMAc was heated to 100 °C. Upon cooling to 60 °C lauryl chloride (15.8 g, 14.3 mL, 0.065 moles) was added via an addition funnel. After 10 minutes of stirring the reaction began to gel to a honey like consistency. With 10 additional minutes, the gel began to re-disperse to lower viscosity. After 3 additional hours the polymer was isolated as 12.7 g white fluffy powder. NMR in CDCl₃ showed conversion to 1.2 DoS.

20

Example 13

This example reached a DoS of 0.5 and approximately 10% functional solids. In a 250 mL 3 neck flask with stir bar, nitrogen purge, condenser, glucan (5 g, 99.8% solids, 0.031 moles) was added, then DMAc was added. The glucan/DMAc was heated to 100 °C. Upon cooling to 60 °C lauryl chloride (6.75 g, 7.13 mL, 0.031 moles) was added via an addition funnel. After 5 minutes of stirring the reaction began to gel to a honey like consistency and some graniness. After 3 additional hours

25

30

the polymer was isolated as 8.35 g white fluffy powder. NMR in DMSO showed conversion to 0.5 DoS.

Example 14

5 This example targeted a 1 DoS with approximately 10% functional solids. In a 2L 4-port round bottom flask with nitrogen purge vertical condenser and distillation condenser, collection flask and vacuum port, Glucan #1 100.5 g (0.62 moles) and 1118 g DMAc (3126.55 ppm water) were added. Under reduced pressure using an aspirator and controller,
10 water was distilled from the slurry over a period of an hour at 95 °C. In the collection flask 30 mL water was collected. The vacuum was removed and the system was equilibrated under nitrogen. The temperature was reduced to 45 °C over 30 additional minutes. When the mixture reached 45 °C, acetyl chloride (52.78 g, 48 mL, 0.67 moles) was added over 3
15 minutes. A temperature rise was observed of 11 °C. Viscosity also increased after the addition of the acetyl chloride. After 30 minutes of reaction, the solution was clear. Vacuum was applied for 2 minutes then returned to nitrogen purge for storing until used.

Application Examples

Example 15 Water Retention Value

25 Solids (powders) isolated from the material prepared in Example 3 and the material prepared in Example 6 were measured for water retention value (WRV) according to the standard method “Water Retention of Textile Fibers – ASTM D2402-07. Results are given in Table 2.

The water retention value of poly(alpha-1,3-glucan) without modification (i.e. with no esterification) was 80 units.

Table 2

Solids isolated from Example	3	6
Polysaccharide Ester	Glucan acetate	Glucan Benzoate, DoS 0.74
WRV	43	43

Example 16 Film Application.

5 The material prepared in Example 1 and the material prepared in Example 2 were cast into films using a casting blade. Solutions were cast using a doctor blade and coagulated into methanol. Both gave clear films with no observable particles.

10

In Situ Preparation of Glucan Acetate**Example 17**

To a 3L jacketed reactor equipped with a U-shaped Teflon coated motor driven stirrer, nitrogen inlet, thermocouple, vigreux column
15 connected to second condenser with collection funnel, and vacuum with valves to change vacuum/nitrogen flow was charged 1130 g DMAc and 56 g of calcium chloride. After the salt was dissolved, 80 g (0.49 moles) of glucan #1 was added under rapid agitation. The contents were held at 65 °C overnight to ensure complete dissolution of the glucan. Vacuum was
20 then slowly applied to 27-29 inches Hg to pull over DMAc and any water present. After 161 g were removed, the pressure was brought back to atmospheric and the reactor was held under a slow nitrogen purge. Using a syringe, 48 mL (0.25 moles) of tripropylamine were added. This was followed immediately by the addition of 93 mL (0.98 moles) of acetic
25 anhydride. The batch temperature was held at 80 °C for 3 hours. The heater was turned off and vacuum was applied to remove DMAc to cool the reactor contents and raise the viscosity of the reactor liquor.

