CURABLE BIOPOLYMER NANOPARTICLE LATEX BINDER FOR MINERAL, NATURAL ORGANIC, OR SYNTHETIC FIBER PRODUCTS AND NON-WOVEN MATS

Inventors: Alexander Tseitlin, Halton Hills (CA); David Van Abstyn, Burlington (CA); Steven Bloembergen, Okemos, MI (US)

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ABSTRACT
A curable aqueous binder composition includes a dispersion of biopolymer particles, optionally with and an inter-particle crosslinking agent, for use in the formation of composite materials such as mineral, natural organic, or synthetic fiber products, including mineral fiber insulation, non-woven mats, fiberglass insulation and related glass fiber products, and wood based products, and construction materials. In an application of the curable aqueous composition to making fiberglass insulation, the composition may be blended with a second resin which may be a non-formaldehyde resin. In an application of the composition to making fiberglass roofing shingles, the biopolymer particles may be mixed into a formaldehyde based resin during or after the polymerization of the resin.
Stage 1: Free-Flowing Binder Composition

Interim Stages: Mat Formation & Fluffing

Final Stage: Drying & Curing

Aqueous dispersion of internally crosslinked nanoparticles plus a multi-functional crosslinker R

Biopolymer nanoparticles are film forming to form clusters that contain additional crosslinker R adsorbed onto their surfaces

Biopolymer nanoparticles clusters undergo drying & inter-particle crosslinking to bond mineral fibers

FIGURE 2
CURABLE BIOPOLYMER NANOPARTICLE LATEX BINDER FOR MINERAL, NATURAL ORGANIC, OR SYNTHETIC FIBER PRODUCTS AND NON-WOVEN MATS

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This patent claims the benefit of U.S. provisional patent application No. 61/493,266 filed on Jun. 3, 2011 which is incorporated herein by this reference to it.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

[0002] Not Applicable.

BACKGROUND OF THE INVENTION

[0003] 1. Field of the Invention
[0004] This invention relates to a curable composition, for example a composition useful for forming a composite material comprising biopolymer particles, and to composite materials, for example mineral fiber insulation and roofing shingles.
[0005] 2. Description of the Related Art
[0006] The following discussion is not an admission that anything described below is common knowledge of persons skilled in the art, or citable as prior art.
[0007] Mineral fibers used in insulation products and non-woven mats are usually bonded together with a crosslinked binder resin. The binder has to provide the resilience for recovery after packaging (in the case of insulation products) as well as stiffness and compatibility between individual fibers.
[0008] The process for making mineral fiber products such as fiberglass insulation typically includes melting minerals, sand or recycled glass, producing a molten glass stream that is passed through high pressure air fiberizers or “spinning wheels” where the glass is then spun into thin fibers and transported onto a belt to form the fiberglass insulation product. Given the enormous volume and surface area expansion, the temperature drops almost instantaneously from the red hot mineral stream to the relatively cool mineral fibers. This rapid drop in temperature facilitates the application of an aqueous polymeric binder composition immediately following the fiberizer without substantially degrading the polymer and other binder components, and even more importantly, without triggering premature curing and crosslinking such that the subsequent sections of the manufacturing process can be used to control the dimensions of the fiberglass mat product. The fibers are then blown to a conveyor or forming chamber where they are dried and cured. As part of this process, the coated mat is generally transferred to a forming or air-fluffing chamber and subsequently a curing oven to cure the binder and bond the glass fibers together. Prior to the curing process, the degree of fluffing facilitates the control over the dimensions of the particular grade of mineral fiber product.

[0009] The dominant binders for insulation and non-woven mats as well as for wood products are formaldehyde based resins, such as phenol-formaldehyde (PF), melamine-formaldehyde (MF), and urea-formaldehyde (UF) resins and the like, as well as mixed phenol/urea-formaldehyde (P/UF) resins and the like. A serious disadvantage of formaldehyde-based resins is the release of free formaldehyde to the environment during manufacturing and use, contaminating the air that we breathe which is undesirable for health and ecological reasons. Note that formaldehyde has been reported to be a human carcinogen (IARC 2004). IARC classified Formaldehyde as Carcinogenic to Humans. IARC Press Release No. 153, International Agency for Research on Cancer, available at www.iarc.fr/en/media-centre/pr/2004/pr153.html. Substances Profile: Formaldehyde Gas. Report on Carcinogens, 11th Edition. National Toxicology Program, available at http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s089form.pdf; and National Emissions Standard for Formaldehyde in Composite Wood Products Becomes Law, found at http://www.augs.com/ DesktopDefaultaspx?mid=168&tabid=82&ItemID=30). In addition to the health and environmental problems, further compounding the problem is that the lowest cost formaldehyde based binders are based on UF resins. Therefore, UF has traditionally been the dominant binder system used in mineral fiber products, fiberglass insulation, nonwovens as well as wood products, such as particle board, plywood and oriented strand board (OSB) products. Of all the formaldehyde based resins, UF is the least stable to hydrolysis especially at elevated temperature (30-45°C, or higher) and humidity, it has commonly been the preferred binder for indoor uses (such as particle board used in kitchen cabinets, countertops, furniture, etc.), where air contamination and human exposure risks are highest. This problem recently gained visibility in the US when hurricanes Katrina and Rita devastated the Louisiana, Mississippi and Alabama coastlines. The problem was brought to the forefront following serious health and air quality complaints by displaced hurricane victims and concerns arose over high levels of formaldehyde found in some travel trailers and temporary housing (FEMA trailers). Survivors housed in the trailers were exposed to high levels of formaldehyde due to the hot and humid conditions of the local climate (Four Years Later: Formaldehyde Exposure & Emissions Standards, Product Evaluations Technology Brief by Air Quality Sciences, Inc., Volume 9, Issue 9). The somewhat more costly pure PF and MF resins are generally more stable to hydrolysis. These resins are typically used in outdoor applications, and therefore their main challenge is worker exposure during manufacturing, while in-use release of formaldehyde is less of a concern, especially in outdoor applications. Note, however, that PF resin products shipped by the resin supplier may contain a significant level of free formaldehyde, which then needs to be reduced by the downstream (e.g. fiberglass) manufacturer in a pre-reaction. This is commonly done using urea to capture most of the free formaldehyde to result in mixed P/UF binder systems. Thus, the so-called PF binders used in these applications actually are P/UF systems which are prone to more free formaldehyde release in use given the UF portion is less stable to hydrolysis, especially at temperatures between 30-45°C, or higher.

[0010] In addition, formaldehyde based binders are petroleum-based synthetic products. In an era of depleting oil reserves and increasing costs of petrochemicals, the need to wean our industries away from their dependence on foreign oil has become paramount. Plant, animal and agro-based materials are in balance with nature and are “carbon neutral”, whereas petro-based materials are not because they are “carbon positive” (see Phil Greenall and Steven Bloembergen, “New generation of biobased latex coating binders for a sustainable future”, Paper Technology 52, No. 1, Paper Industry Technical Ass’n, p. 10-14, February 2011; and Do Ik Lee, Steven Bloembergen, and John van Leeuwen, “Development
of New Biobased Emulsion Binders”, PaperCon2010 Meeting, “Talent, Technology and Transformation”, Atlanta, Ga., May 2-5, 2010. Biobased materials offer a much reduced carbon footprint, and green agro-based products are becoming more and more important in an age where greenhouse gas (GHG) emissions are escalating.

However, traditional biobased industrial materials derived from agricultural crops are generally viewed by manufacturing and packaging industries as less consistent and inferior to the dominant petrochemical-based synthetic products.

Various attempts have been made to reduce undesirable formaldehyde emissions as well as developing formaldehyde-free binders and use other synthetic oil-derived polymer resins, as well as traditional modified soluble starches, dextrins or other low performance biobased materials. However, these have serious shortcomings such as high cost, high corrosion, high viscosity, dark color, lack of rigidity, water sensitivity, poor bond strength, etc.

A number of formaldehyde-free compositions have been developed for use as a binder for making nonwoven products.

U.S. Pat. No. 5,977,232 discloses a formaldehyde-free binder for glass wool insulation based on carboxylic acid which is corrosive due to the low pH of the system. This technology has been found to result in major corrosion problems with the equipment used to manufacture fiberglass insulating products, as well as in-use applications where metal wall studs and other metal components are being used in combination with the fiber glass insulation product.

U.S. Patent Application No. 2003/0008586 discloses the use of polyvinyl alcohol (PVOH) as a formaldehyde-free binder solution for low binder nonwoven fiber mat useful for making wood product laminates. The binder produces high bonding strength with wood and is characterized by a relatively good storage stability (relative to formaldehyde resins). The binder is used at 5% concentration. The problem is the much higher cost of PVOH relative to conventional formaldehyde binder systems. In addition, since it is petroleum based it is a carbon positive material which is not environmentally preferred. Without any additional enhancer, this binder does not provide sufficient wet strength and water resistance.