Gravimetric analysis of a sample precipitated into methanol/isopropyl alcohol indicated the presence of 10.4% solids in the final liquor. Dried powder was dissolved in DMSO with 2% w/v LiCl to yield a reduced viscosity of 1.60 dL/g. The ¹H NMR spectra obtained in
5 DMSO/LiCl indicated an acetate DOS of 0.70. No undissolved particles were seen by microscopic examination in a dope consisting of 10% dried powder in DMF.

Example 18

10 To a 1L reactor submerged in a hot oil bath equipped with a Teflon coated motor driven anchor stirrer, nitrogen inlet, thermocouple, vigreux column connected to second condenser with collection funnel, and vacuum with valves to change vacuum/nitrogen flow was charged 500 g DMF followed by 50.8 g (0.31 moles) of glucan #1. The reactor was held
15 under a slow nitrogen purge while the temperature of the contents was raised to 86 °C. Using a syringe, 34 mL (0.24 moles) of triethylamine were added. This was followed immediately by the addition of 73 mL (0.77 moles) of acetic anhydride. The batch temperature was held at 85-90 °C for 7 hours. Samples were pulled for microscopic examination to
20 determine the extent of solids dissolution. When clear, the oil bath was lowered away from the reactor to allow the contents to cool. Vacuum was applied briefly to remove unreacted amine and anhydride.

Gravimetric analysis of a sample precipitated into 50/50 v/v methanol/water indicated the presence of 11.7% solids in the final liquor.
25 Dried powder was dissolved in DMSO with 2% w/v LiCl to yield a reduced viscosity of 1.91 dL/g. The ¹H NMR spectra obtained in DMSO/LiCl indicated an acetate DOS of 2.5. No undissolved particles were seen by microscopic examination of a dope consisting of 10% dried powder in DMF.

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Example 19

To a 1L jacketed reactor equipped with a Teflon motor driven half-moon shaped stirrer, nitrogen inlet, react-IR probe, thermocouple, short-path column condenser with collection flask and sparging aspiration flask, and vacuum with valves to change vacuum/nitrogen flow was charged 490 g DMF followed by 15 g (0.09 moles) of glucan #1. The reactor was held under a slow nitrogen purge while the temperature of the contents was raised to 90 °C. Using a syringe, 1.2 mL (0.008 moles) of 1,8-Diazabicyclo[5.4.0]undec-7-ene were added. This was followed immediately by the addition of 29.6 mL (0.32 moles) of vinyl acetate. The batch temperature was held at 90 °C for 1 hour while monitoring the progress of the reaction by react-IR. When the product ester peak at 1742 cm^{-1} leveled and reactor contents were clear, the contents were cooled by applying cooling to the jacket.

For analysis, a sample was precipitated into water, washed several times with water, then methanol. The ^1H NMR spectra obtained in DMSO/LiCl indicated an acetate DOS of 1.9.

Example 20

To a 1L jacketed reactor equipped with a Teflon motor driven half-moon shaped stirrer, nitrogen inlet, react-IR probe, thermocouple, short-path column condenser with collection flask and sparging aspiration flask, and vacuum with valves to change vacuum/nitrogen flow was charged 490 g DMF followed by 40 g (0.25 moles) of glucan #1. The reactor was held under a slow nitrogen purge while the temperature of the contents was raised to 90 °C. Using a syringe, 3.7 mL (0.025 moles) of 1,8-Diazabicyclo[5.4.0]undec-7-ene were added. This was followed immediately by the addition of 45.5 mL (0.49 moles) of vinyl acetate. The batch temperature was held at 90 °C for 1 hour while monitoring the progress of the reaction by react-IR. When the product ester peak at 1742

cm⁻¹ leveled and reactor contents were clear, the contents were cooled by applying cooling to the jacket.

For analysis, a sample was precipitated into water, washed several times with water, then methanol. The ¹H NMR spectra obtained in

5 DMSO/LiCl indicated an acetate DOS of 1.9.

Example 21

To a 1L jacketed reactor equipped with a Teflon motor driven half-moon shaped stirrer, nitrogen inlet, react-IR probe, thermocouple, short-path column condenser with collection flask and sparging aspiration flask,
10 and vacuum with valves to change vacuum/nitrogen flow was charged 490 g DMF followed by 40 g (0.25 moles) of glucan #1. The reactor was held under a slow nitrogen purge while the temperature of the contents was raised to 90 °C. Using a syringe, 3.7 mL (0.025 moles) of 1,8-
15 Diazabicyclo[5.4.0]undec-7-ene were added. This was followed immediately by the addition of 22.75 mL (0.25 moles) of vinyl acetate. The batch temperature was held at 90 °C for 1 hour while monitoring the progress of the reaction by react-IR. When the product ester peak at 1742 cm⁻¹ leveled and reactor contents were clear, the contents were cooled by
20 applying cooling to the jacket.

For analysis, a sample was precipitated into water, washed several times with water, then methanol. The ¹H NMR spectra obtained in DMSO/LiCl indicated an acetate DOS of 0.6.

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Example 22

To a 1L jacketed reactor equipped with a Teflon motor driven half-moon shaped stirrer, nitrogen inlet, react-IR probe, thermocouple, short-path column condenser with collection flask and sparging aspiration flask, and vacuum with valves to change vacuum/nitrogen flow was charged 490
30 g DMF followed by 40 g (0.25 moles) of glucan #1. The reactor was held under a slow nitrogen purge while the temperature of the contents was

raised to 90 °C. Using a syringe, 0.92 ml (0.006 moles) of 1,8-Diazabicyclo[5.4.0]undec-7-ene were added. This was followed immediately by the addition of 45.5 mL (0.49 moles) of vinyl acetate. The batch temperature was held at 90 °C for 1 hour while monitoring the progress of the reaction by react-IR. When the product ester peak at 1742 cm⁻¹ leveled and reactor contents were clear, the contents were cooled by applying cooling to the jacket.

For analysis, a sample was precipitated into water, washed several times with water, then methanol. The ¹H NMR spectra obtained in DMSO/LiCl indicated an acetate DOS of 1.8.

In Situ Preparation of Glucan Benzoate

Example 23

To a 3L jacketed reactor equipped with a U-shaped Teflon coated motor driven stirrer, nitrogen inlet, thermocouple, vigreux column connected to second condenser with collection funnel, and vacuum with valves to change vacuum/nitrogen flow was charged 1130 g DMAc and 56 g of calcium chloride. After the salt was dissolved, 80 g (0.49 moles) of glucan #1 was added under rapid agitation. The contents were held at 65 °C overnight to ensure complete dissolution of the glucan. Vacuum was then slowly applied to 27-29 inches Hg to pull over DMAc and any water present. After 151 g were removed, the pressure was brought back to atmospheric and the reactor was held under a slow nitrogen purge. Using a syringe, 48 mL (0.25 moles) of tripropylamine were added. This was followed immediately by the addition of 222 g (0.98 moles) of benzoic anhydride dissolved in 100 g of DMAc. The batch temperature was held at 80 °C for 7 hours. The heater was turned off and vacuum was applied to remove DMAc to cool the reactor contents and raise the viscosity of the reactor liquor. A total of 218 g of liquid was removed.

Gravimetric analysis of a sample precipitated into water followed by 3 methanol washes indicated the presence of 9.0 % solids in the final liquor. Dried powder was dissolved in DMSO with 2% w/v LiCl to yield a reduced viscosity of 1.58 dL/g. The ¹H NMR spectra obtained in
5 DMSO/LiCl indicated a benzoate DOS of 0.76. No undissolved particles were seen by microscopic examination in a dope consisting of 10% dried powder in DMF.