U.S. Pat. Nos. 6,221,973 and 6,331,350 describe a formaldehyde-free fiberglass binder including a polyacid, such as polycrylic acid, and a polyal, with a molecular weight less than about 1000, such as, for example, glycerol, triethanolamine, sorbitol, or ethylene glycol. A phosphorous catalyst is used to accelerate the cure of the composition. The major disadvantage of this binder is high cost and low pH which causes corrosion of fiber glass mat production equipment and during in-use applications.

PCT Patent Application No. WO 2006/120523 describes a polyvinyl alcohol-based formaldehyde-free curable aqueous composition comprising PVOH crosslinked with multifunctional crosslinking agent (e.g. nonpolymeric polyacid, polyaldehyde or anhydride). Disadvantages of this system are low pH and high viscosity at relatively low solids content. The problems as mentioned above include the much higher cost of PVOH relative to conventional formaldehyde binder systems, and since it is petroleum based it is a carbon positive material which is not environmentally preferred. This binder is also corrosive due to relatively low pH (about 4) and does not provide the required water resistance.

U.S. Pat. No. 6,884,849 describes a polyalcohol-based binder composition comprising a low molecular weight polyalcoholic acid and a low molecular weight polyalcohol, such as PVOH having an average molecular weight between 200 and 13,000. The binder solution preferably comprises at least one cule catalyst or accelerator, such as sodium hypophosphate. The binder exhibits a high cure rate and provides a good recovery of the final nonwoven product. However, a practical use of such a composition for insulation production is limited because the high acidity of these binder compositions will cause corrosion of production lines and during the in-use applications. Moreover, whilst the strength of this binder is acceptable for some applications it is not as good as the commonly used formaldehyde based binders. In addition, since it is petroleum based it is a carbon positive material which is not environmentally preferred.

U.S. Patent Application No. 2004/0038017 describes a binder composition containing a substantially infinitely water-dilutable or dispersible adduct of a monomeric polyalcoholic acid component and a monomeric polyal component to yield a polyester. This binder requires a much longer time (up to 15 minutes) for curing under standard curing conditions, or a much higher temperature (of about 300° C.), which is a serious disadvantage.

U.S. Patent Application No. 2010/0080976 discloses formaldehyde-free mineral fiber insulation product based on a combination of polycarboxylic acid, sugar and ammonia. Such a system has relatively low water resistance, is dark in color and generates ammonia emissions upon cure. In addition, since it is petroleum based it is a carbon positive material which is not environmentally preferred.

Formaldehyde free binders disclosed in U.S. Patent Application No. 2007/0142596 and GB 2451719A relate to binders comprising Maillard reactants, in particular dextrone systems derived from a mixture of dextrose monohydrate, inhydros citric acid, water and aqueous ammonia. These binders turn dark brown on curing and have poor water and biological resistance.

While these references and other prior art systems disclose various formaldehyde-free systems for insulation and non-woven mats, they all have limitations with respect to developing binders that are effective as well as environmentally friendly.

High strength fiber mats are extremely popular in the building materials industry. Most non-woven fiber mats have numerous applications, including use in roofing, siding and floor underlayment, insulation facers, floor and ceiling tiling, and vehicle parts. The most common use of fiber mats is in roofing shingles, and in particular in asphalt roof shingles.

Various fiber mats and methods of making the same have been previously described. For example, U.S. Pat. Nos. 4,135,029, 4,258,098, 5,919,365, and 6,642,299 describe glass fiber mats made by a wet-laid process. Glass fiber mats made by the wet-laid process are formed from glass fibers held together by a binder material. The last two patents (U.S. Pat. Nos. 5,919,365 and 6,642,299) relate to improved wet
web strength with styrene-maleic anhydride copolymer (SMA), styrene-acrylate copolymers, and mixtures thereof. These binders have limited application due to high cost. In addition, they are petroleum based carbon positive materials which are not environmentally preferred.

[0025] Typically, in wet processed glass fiber mats, the binder is applied in liquid form and dispersed onto the glass fibers by a curtain type applicator. Conventional wet processes strive to produce a uniform coating of binder on the glass fibers. After the binder and glass fibers have been dried and cured, the glass fiber mat is cut as desired.

[0026] A major problem in the manufacturing process and use of some known fiber mats is inadequate wet web strength. The wet web strength of wet glass mat has significant impact on runability of glass mat production and mat properties. In order to prevent the wet web (glass mat) web from breaking during production, the production line speed has to be reduced due to lower wet web strength of the glass mat prior to curing. Also, lower wet web strength requires higher vacuum draw to support the wet web and minimize web breaks. But higher vacuum draw will lead to undesired mat properties, such as a high mat tensile ratio (i.e., the ratio of dry to wet tensile strengths).

[0027] Inadequate dry mat tensile strengths also can reduce the ability of the finished rood to resist stresses during its service lifetime on the roof. Because building materials generally, and roofing shingles in particular, are often subjected to a variety of weather conditions, the fiber mats should also maintain their strength characteristics under a wide range of conditions.

[0028] Among the attempts of improving glass fiber mat tensile strength, U.S. Pat. No. 4,430,158 claims improved tensile strength to a sized glass fiber mat by adding an anionic surfactant, such as sodium dodecylbenzene sulfonate, to the urea formaldehyde binder system, and U.S. Pat. No. 4,542,068 discloses a method of making a glass fiber mat in which the synthetic styrene butadiene binder system plus an alkyolated alkylamine is employed, while U.S. Pat. No. 7,272,915 describes a urea formaldehyde binder modified with acrylonitrile-butadiene-styrene copolymer providing increased tensile strength. A major problem in the manufacturing process and use of fiber mats is inadequate wet web strength, which cannot be provided by a urea formaldehyde resin without an additive, as illustrated by the related art described in this paragraph. In addition, since these binders are all petroleum based they are carbon positive materials and therefore not environmentally preferred.

[0029] U.S. Pat. No. 7,268,091 discloses a urea-formaldehyde binder, and a vinlypyrrolidone/acylic acid/lauryl methacrylate terpolymer. An aqueous binder composition containing a urea-formaldehyde resin modified with a watersoluble styrene-maleic anhydride copolymer is used in the preparation of fiber mats is described in U.S. Pat. No. 6,084,021. The main disadvantage of these binders is a necessity of preparing the binder before applying it on the glass fiber mat due to a limited stability of a resin/latex mixture. In addition, since these binders are petroleum based they are carbon positive materials which are not environmentally preferred.

[0030] In summary, various attempts have been made to reduce undesirable formaldehyde emissions as well as developing formaldehyde-free binders and use traditional modified starches and dextrins or other low performance bio-based materials. However, all of these to date have serious shortcomings such as high cost, high corrosivity, high viscosity, dark color, lack of rigidity, water sensitivity, poor bond strength, etc.

[0031] Multiple disclosures have been made regarding the composition and use of various forms of biopolymer nanoparticles. For instance, U.S. Pat. No. 6,677,386 (which corresponds to WO 00/69916) describes a process for producing biopolymer nanoparticles, which in one form are starch nanoparticles. In the process, the biopolymer is plasticized using shear forces, and a crosslinking agent is added during the processing. After the processing, the biopolymer nanoparticles can be dispersed in an aqueous medium. One version of the process results in starch nanoparticles which are characterized by an average particle size of less than 400 nanometers. The nanoparticles can be used as a matrix material wherein the matrix material may be a film-forming material, a thickener, a rheology modifier, an adhesive or an adhesive additive (tackifier). The nanoparticles or dispersions thereof may also be used for their barrier properties, as a carrier, fat replacer or medicament for mitigating dermal disorders. Further examples of applications for the nanoparticles or dispersions thereof are in the paper-making and packaging industry, agriculture and horticulture fields. The nanoparticles can also be used as excipients or carriers in medicines, where they may be complexed or covalently coupled to active substances such as slow-release drugs. The nanoparticles can also be processed into a foam at relatively high density.

[0032] Other uses of the nanoparticles of U.S. Pat. No. 6,677,386 can be found in: (i) U.S. Pat. No. 7,160,420 which describes the use of the starch nanoparticles as a wet-end additive in papermaking pulp slurry, or applied to the surface of the paper as a surface sizing agent; (ii) U.S. Pat. No. 6,825,252 which describes the use of the starch nanoparticles in a binder in a pigment paper coating composition; (iii) U.S. Patent No. 6,921,430 which describes the use of the starch nanoparticles in environmentally friendly adhesives; and (iv) U.S. Patent Application Publication No. 2004/0241382 which describes the use of the starch nanoparticles in an adhesive for producing corrugated board. The disclosure of these patents and published applications, and of all other publications referred to herein, are incorporated by reference as if fully set forth herein.

[0033] The invention in U.S. Pat. No. 6,677,386 relates to a process for producing biopolymer nanoparticles which in one form are starch nanoparticles characterized by an average particle size of less than 400 nanometers. The structure of the biopolymer nanoparticles has been described in the literature (see Bloembergen et al., “Specialty Bio-based Monomers and Emulsion Polymers Derived from Starch”, 2010 PTS Advanced Coating Fundamentals Symposium, Munich, Germany, Oct. 11-13, 2010). In dry form, the product consists of larger agglomerates with an average agglomerate particle size of ~300 mi (300,000 nm), from which nanoparticles are released when they are dispersed in water. In dispersed form, the biopolymer nanoparticles exist as insoluble colloidal particles that form a biopolymer latex dispersion with an average size of ~100 nanometers. Each of the nanoparticles can be thought of as internally crosslinked macromolecular units with intra-particle crosslinks (FIG. 1). No inter-particle crosslinks exist, as this would result in poor rheology and reduced binding power (reduced surface area). Excellent paper coating binding strength and rheological properties (superior machine runability) have been reported by coated paper and board manufacturers and paper industry experts.
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(see Klass, C. P., “New Nanoparticle Latex offers Natural Advantage”, Paper360° Magazine, p. 30-31, January, 2007; Figliolino et al., “Reducing Carbon Footprint with Biolatex”, Paper360° Magazine, p. 25-28, August, 2009; Lee et al., “Development of New Biobased Emulsion Binders”, PaperCon2010, “Talent, Technology and Transformation”, Atlanta, Ga., May 2-5, 2010; Greenall et al., “New generation of biobased latex coating binders for a sustainable future”, Paper Technology 52, No. 1, Paper Industry Technical Ass’n, p. 10-14, February 2011; and Oberndorfer et al., “Coating & print performance of bio-based latex in European graphic papers”, PaperCon2011, “Rethink Paper: Lean and Green”, Cincinnati, Ohio, May 1-5, 2011). The biopolymer latex binder provides a high performance substitute to the petrochemical-based binders used in coated paper and paperboard manufacturing processes at a lower cost per pound. Carboxylated or acrylonitrile or otherwise modified styrene butadiene (SB latex) and styrene acrylate (SA latex) are the dominant petrochemical-based binders used in coated paper and paperboard manufacturing. Currently, the industry consumes over 4 billion pounds of SB and SA latex per annum. As the price of oil continues to escalate, and as the price of synthetic binders has increased by more than 100% over the past few years, paper producers have faced increased production costs forcing them to find efficiencies, pass increases on to the consumer, or cease production. The biopolymer latex binder of U.S. Pat. No. 6,667,836 provides performance that is comparable to the petro-based SB and SA latex products for important paper properties such as coating gloss, brightness, whiteness, fluorescence, ink gloss, and printability, while providing superior performance to SB and SA Latex for water retention, opacity, dry pick, print mottle, porosity (blister resistance) and paper stiffness.

SUMMARY OF THE INVENTION
[0034] The following discussion is intended to introduce the reader to the detailed description, and not to limit any claimed invention. An invention may reside in any combination or sub-combination of elements or steps described in this summary, the figures or the detailed description.
[0035] This specification describes compositions useful, for example, in providing an alternative means of making one or more of mineral, natural organic or synthetic fibers products.
[0036] The inventors demonstrate, among other things, novel and non-obvious uses for biopolymer nanoparticles such as those described in U.S. Pat. No. 6,667,836, a new curable binder composition comprising a biopolymer nanoparticles, in some applications with a multifunctional crosslinking agent, for use for example in the formation of mineral, natural organic, or synthetic fiber products, for example mineral fiber insulation, non-woven mats, fiberglass insulation and related glass fiber products, and wood based products, and construction materials. By “multifunctional crosslinking agent”, we mean a crosslinking agent in addition to a crosslinking agent used to form the biopolymer nanoparticle. The multifunctional crosslinking agent has two or more functional groups (which may be the same type of functional group) capable of forming a bond, for example a covalent or ionic bond, with the nanoparticles and preferably with the fibers.
[0037] Curable aqueous compositions are described, for example a formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent. Whereas the biopolymer nanoparticles in the aqueous dispersion are already internally crosslinked within the nanoparticles via intra-particle crosslinks, the additional multifunctional crosslinking agent facilitates interfacial inter-particle crosslinks. In an application wherein a curable aqueous composition is used to make fiberglass insulation, a multifunctional crosslinking agent is selected which lies at least partially dormant during the binder application stage and fiber mat formation and flushing stages, but is triggered in the curing stage to react, or react further, and lock in the desired fiber mat dimensions. The high surface area of the biopolymer nanoparticles in the aqueous composition provides bonding for mineral, natural organic or synthetic fibers which is superior to, or at least offers an alternative to, water-soluble sugars, dextrins, industrial starches, carbohydrates or other natural polymers. The additional multifunctional crosslinking agent facilitates interfacial inter-particle crosslinks to provide useful fiber mat recovery (for insulation products) and dry and wet tensile strength properties.
[0038] The multifunctional crosslinker may be selected from dialdehydes, polyaldehydes, anhydrides such as acid anhydrides or mixed anhydrides, (e.g. succinic and maleic anhydrides), glutaraldehyde, glyoxal, oxidized carbohydrates, periodate-oxidized carbohydrates, epichlorohydrin, epoxides, triphosphates, petroleum-based monomeric, oligomeric and polymeric crosslinkers, biopolymer crosslinkers, divinylation sulphone, borax (Na2B4O7.10H2O), isocyanates, polyacids and hydrolysable organo alkyl silanes producing silanols. The crosslinking reaction may be acid-catalyzed or base-catalyzed. In one embodiment, suitable dialdehydes and polyaldehydes include glutaraldehyde, glyoxal, periodate-oxidized carbohydrates, and the like. Glyoxal, borax, epichlorohydrin, isocyanates, anhydrides, polyacids and silicates such as tetraethyl orthosilicate (TEOS) are particularly suitable crosslinkers. Such crosslinkers may be used alone or as a mixture of crosslinkers. The level of crosslinking agent can conveniently be between 0.1 and 10 weight % with respect to the total dry weight of the curable aqueous composition. The level of crosslinking agent can also be between 0.1 and 5 weight % with respect to the total dry weight of the curable aqueous composition. The level of crosslinking agent can also be between 0.5 and 5 weight % with respect to the total dry weight of the curable aqueous composition. The level of crosslinking agent can also be between 0.1 and 2 weight % with respect to the total dry weight of the curable aqueous composition.
[0039] A cured composition is described in this specification comprising a nonwoven fiber in a cured binder wherein the cured composition is formed by mixing fibers in a curable aqueous composition to form a mixture and curing the mixture.
[0040] A method for forming a non-woven material is described in this specification comprising: mixing fibers a said curable aqueous composition, and heating the curable composition and fibers at 130° C. to 230° C. for sufficient time to cure.
[0041] A method for binding together a loosely associated mat of glass fibers is described in this specification comprising contacting the glass fibers with an aqueous binder composition comprising an aqueous mixture of a substantially infinitely water-dilutable or dispersible adduct of co-condensation of urea, formaldehyde and nanoparticles of crosslinked
biopolymer containing plurality of pendant hydroxyl groups and heating said composition at an elevated temperature to effect cure.

A glass fiber product is described in this specification comprising a crosslinked (cured) composition obtained by curing (drying at elevated temperature) an aqueous binder composition comprising a substantially infinitely water-dilutable or dispersible adduct of co-condensation of urea, formaldehyde and nanoparticles of crosslinked biopolymer containing plurality of pendant hydroxyl groups applied to a mat of nonwoven glass fiber.

A mineral, natural organic, or synthetic wool product is described in this specification comprising a crosslinked (cured) composition obtained by curing (drying at elevated temperature) an aqueous binder composition comprising a substantially infinitely water-dilutable or dispersible adduct of co-condensation of urea, formaldehyde and nanoparticles of crosslinked biopolymer containing plurality of pendant hydroxyl groups applied to a mat of nonwoven mineral, natural organic, or synthetic wool.

A composition is described in this specification comprising an aqueous solution comprising a curable binder, a dispersion of at least 25 wt % of particles in the aqueous solution and a crosslinker adapted to bond to the particles and to mineral fibers. The composition may be used to make mineral fiber insulation, for example fiberglass insulation. The curable binder may be a non-formaldehyde resin, for example polyacrylic acid (PAA) or polyester (PE).

A composition is described in this specification comprising a formaldehyde resin and a dispersion of up to 15 wt % of particles comprising crosslinked biopolymers. The composition may be used to make fiberglass roofing shingles.