Example 24

10 To a 1L jacketed reactor equipped with a Teflon motor driven half-moon shaped stirrer, nitrogen inlet, react-IR probe, thermocouple, short-path column condenser with collection flask and sparging aspiration flask, and vacuum with valves to change vacuum/nitrogen flow was charged 490 g DMF followed by 15 g (0.09 moles) of glucan #1. The reactor was held
15 under a slow nitrogen purge while the temperature of the contents was raised to 90 °C. Using a syringe, 1.2 mL (0.008 moles) of 1,8-Diazabicyclo[5.4.0]undec-7-ene were added. This was followed immediately by the addition of 44.4 mL (0.32 moles) of vinyl benzoate. The batch temperature was held at 90 °C for 1 hour while monitoring the
20 progress of the reaction by react-IR. When the product ester peak at 1742 cm⁻¹ leveled and reactor contents were clear, the contents were cooled by applying cooling to the jacket.

For analysis, a sample was precipitated into water, washed several time with water, then methanol. The ¹H NMR spectra obtained in
25 DMSO/LiCl indicated an acetate DOS of 1.2.

CLAIMS

What is claimed is:

- 5 1. A process comprising the step:
 a) contacting an esterifying agent and a polysaccharide in the
 presence of a solvent and suitable reaction conditions for a reaction time
 sufficient to form a product comprising a polysaccharide ester composition,
 the polysaccharide ester composition comprising a polysaccharide ester
10 compound having a degree of substitution of about 0.001 to about 3;
 wherein the esterifying agent comprises an acyl halide, a
 phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a
 carbonic acid ester, or a vinyl ester; and
 the ratio of esterifying agent to polysaccharide is in the range of
15 about 0.001:1 to about 3:1 on a molar equivalent basis.
2. The process of claim 1, wherein the esterifying agent comprises an
 acyl halide, and the acyl halide comprises acetyl chloride, benzoyl
 chloride, propanoyl chloride, hexanoyl chloride, acetyl bromide, benzoyl
20 bromide, propanoyl bromide, acetyl iodide, benzoyl iodide, or propanoyl
 iodide.
3. The process of claim 1, wherein the esterifying agent comprises a
 phosphoryl halide, a haloformic acid ester, or a carbonic acid ester.
25
4. The process of claim 1, wherein the esterifying agent comprises a
 carboxylic acid anhydride or a vinyl ester.
5. The process of claim 1, wherein the esterifying agent comprises an
30 acyl halide, and the solvent is selected from dimethylacetamide,

tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof.

6. The process of claim 1, wherein the esterifying agent is a
5 phosphoryl halide, a carboxylic acid anhydride, a haloformic acid ester, a carbonic acid ester, or a vinyl ester, and the solvent is selected from dimethylacetamide, dimethylformamide, tetrahydrofuran, acetonitrile, acetone, methyl ethyl ketone, or a mixture thereof.

10 7. The process of claim 1, wherein the suitable reaction conditions include a reaction temperature in the range of about 30 °C to about 175 °C.

8. The process of claim 1, wherein the polysaccharide comprises poly
15 alpha-1,3-glucan, poly alpha-1,3-1,6-glucan, or dextran.

9. The process of claim 1, wherein the polysaccharide ester composition comprises a polysaccharide ester compound wherein at least one ester group comprises a C₂-C₂₀ acyl group.

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10. The process of claim 1, wherein the step a) contacting an esterifying agent with a polysaccharide in the presence of a solvent further comprises the steps of:

25 i) contacting the polysaccharide and the solvent to form an initial mixture comprising water;

ii) heating the initial mixture;

iii) removing at least a portion of the water from the initial mixture under reduced pressure to obtain a mixture comprising a reduced water content; and

30 iv) adding the esterifying agent to the mixture comprising a reduced water content.

11. The process of claim 1, further comprising a step of removing at least a portion of the byproduct acid halide formed in the contacting step a).

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12. The process of claim 1, further comprising a step of combining the product comprising a polysaccharide ester composition with a polymer dispersed in or dissolved in a second solvent to form a blend of the polysaccharide ester composition and the polymer.

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13. The process of claim 12, further comprising a step of casting a film from the blend, coating a substrate with the blend, or spinning fibers from the blend.