A composite material is described in this specification comprising particles, fibers, and a crosslinker bonded to the fibers and the particles wherein the particles are one or more particles selected from the group of crosslinked biopolymers, particles with an average size of less than 400 nm, and particles with a volume swell ratio greater than 6.

A curable aqueous compositions for fiber mat formation described in this specification comprises a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent. The multifunctional crosslinking agent may lie dormant during a binder application stage and fiber mat formation and flashing stages, but is triggered in the curing stage to react and lock in the desired fiber mat dimensions.

A curable aqueous composition for fiber mat formation described in this specification comprises a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent wherein said multifunctional crosslinking agent facilitates interfacial inter-particle crosslinks.

A curable aqueous composition for fiber mat formation described in this specification comprises a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent wherein said multifunctional crosslinking agent facilitates a useful fiber mat recovery and dry and wet tensile strength properties.

A reduced total emission process for preparing of a binder-coated nonwoven product described in this specification includes the preparation of a curable aqueous binder composition comprising a biopolymer nanoparticles; applying the binder to the nonwoven fibers to form a binder-containing nonwoven mat; curing the binder-containing nonwoven mat at elevated temperatures to form the binder-coated nonwoven product.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**FIG. 1** is a schematic that illustrates the intra-particle crosslinked structure of a biopolymer nanoparticle, with “—R—” representing a crosslink between different starch polymers located within the biopolymer nanoparticle.

**FIG. 2** is a schematic illustrating delayed inter-particle crosslinking of a biopolymer nanoparticle composition during the final drying and curing stage of a fiberglass insulation product, where “R” represents an unreacted multifunctional crosslinking reagent and “X” represents the reacted reagent facilitating inter-particle crosslinks; the interfacial inter-particle crosslinking agent lies dormant during the binder application stage and the fiber mat formation and flashing stages, but is triggered in the curing stage to lock in the desired fiber mat dimensions.

**FIG. 3** is a schematic of a cured mineral, natural organic, or synthetic fiber product made from a curable aqueous composition comprising biopolymer nanoparticles of crosslinked starch and a multifunctional crosslinking agent.

**FIG. 4** is an SEM micrograph (at 500x magnification) of a glass fiber mat to which a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent has been added following which it was cured, and serves to illustrate “spot welding”, or fiber to fiber bonding, with the biopolymer latex binder composition containing a multifunctional crosslinker.

**FIG. 5** is an SEM micrograph (at 2,500x magnification) of a glass fiber mat to which a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent has been added following which it was cured, and serves to illustrate extensive interfiber “spot welding”, or fiber to fiber bonding, with the biopolymer latex binder/multifunctional crosslinker composition.

**FIG. 6** is a High Resolution SEM micrograph (at 30,000x magnification) of a spot weld, or fiber to fiber bond, area in a fiber mat made with a cured binder composition consisting of 50% polyacrylic acid (PAA) resin-50% biopolymer latex binder by solids weight composition containing a multifunctional crosslinker.

**DETAILED DESCRIPTION OF THE INVENTION**

Before the present materials and methods are described, it is understood that this invention is not limited to the particular methodology, protocols, materials, and reagents described, as these may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention.

It must be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise. As well, the terms “a” (or “an”), “one or more” and “at least one” can be used interchangeably herein. It is also to be noted that the terms “comprising”, “including”, and “having” can be used interchangeably.

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art to which this
invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described. All publications and patents specifically mentioned herein are incorporated by reference for all purposes including describing and disclosing the chemicals, instruments, statistical analysis and methodologies which are reported in the publications which might be used in connection with the invention. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

By “biopolymer” we mean biopolymers such as starch, starch derivatives, and carbohydrates or other polysaccharides including cellulose, hemicellulose and gums, as well as proteins (e.g. gelatin or whey protein) that can be formed into nanoparticles. The biopolymers may be previously modified, e.g. with cationic groups, carboxymethyl groups, by acylation, phosphorylation, hydroxylalkylation, oxidation and the like. Starch, and mixtures of different starch species, and mixtures of starch with other (bio)polymers containing at least 50% starch are preferred. Especially preferred is high-amylopectin starch (i.e. low-amylose starch), i.e. starch having a content of at least 75%, especially at least 90% of amylopectin, such as waxy starch.

By “biopolymer nanoparticle” we mean a particle comprising crosslinked biopolymer molecules. A dispersion of biopolymer nanoparticles may include particles, or may have an average size (by number or mass, or the D50 value of an NTA measurement) of particle, between 1 and 2500 nanometers (nm), or between 1 and 1000 nm or between 1 and 400 nm. Particles within the smaller size ranges are preferred because they provide increased surface for inter-particle bonding. Smaller particles are also easier to disperse or maintain in dispersion, and are more likely to form a colloid. However, in some applications, particles with an average size even larger than 2500 nm might be used.

The size of the nanoparticles can be determined by forming a dispersion of the particles and making a measurement using, for example, NanoPartica Tracking Analysis (NTA) using an L/M 20 tracking analysis device (NanoSight Ltd.) equipped with a blue laser (405 nm). This device uses a 50 mW laser operating in the CW mode to illuminate the particles. The light scattered by the particles is captured using a digital camera and the motion of each particle is tracked from frame to frame using NanoSight software. A high speed video is obtained (50 frames per second, average video about 30 s). The trajectories of individual nanoparticles are generated from the video sequence and the mean squared displacement determined for each particle. Typically at least 20 trajectories are acquired and 250 to 500 sets of trajectories (each set corresponding to an individual particle) are accumulated in a video sequence. The analysis of the mean squared displacement is used to calculate the diffusion coefficient and the hydrodynamic radius ($r_h$) is determined using the Stokes-Einstein equation. Thus, the diameter of each particle in the sample can be determined and a particle size distribution derived. Because a diffusion coefficient is obtained for each particle in the field of view, a particle size distribution can be obtained which does not assume a particular mathematical model as in dynamic light scattering (DLS) analysis.

As an alternative, DLS measurements may also be used. In that case, the dispersion is diluted as required by the instrument and preferably filtered to remove any remaining agglomerates. DLS and NTA are complementary, given that the NTA technique is a direct measurement of the diffusion coefficient for individual particles tracked via video tracking software (and relates that to particle diameter via the Stokes-Einstein equation), and can measure particles in the range of 50-1000 nm, while DLS can measure to smaller particle sizes below 50 nm. Other useful techniques include oscillating probe Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Environmental SEM (ESEM), Transmission Electron Microscopy (TEM) and Scanning/Transmission Electron Microscopy (STEM).

By “biopolymer nanoparticle latex”, “biopolymer latex” we mean a colloidal dispersion of biopolymer nanoparticles. The particles in a biopolymer latex typically have an average size between about 1 and 1000 nm.

By “starch” we mean a complex carbohydrate polymer which is insoluble in water. Starch is often found in the fruit, seeds, or tubers of plants. The major resources for starch production and consumption are corn, potatoes, wheat, tapioca and rice. Starch is a mix of two polymeric carbohydrates (polysaccharides) called amylose and amylopectin, in which the monomers are glucose units joined to one another head-to-tail forming alpha-1,4 linkages. The overall structure of amylopectin is not, however, simply a linear polysaccharide chain, since occasionally, two glucose units are joined to one in an alpha-1,6 linkage, forming a branch point. Structurally, the starch forms clusters of linear polymers, where the alpha-1,4 linked chains form linear columns of glucose units branching at the alpha-1,6 links. The relative content of amylose and amylopectin varies between starch species.

Note that EcoSynthetic®, EcoSphere®, and Biolatex®, are registered trademarks of EcoSynthetic Ltd. of Lansing, Mich., USA. EcoSphere 2202™ is a starch based, internally crosslinked colloid forming hydrogel particle having an average particle size under 400 nm available commercially from EcoSynthetic Ltd., or EcoSynthetic Inc. of Burlington, Ontario, Canada. In particular, the EcoSphere 2202™ particles have a number average particle size in the range of 50 to 150 nm and, considering a distribution of their particle sizes, are also predominantly in the range of 50 to 150 nm in size. These products are made primarily from starch including amylose and amylopectin. The product is normally sold for to replace petroleum based latex binders in industrial applications, such as coated paper and paperboard. The product is provided in the form of a dry powder of agglomerated nanoparticles with a volume mean diameter of about 300 microns. When mixed in water and stirred, the agglomerates break apart and form a stable dispersion of the nanoparticles.

This specification describes, among other things, a novel and non-obvious use for biopolymer nanoparticles, such as those described in U.S. Pat. No. 6,667,836, in achieving a new curable binder composition comprising a biopolymer nanoparticle latex and a multifunctional crosslinking agent for use in the formation of mineral, natural organic, or synthetic fiber products, including mineral fiber insulation, non-woven mats, fiberglass insulation and related glass fiber fiber products. The fibers may comprise natural fiber such as cellulose, sisal, wool, jute; synthetic fibers such as polyolefins, polystyrenes, acrylics, nylon, polyamides, ceramics, molten stone, stone wool, glass fibers, carbon fibers, aramid fibers, and the like, alone or in combinations with one another.

This specification describes a curable aqueous composition comprising a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent. FIG. 1 illustrates how the biopolymer...
nanoparticle 10 can be thought of as one crosslinked macro-molecular unit, with —R— representing crosslinks between polymer molecules 12, for example starch polymer molecules, located within the nanoparticle 10. Whereas the biopolymer nanoparticles in the aqueous dispersion are already internally crosslinked within the nanoparticles via intra-particle crosslinks (see FIG. 1), an additional multifunctional crosslinking agent may optionally be added to facilitate interfacial inter-particle crosslinks (shown as R or X in FIG. 2). Although crosslinking agents are inherently multifunctional, the term multifunctional crosslinking agent is used herein to help avoid confusion with the crosslinking agent used to form the nanoparticle. Said multifunctional crosslinking agent is preferably designed to be dormant, or at least to not fully react, during the binder application stage and the fiber mat formation and fluffing stages, but is triggered in the curing stage by heat, an increasing solids content, or both, to react, or further react, and lock in the desired fiber mat dimensions. The multifunctional crosslinking agent may further crosslink particles to a reinforcement material such as fibers or wood in a non-fibrous form, i.e. a form other than pulp. For example, TEOS has four reaction sites. One or more of these reaction sites may bond with a biopolymer nanoparticle before curing, but reactions at all four sites, with other nanoparticles, a fiber or wood, are not believed to occur until the composition is heated.

As indicated in FIG. 2, biopolymer nanoparticles 10 of the type formed by crosslinking essentially non-crystalline starch molecules swell in water. The starch molecules are hydrophilic. At low concentrations (i.e. low volume fraction), for example at a solids content of 20 wt% or less, the particles achieve a maximum swelling value that is balanced between their elastic constraint due to their crosslinked network and the osmotic pressure. The maximum swelling value (or volume factor) of the particles may be determined by measuring the relative viscosity, \( \eta_r \), of a low concentration dispersion of the particles. The relative viscosity (\( \eta_r = \eta/\eta_s \)) of the dispersion is obtained by measuring the flow times between two demarcations of a glass Ubbelohde viscometer for the dispersion (ii) and for its dispersion medium (\( \eta_s \)), which is water. Using the Einstein equation, \( \eta_r = 1 + 2.5 \times 10^{-3} \phi \), where \( \phi \) is the effective volume factor and \( \phi \) is the volume fraction, one can obtain the effective volume factor (i) that is equal to the maximum volume swelling of the particles at low concentrations. The effective volume factors (i.e. the maximum volume swell ratios) of the particles varies with different crosslink densities, for example between about 6 and about 16. The Ecosphere 2202™ product has a volume factor greater than 6.

The swelling occurs primarily in the core 14 (see FIG. 1) of the particle. The shell 16 (see FIG. 1) provides a steric stabilization mechanism that enhances the colloidal forming nature of the particles.

The particles de-swell to some extent when solids concentration increases, as occurs when water is evaporated out of a dispersion during heat curing, so that their composition can be made at higher solids, as shown in FIG. 1. In particular, de-swelling will take place when the concentration of the dispersion exceeds that of the starch network in the nanoparticles which is equal to the reciprocal 1/SR(W) of the weight swell ratio, SR(W). For example, if SR(W) is 5, then starch nanoparticles will start de-swelling when the concentration of a crosslinked starch dispersion approaches or exceeds 20% solids.

Internal crosslinking in the particles prevents them from de-swelling completely and so the particles can be described as a hydrogel. When dried during curing, crosslinked starch based particles have a density less than the density of a native starch granule. For example, a native starch granule may have a relative density of about 1.6 whereas a crosslinked starch particle may have a relative density of about 1.0. While this hydrogel nature of certain particles may not be required in all applications, it is advantageous in at least some applications.

In general, the cost and energy required to produce a material varies with its weight. However, the ability of the particles to function as a binder is related to their volume. Accordingly, a less dense particle can provide a more efficient use of material, and a lighter finished product. Further, in the case of insulating products, the rate of heat transfer tends to decrease with density and so a hydrogel form of a material may provide better thermal performance in an insulation product.

In the case of an insulation product, the hydrogel nature of some particles is also well adapted to standard fiberglass insulation production methods. In stage 1 (see FIG. 2) the dispersion is free flowing, and may be applied by sprayers typically used in fiberglass insulation making. Stage 2 may be viewed as covering the time from when the spray contacts the fibers to when fiber temperature begins to rise again when the fiber mat enters Stage 3. During stage 2, some water evaporates and the dispersion reaches a solids concentration in which the particles contact each other. The dispersion then becomes film forming but is still flowable and tends to accumulate at binding locations such as intersections between fibers where the fibers contact each other or come close to contacting each other. During stage 3, as the particles de-swell towards their maximum density, they become immobile across intersections between fibers and so bind the fibers together.

FIG. 3 illustrates a schematic of a cured product 20 made with mineral, natural organic, or synthetic fibers 22 bound with biopolymer nanoparticles 12. The product has effective chamber formation that results from the curable aqueous composition, for example a composition comprising biopolymer nanoparticles, for example a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent. Effective chamber formation is important in fiberglass manufacturing in order to provide acceptable insulation, fiber mat strength, compactability and recovery properties.

FIG. 4 provides an SEM micrograph (at 500x magnification) of a non-woven mat of glass fibers 32 to which a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent has been added following which it was cured. Binding locations 32 comprising cured products of the formulation are visible at fiber intersections.

FIG. 5 is an SEM micrograph of a glass fiber 32 mat to which a biopolymer latex formulation comprising nanoparticles of crosslinked starch and a multifunctional crosslinking agent has been added following which it was cured, and this higher resolution SEM micrograph (at 2,500x magnification) serves to illustrate extensive interfiber “spot welding”, or fiber to fiber bonding, at binding locations 30 with the biopolymer latex binder/multifunctional crosslinker composition. FIG. 6 is a high resolution SEM micrograph at 50,000x of a spot weld, or fiber to fiber bond, area within a
binding location 30 in a fiber mat cured with a binder composition consisting of 50% polyacrylic acid (PAA)-50% biopolymer latex, by weight of PAA and biopolymer nanoparticles, binder composition containing a multifunctional crosslinker. The biopolymer nanoparticles 12 are clearly visible in the high resolution micrograph depicted in FIG. 6, that is at least those located at or near the surface of the cured polymer blend.

[0077] The high surface area of the biopolymer nanoparticles in the aqueous dispersion, an in particular a biopolymer latex, in itself provides bonding for mineral fibers while the additional multifunctional crosslinking agent facilitates interfacial inter-particle crosslinks, and/or crosslinks to the fibers. The bonding provides fiber mat recovery when used to make insulation products and dry and wet tensile strength sufficient for various products, such as asphalt shingles. Biopolymer nanoparticles can be formed as prescribed in U.S. Pat. No. 6,677,386 (which corresponds to International Publication WO 00/69916). In that process, a biopolymer, such as starch comprising amyllose or amylopectin or both, is combined with a plasticizer. This combination is mixed under high shear forces, preferably in a twin screw fully intermeshing co-rotating extruder, to plasticize the biopolymer and create a thermoplastic melt phase in which the crystalline structure of the biopolymer is removed. A crosslinking agent is then added while mixing continues to form cross-linked nanoparticles. The nanoparticles exit the extruder as a strand, which is ground to a fine dry powder. The starch based nanoparticles are present in the powder in agglomerated form, and can be dispersed in an aqueous medium.

[0078] The biopolymers may be starch or other polysaccharides such as cellulose and gums, as well as proteins (e.g. gelatin, whey protein). The biopolymers may be previously modified, e.g. with cationic groups, carboxy-methyl groups, by acylation, phosphorylation, hydroxalkylation, oxidation and the like. Starch and mixtures of at least 50% starch with other polymers are preferred. The starting material may be a native or granular starch selected from the group consisting of, for example, potatoes, rice, tapioca, corn, peas, rye, oats, wheat, and combinations thereof. The starch, whether used alone or in a mixture, is preferably a high molecular weight starch, for example a molecular weight of at least 10,000, and not dextrin or dextrin. For example, the starch may be made up of amyllose or amylopectin or both. Waxy starches, such as waxy corn starch, are particularly preferred.

[0079] The following five paragraphs are repeated or summarized from U.S. Pat. No. 6,677,386 to further describe the process of making the nanoparticles.