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14. The process of claim 12, wherein the polymer comprises polyacrylates, polyaramids, polyphenylene isophthalamide, poly-m-phenylene isophthalamide, polyphenylene terephthalamide, vinyl polymers, polyethylene, polypropylene, poly(vinyl chloride), polystyrene, polytetrafluoroethylene, poly(alpha -methylstyrene), poly(acrylic acid), poly(isobutylene), poly(methacrylic acid), poly(methyl methacrylate), poly(1-pentene), poly(1,3-butadiene), poly(vinyl acetate), poly(2-vinyl pyridine), 1,4-polyisoprene, 3,4-polychloroprene, polyethers, poly(ethylene oxide), poly(propylene oxide), poly(trimethylene glycol), poly(tetramethylene glycol), polyacetals, polyformaldehyde, polyacetaldehyde, polyesters, poly(3-propionate), poly(10-decanoate), poly(ethylene terephthalate), poly(m-phenylene terephthalate); polyamides, polycaprolactam, poly(11-undecanoamide), poly(hexamethylene sebacamide), poly(tetramethylene-m-benzenesulfonamide), polyetheretherketone, polyetherimide, poly(phenylene oxide), polyamide (including polyureas), polyamideimide, polyarylate, polybenzimidazole, polycarbonates, polyurethane, polyimide,

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polyhydrazide, phenolic resins, polysilane, polysiloxane, polycarbodiimide, polyimine, azo polymers, polysulfide, polysulfane, cellulose polymers, or starch polymers.

- 5 15. A polysaccharide ester composition obtained by the process of claim 1.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/062515

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08B37/00
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)
C08B

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, BIOSIS, EMBASE, 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	EP 1 666 930 A1 (NIPPON KAYAKU KK [JP]; POLATECHNO CO LTD [JP]) 7 June 2006 (2006-06-07) examples 1-3	1,2,5, 7-15
X	WO 2013/133436 A1 (UNIV KYOTO [JP]) 12 September 2013 (2013-09-12) paragraph [0251] - paragraph [0576]	1,2,5, 7-15
X	US 2 992 214 A (MENCH JOHN W ET AL) 11 July 1961 (1961-07-11) claims 1-3	1,2,5, 7-15
X	EP 1 983 006 A1 (DAICEL CHEM [JP]) 22 October 2008 (2008-10-22) paragraphs [0000], [400069], [0092]	1,2,5, 7-15
	-/-	



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 application or patent 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

26 January 2018

Date of mailing of the international search report

16/04/2018

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/062515

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1, 2, 5, 7-15(all partially)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2017/062515

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	IAN CUMPSTEY: "Chemical Modification of Polysaccharides", ISRN ORGANIC CHEMISTRY, vol. 2013, 1 January 2013 (2013-01-01), pages 1-27, XP055351340, DOI: 10.1155/2013/417672 the whole document	1,2,5, 7-15
X,P	----- WO 2017/175752 A1 (DAICEL CORP [JP]) 12 October 2017 (2017-10-12) example 7 -----	1,2,5, 7-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/062515

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			TW 200806692 A 01-02-2008
			US 2010228019 A1 09-09-2010
			WO 2007086318 A1 02-08-2007
WO 2017175752	A1	12-10-2017	NONE

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1, 2, 5, 7-15(all partially)

Esters from a polysaccharide and an acyl halide

2. claims: 1, 3, 5-15(all partially)

Ester from a polysaccharide and an phosphoryl halide.

3. claims: 1, 4-15(all partially)

Ester from a polysaccharide and a carboxylic acid anhydride.

4. claims: 1, 3, 5-15(all partially)

Ester from a polysaccharide and a haloformic acid ester.

5. claims: 1, 3, 5-15(all partially)

Ester from a polysaccharide and a carbonic acid ester.

6. claims: 1, 4-15(all partially)

Ester from a polysaccharide and a vinyl ester.

7. claims: 1-15(partially)

Ester from an alpha-1,3-glucan.

8. claims: 1-15(partially)

Composites from a polysaccharide ester with a further polymer.