[0080] The biopolymer preferably has a dry substance content of at least 50% by weight at the time when processing starts. Processing is preferably done at a temperature of at least 40 degrees C., but below the degredation temperature of the polymer, for example 200 degrees C. The shear can be effected by applying at least 100 J of specific mechanical energy (SME) per g of biopolymer. Depending on the processing apparatus used the minimum energy may be higher; also when non-pregelatinised material is used, the minimum SME may be higher, e.g. at least 250 J/g, especially at least 500 J/g.

[0081] The plasticiser may water or a polyol (ethylene glycol, propylene glycol, polyglycols, glycerol, sugar alcohols, urea, citric acid esters, etc.). The total amount of plasticisers (i.e. water and others such as glycerol) is preferably between 15 and 50%. A lubricant, such as lecithin, other phospholipids or monoglycerides, may also be present, e.g. at a level of 0.5-2.5% by weight. An acid, preferably a solid or semi-solid organic acid, such as maleic acid, citric acid, oxalic, lactic, gluconic acid, or a carbohydrate-degrading enzyme, such as amylase, may be present at a level of 0.01-5% by weight of biopolymer. The acid or enzyme assists in slight depolymerisation which is assumed to be advantageous in the process of producing nanoparticles of a specific size.

[0082] The crosslinking is preferably reversible, i.e. the crosslinks are partly or wholly cleaved after the mechanical treatment step. Suitable reversible crosslinkers include those which form chemical bonds at low water concentrations, which dissociate or hydrolyse in the presence of higher water concentrations. This mode of crosslinking results in a temporary high viscosity during processing followed by a lower viscosity after processing. Examples of reversible crosslinkers are dialdehydes and polyaldehydes, which reversibly form hemiacetals, acid anhydrides and mixed anhydrides (e.g. sucinic and acetic anhydride) and the like. Suitable dialdehydes and polyaldehydes are glutaraldehyde, glyoxal, periodate-oxidised carbohydrates, and the like. Glyoxal is a particularly suitable crosslinker.

[0083] Such crosslinkers may be used alone or as a mixture of reversible crosslinkers, or as a mixture of reversible and non-reversible crosslinkers. Thus, conventional crosslinkers such as epichlorohydrin and other epoxides, triplosphates, divinyl sulphone, can be used as non-reversible crosslinkers for polysaccharide biopolymers, while dialdehydes, thiol reagents and the like may be used for proteinaceous biopolymers. The crosslinking reaction may be acid- or base-catalysed. The level of crosslinking agent can conveniently be between 0.1 and 10 weight % with respect to the biopolymer. The crosslinking agent may already be present at the start of the mechanical treatment, but in case of a non-pre-gelatinised biopolymer such as granular starch, it is preferred that the crosslinking agent is added later on, i.e. during the mechanical treatment.

[0084] The mechanically treated, crosslinked biopolymer is then formed into a latex by dispersion in a suitable solvent, usually water and/or another hydroxylic solvent such as alcohol), to a concentration of between 4 and 50 weight % especially between 10 and 40 wt. %. Prior to the dispersion a cryogenic grinding step may be performed, but stirring with mild heating may work equally well. This treatment results in a gel which either spontaneously or after induction by water adsorption, is broken into a latex. This viscosity behaviour can be utilised for applications of the particles, such as improved mixing, etc. If desired, the dispersed biopolymer may be further crosslinked, using the same or other crosslinking agents as described above. The extrudate is characterised by swelling in an aqueous solvent, e.g. water or a mixture of at least 50% water with a water-miscible solvent such as an alcohol, and by exhibiting a viscosity drop afterwards to produce a dispersion of nanoparticles.

The production of biopolymer nanoparticles similarly formed by reactive extrusion and comprising starch essentially without crystalline structures is described in Starch nanoparticle formation via reactive extrusion and related mechanism study, Delong Song et al., Carbohydrate Polymers 85 (2011) 208-214. Using various materials and reaction conditions, dispersions having particles with number average particle sizes up to about 2000 nm were produced.

Another method of producing biopolymer nanoparticles by reactive extrusion process from waxy corn starch is described in International Publication Number WO 2011/071742 A2, Process for Preparing Stable Starch Dispersions, by Welsch et al., published on Jun. 16, 2011. This process comprises introducing a feed starch and an hydroxylic liquid to an extruder. Shear forces are applied in the extruder to the starch and the liquid in the substantial absence of a cross-linker under conditions sufficient to prepare a stable dispersion of starch particles in the hydroxylic liquid.

Another method of producing biopolymer nanoparticles is described in International Publication Number WO 2011/155979 A2, Process for Preparing Stable Dispersions of Starch Particles, by Welsch et al., published on Dec. 15, 2011. In this process, a feed starch and an aqueous liquid are introduced into a rotor stator mixer. The feed starch and aqueous liquid are maintained in the rotor stator mixer at a temperature ranging from a gelation temperature to less than a solubilization temperature. The feed starch is sheared into starch particles with the rotor static mixer to form the dispersion of starch particles in the aqueous liquid.

Another method of producing a starch nanoparticle is described in U.S. Pat. No. 6,755,915 to Van Soest et al. (June 29, 2004) which teaches a method of preparing starch particles with a size range of 50 nm to 100 nm. The method includes the steps of: dispensing starch in a first water phase; dispersing a second hydrophobic phase in the first phase to form an oil-in-water emulsion; inverting the oil-in-water emulsion to a water-in-oil emulsion; cross-linking the starch in the first phase; and separating the formed starch particles. The phase inversion can occur by including a surfactant that stabilizes a water-in-oil emulsion or the surfactant can be temperature sensitive and increasing the reaction temperature. The inversion can also occur by the addition of further hydrophobic liquids or various suitable salts. In this process the starch molecules can remain partially granular during both the cross-linking reaction and complete gelatinisation of the granular starch can be effected before, during or after the phase inversion. Gelatinization occurs by increased temperature, salts or combinations thereof.

Another method of making biopolymer nanoparticles is described in WO 2010/084088 to Santander Ortega et al. (international publication Jul. 29, 2010). The method includes the steps of preparing starch derivatives by a first disintegration step, with solvent and increased temperatures, followed by common substitution methods, such as esterification, etherification. The starch derivatives are added to an organic solvent and an oil/water emulsion is prepared with a high shear mixer. Sonication may be used to improve the oil droplet distribution. The organic phase is then removed through a membrane, which results in an aqueous dispersion of starch-based nanoparticles.

Another method of making biopolymer nanoparticles is described in GB 1,420,392 to Beersma which teaches a method of forming starch particles by cross-linking native starch granules and then fragmenting the cross-linked starch granules with heat and pressure in an extruder.

Another method of making biopolymer nanoparticles is described in WO 2010/065750 to Bloembergen et al. which teaches that Brabender static high shear mixers and Sigma Blade mixers may be used in place of an extruder to produce nanoparticles by way of shearing starch granules in the presence of a crosslinker.

The nanoparticles may form a colloid or latex in water. The particles may be made up of water-swollen crosslinked hydrophilic polymers. The polymers may have hydroxyl functional groups. The particles may swell by an effective volume factor (maximum volume swell ratio in water) of 6 or more, but deswell at increasing solids content, for example when water is evaporated from them by heat while curing.

The binder composition may include as the multifunctional crosslinking agent polyacids having at least two acidic functional groups that will react with the alcohol moieties on the starch particles. It is preferred to use nonpolymeric polyacids. These nonpolymeric polyacids include at least one of citric acid, maleic acid, succinic acid, phthalic acid, glutaric acid, maleic acid, phthalic acid or the like, and salts thereof.

The binder composition may include as the multifunctional crosslinking agent an anhydride of the nonpolymeric polyacid. These anhydrides include at least one of maleic anhydride, succinic anhydride, phthalic anhydride and the like.

The binder composition may contain as a plasticizer and/or processing aid a polyol of a wide variety of materials, including, but not limited to, ethylene glycol (to make 2,3-dihydroxydioxane), diethylene glycol, dialkylene glycol (to make an oligomeric condensation product) such as 1,2-propylene glycol, 1,3-propanediol glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, polyethylene glycols having the formula HO(CH₂CH₂OH)ₙH where n is 1 to about 50, silanols (as products of hydrolysis of organosilanes), and the like, and their mixtures. Other suitable polyols (i.e. containing at least three hydroxy groups) can be used, such as glycerin, (to make 2,3-dihydroxy-5-hydroxymethyl dioxane) as well as unalkylated or partially alkylated polymeric glycolal derived glycols such as poly(N,1',2'-dihydroxyethyl-ethylene urea), dextran, glyceryl monostearate, ascorbic acid, erythrobic acid, sorbic acid, ascorbil palmitate, calcium ascorbate, calcium sorbate, potassium sorbate, sodium ascorbate, sodium sorbate, monoglycerides of edible fats or oils or edible fat-forming acids, inositol, sodium tartarate, sodium potassium tartrate, glycerol monopropionate, sorbose monoglyceride citrate, polyvinyl alcohol, cr-di-methylglucoside, sorbitol, dextrin, and their mixtures.

The binder, alternatively called a curable aqueous composition, is prepared in one form of biopolymer nanoparticles and a multifunctional crosslinker. The biopolymer nanoparticles are dispersed in water and/or hydroxylic solvent (such as an alcohol), to a concentration of biopolymer nanoparticles of between 4 and 50 wt %, or between 10 and 20 wt %, prior to curing, usually at the application site where it
is combined with the fibers and then cured. Optionally, the binder may also contain, or be mixed with, other binders, alternatively called resins or aqueous curable compositions, know in the art (for example the binders described in the background section herein) or other binders, known now or developed in the future, useful for binding fibers or wood together. Optionally, the binder or curable aqueous composition may contain a multifunctional crosslinker or other additives. Optionally, the binder may contain another latex, for example an SB latex, or an extender. The curable aqueous composition may provide a partial or complete replacement for a formaldehyde-based binder or polymer binder, or a latex component of a binder system. The curable aqueous composition may be used in combination with a formaldehyde-based binder or other petro-chemical based soluble polymer or latex component of a binder system. A formaldehyde free binder system may be made by using the curable aqueous composition alone or in combination with a non-formaldehyde binder system, which may be an organic, for example petro-chemical based, system such as one using polyacrylic amide (PAA) or polyester (PE) resins, or a biopolymer system using, for example, a soluble protein, starches, dextrin or other biopolymer.

One method for forming a non-woven material comprises: mixing fibers with a binder, and heating the binder and fibers at 130°C to 230°C for sufficient time to cure. Preferably, the binder comprises up to 95% by weight of water immediately prior to curing. Most preferably, the binder comprises 85 to 95% by weight of water immediately prior to curing. The binder and fibers can also be heated at 180°C to 220°C for sufficient time to cure.

A biopolymer latex is substantially water-dilutable. The binder can be mixed with the nonwoven fiber material by spraying, soaking or other suitable methods commonly used by the industry. The material is then dried and the binder is cured in an oven at elevated temperatures, generally at 130°C to 230°C for providing the formation of a rigid thermoset polymer.

The curable aqueous composition may includes other components, e.g., emulsifiers, plasticizers, anti-foaming agents, biocide additives, anti-mycosis including, e.g., fungicides and mold inhibitors, adhesion promoting agents, colorants, waxes, antioxidants, and combinations thereof.

The curable aqueous composition can be used to prepare nonwoven products by a variety of methods known in the art, which, in one embodiment, involves the impregnation of a loosely assembled mass of fibers with the binder solution to form a mat. The fibers may comprise natural fiber such as cellulose, sisal, wool, jute; synthetic fibers such as polyolefins, polyesters, acrylics, nylon, polyamides, ceramics, molten stone, stone wool, glass fibers, carbon fibers, aramid fibers, and the like, alone or in combinations with one another. The product may be used, for example, in building insulation, a roofing fiberglass mat, construction materials, or a nonwoven filtration material.

In various trials, fiberglass insulation batts were made using binder compositions comprising a blend of 100 parts EcoSphere 2202 starch-based biopolymer nanoparticles with an average size of less than 400 nm, 100 parts of a second binder and 1 part of TEOS, all parts on a dry solids basis. In different trials, PAA and polyester (PE) were used as the second binder. The compositions were used to manufacture a glass fiber insulation product on a standard fiberglass bat manufacturing line. The binder was sprayed onto glass fibers using high pressure nozzles already present in the manufacturing line. The fibers were then collected, formed into a mat, flattened, and heated in an oven to the cure temperatures of the binder mix. The cured glass fiber insulation samples had cured binder contents between 3 and 10% by weight as determined by loss on ignition (LOI); thicknesses of 70 to 300 mm; and, densities of 7 to 10 kg/m³. The binder content, thickness and densities were varied to produce different grades (R values) of the resulting insulation products. The product was then downsized to an appropriate length and width, compressed and packaged in a bag. The bags recovered their design thickness after the bags were opened.
EXAMPLES

[0106] The following Examples and are not intended to limit the claims.

Example 1
Preparation of Biopolymer Binder Composition

[0107] The technique described in U.S. Pat. No. 6,677,386 has been used to prepare biopolymer nanoparticles by reactive extrusion processing. Native potato starch, corn starch, tapioca and waxy corn starch have been used to prepare nanoparticles. Agglomerated particles of such nanoparticles are commercially available, sold under the trade mark EcoSphere, from Ecosynthetix Inc. EcoSphere 2202 extruded pellets comprised of starch nanoparticles were dispersed in water using mechanical agitation. The nanoparticles at 35% (w/v) solids were dispersed in 15 minutes at 45° C. using a 3-blade mixer at 200 rpm. A crosslinker (tetraethyl orthosilicate) was added in amount of 1 wt% (based on dry solids) and mixed for 30 minutes. After that the pH was adjusted to 7.0 with aqua ammonia. The binder is a low viscosity liquid. The stability of the resulting biopolymer binder is about 1 month at room temperature.

Example 2
Preparation of Blends of Biopolymer Binder

[0108] Glass fiber binder compositions were prepared using the biopolymer of Example 1 mixed with 25, 40 and 50 parts (dry basis) of polyester as described in example 3 of WO 03/106561 at room temperature. A crosslinker (tetraethyl orthosilicate) was added in the amount of 1% by weight (based on dry solids) and mixed for 30 minutes. No crosslinker was added to the control binder compositions. After that the pH was adjusted to 7.0 with aqua ammonia. In addition, a glass fiber binder composition was prepared using the biopolymer of Example 1 mixed with 50 parts (dry basis) of polyacrylic binder as described in the example of U.S. Pat. No. 6,331,350 at room temperature. A crosslinker (tetraethyl orthosilicate) was added in the amount of 1% wt (based on dry solids) and mixed for 30 minutes. After that the pH was adjusted to 7.0 with aqua ammonia. No crosslinker was added to the control binder composition.

Example 3
Tensile Testing of Cured Glass Fiber Specimens

[0109] The biopolymer binder composition of Example 1 prepared from dry EcoSphere® 2202 biopolymer latex powder to give a 35% solids dispersions was subsequently diluted with water to give a binder dispersion having 15% non-volatiles, and the binder solution was applied to a glass fiber substrate as follows. Glass paper (Whatman 934-AH) was soaked in the binder solution for 5 minutes, then the excess liquid was removed by vacuum. The samples were put into an oven at 200° C. for 5 minutes for curing of the binder resin. The cured samples were cut into specimens having the dimensions of 6cm x 1cm and tested for dry tensile strength by an Instron tensile tester. For wet tensile testing, the specimens were treated with hot water at 80° C. for 10 minutes, and then tested for tensile strength while still wet. The test results are presented in the Table 1, where Comparative A is polyester binder as described in WO 03/106561; comparative B is a pure polyacrylic binder at 15% solids as described in U.S. Pat. No. 6,331,350; C is a pure biopolymer nanoparticle biopolymer latex binder dispersion at 15% solids (based on EcoSphere® 2202 biopolymer latex binder); C* is as C, but with 1% of tetraethyl orthosilicate (TEOS) crosslinker added; D is a 40/60 blend of A and C; D* is a 40/60 blend of A and C* (with 1% TEOS crosslinker added); E is a 25/75 blend of A and C; F is a 50/50 blend of A and C; G is a 50/50 blend of B and C; and G* is a 50/50 blend of B and C* (with 1% TEOS crosslinker added).

<table>
<thead>
<tr>
<th>Binder</th>
<th>Crosslinker</th>
<th>Dry strength, kgf</th>
<th>Wet strength, kgf</th>
<th>Retention, %</th>
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</thead>
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<tr>
<td>Comparative A</td>
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<td>35.1</td>
<td>18.4</td>
<td>52.4</td>
</tr>
<tr>
<td>Comparative B</td>
<td>No</td>
<td>25.9</td>
<td>17.3</td>
<td>66.8</td>
</tr>
<tr>
<td>C</td>
<td>No</td>
<td>19.4</td>
<td>3.5</td>
<td>18.0</td>
</tr>
<tr>
<td>C*</td>
<td>Yes</td>
<td>18.4</td>
<td>9.5</td>
<td>51.3</td>
</tr>
<tr>
<td>D</td>
<td>No</td>
<td>24.0</td>
<td>17.1</td>
<td>71.3</td>
</tr>
<tr>
<td>D*</td>
<td>Yes</td>
<td>26.6</td>
<td>22.3</td>
<td>83.8</td>
</tr>
<tr>
<td>E</td>
<td>No</td>
<td>24.4</td>
<td>15.6</td>
<td>63.9</td>
</tr>
<tr>
<td>F</td>
<td>No</td>
<td>24.8</td>
<td>17.9</td>
<td>72.2</td>
</tr>
<tr>
<td>G</td>
<td>No</td>
<td>28.9</td>
<td>16.1</td>
<td>55.7</td>
</tr>
<tr>
<td>G*</td>
<td>Yes</td>
<td>28.7</td>
<td>22.2</td>
<td>77.5</td>
</tr>
</tbody>
</table>

[0110] The results indicate that addition of a small amount of a multifunctional crosslinker, such as the TEOS silane crosslinker (0.5 to 1.5 wt%, dry basis), significantly improves the wet strength of the fiber mat and the Retention, a key performance attribute. The Retention was calculated as a ratio of Wet Strength/Dry Strength in percent. The tensile strength was measured as the maximum load in kgf at break.

Example 4
UF-Biopolymer Latex Binder Preparation

[0111] A resin of 60% solids, having a formaldehyde-urea mole ratio of 1.65:1, and having a final viscosity of “O” on the Gardner-Holdt scale was prepared. A stirred reactor was charged with the required quantities of 50 wt % aqueous formaldehyde solution (formalin), urea and nano-starch EcoSphere® 2202 biopolymer latex binder at 15% solids. After an initial 15-minute reflux, the pH was adjusted to 6.5 with formic acid and then the reflux was continued to the desired viscosity (“O” on the Gardner-Holdt scale). The pH was then adjusted to 7.5 with 28% ammonium-hydroxide and the resin solution was concentrated to 60% solids by vacuum distillation. A comparative UF resin containing an additive comprising poly(styrene-co-methacrylic acid) was prepared without the addition of nano-starch, as described in U.S. Pat. No. 6,642,299.

Example 5
Treatment of Nonwovens and Tensile Testing of Treated Nonwovens

[0112] The binder compositions of Example 4 were applied to a glass fiber specimen (Whatman 934-AH) by saturation method and the excess binder was recovered by vacuum, and the specimen was then cured in the oven at 200° C. for 5
minutes. The binder add-on was 28%±2% (dry binder weight based on the weight of glass). The testing procedure is described in Example 3. The test results are presented in Table 2 where Comparative H contains urea-formaldehyde resin modified with an additive comprising poly(styrene-co-methacrylic acid): J contains urea-formaldehyde resin that was first prepared and then modified with an additive comprising EcoSphere® (Post-added); K contains urea-formaldehyde resin that was modified in the presence of an additive comprising EcoSphere® (Cooked-in).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Biopolymer latex Binder</th>
<th>Shelf Life Stability</th>
<th>Dry Tensile (kgf)</th>
<th>Wet Tensile (kgf)</th>
<th>Retention, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative</td>
<td>None</td>
<td>3-5 hrs</td>
<td>5.71</td>
<td>5.64</td>
<td>98.7</td>
</tr>
<tr>
<td>H</td>
<td>Post-added</td>
<td>3 weeks</td>
<td>4.52</td>
<td>3.84</td>
<td>84.0</td>
</tr>
<tr>
<td>J</td>
<td>Cooked-in</td>
<td>&gt;3 months</td>
<td>5.48</td>
<td>4.7</td>
<td>85.8</td>
</tr>
</tbody>
</table>

By "Post-added" we mean blending of a certain amount of biopolymer latex binder with previously cooked urea-formaldehyde polymer resin; by "Cooked-in" we mean addition of the biopolymer latex binder during the polymerization of urea and formaldehyde.

Example 6
Replacement of SB Latex in Roofing Shingle Binder

Example 7
Binders with Varying Amounts of Crosslinker

Example 8
Binders with Different Crosslinkers

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Max Load Dry (kgF)</th>
<th>Max Load Wet (kgF)</th>
<th>Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF with 5% of SB</td>
<td>33.3</td>
<td>28.0</td>
<td>84.1</td>
</tr>
<tr>
<td>UF with 5% of Ecosphere 2202</td>
<td>25.8</td>
<td>24.2</td>
<td>94.1</td>
</tr>
<tr>
<td>UF with SB/Eco 1:3</td>
<td>32.9</td>
<td>28.1</td>
<td>85.5</td>
</tr>
<tr>
<td>UF with 5% of Ecosphere 2202 cooked in</td>
<td>34.3</td>
<td>28.0</td>
<td>81.7</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Wt % TEOS crosslinker</th>
<th>Dry strength (max load in KgF)</th>
<th>Wet strength (max load in KgF)</th>
<th>Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>50.1</td>
<td>7.5</td>
<td>14.9</td>
</tr>
<tr>
<td>0.5</td>
<td>62.9</td>
<td>28.8</td>
<td>45.7</td>
</tr>
<tr>
<td>1.0</td>
<td>66.1</td>
<td>30.6</td>
<td>46.3</td>
</tr>
<tr>
<td>3.0</td>
<td>61.3</td>
<td>22.3</td>
<td>36.3</td>
</tr>
<tr>
<td>5.0</td>
<td>57.4</td>
<td>22.9</td>
<td>40.0</td>
</tr>
</tbody>
</table>
## TABLE 5

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Dry strength (max load in KgF)</th>
<th>Wet strength (max load in KgF)</th>
<th>Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt % TEOS</td>
<td>64.9</td>
<td>50.9</td>
<td>78.3</td>
</tr>
<tr>
<td>3 wt % Ca metasilicate</td>
<td>61.4</td>
<td>47.6</td>
<td>77.4</td>
</tr>
<tr>
<td>1 wt % Ca metasilicate</td>
<td>61.3</td>
<td>37.6</td>
<td>61.3</td>
</tr>
<tr>
<td>1 wt % Na metasilicate</td>
<td>65.3</td>
<td>37.3</td>
<td>57.1</td>
</tr>
</tbody>
</table>

[0118] Thus, the invention provides a curable composition for forming a composite material wherein the composition includes a biopolymer nanoparticle latex including crosslinked nanoparticles, and a multifunctional crosslinking agent for forming a cured crosslinked binder joining a portion of a plurality of reinforcement fibers in the composite material.

[0119] Although the present invention has been described in detail with reference to certain embodiments, one skilled in the art will appreciate that the present invention can be practiced by other than the described embodiments, which have been presented for purposes of illustration and not of limitation. Therefore, the scope of the appended claims should not be limited to the description of the embodiments contained herein.

What is claimed is:

1. A curable composition, the composition comprising:
   a latex including particles comprising crosslinked biopolymer molecules; and
   a crosslinking agent in solution with the latex.
2. The curable composition of claim 1 wherein:
   the biopolymer molecules comprise amylose or amylopectin.
3. The curable composition of claim 1 wherein:
   the particles have an average particle size in the range from
   1 to 1000 nanometers.
4. The curable composition of claim 1 in combination with
   a plurality of fibers or wood in a form other than pulp.
5. The curable composition of claim 1 in combination with
   a plurality of mineral fibers.
6. The curable composition of claim 1 further comprising a
   non-biopolymer binder or a non-biopolymer latex.
7. The curable composition of claim 1 further comprising a
   polycarboxylic acid binder or a polyester binder.
8. The curable composition of claim 1 wherein the
   crosslinking agent is a silicate crosslinking agent.
9. The curable composition of claim 1 wherein the particles
   are formed by reactive extrusion processing.
10. The curable composition of claim 1 wherein:
    the particles are present in the curable composition at a
    concentration of between 4% and 20% by weight of the
    curable composition.
11. A composition comprising,
    a) an aqueous binder;
    b) dispersion of particles in the aqueous binder; and,
    c) a crosslinker in solution with the aqueous binder adapted
    to bond to the particles and to mineral fibers.
12. The composition of claim 11 wherein the particles
    comprise crosslinked starch.
13. The composition of claim 11 wherein the particles form
    a colloidal dispersion in the aqueous binder.
14. The composition of claim 11 wherein the curable
    binder is substantially formaldehyde free of has less than 1
    ppm of formaldehyde based on the weight of the composition.
15. The composition of claim 11 wherein the crosslinker is
    a silicate crosslinker.
16. The composition of claim 11 in combination with a
    non-woven mat of glass fibers.
17. A composition comprising,
    a) an aqueous formaldehyde binder;
    b) a dispersion of particles in the aqueous binder, the par-
    ticles comprising crosslinked biopolymers.
18. The composition of claim 17 wherein the particles are
    added during the polymerization of urea and formaldehyde.
19. The composition of claim 17 in combination with a mat
    of glass fibers and asphalt.
20. A composite material comprising:
    a binder comprising particles selected from the group con-
    sisting of a) particles made of crosslinked biopolymers,
    b) particles having an average size of less than 400 nm,
    c) particles having a volume swell ratio of 6 or more and
    d) particles comprising starch; and,
    a material comprising mineral fibers or non-pulped wood.

* * * * *