EXPANSION AGENTS FOR PAPER-BASED MATERIALS

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Filed: Aug. 15, 2008

Related U.S. Application Data
Continuation-in-part of application No. 12/184,308, filed on Aug. 1, 2008, which is a continuation of application No. PCT/US07/03159, filed on Feb. 5, 2007.

Publication Classification
Int. Cl. D21H 17/56 (2006.01) D21H 21/22 (2006.01) D21H 17/20 (2006.01) D21H 17/24 (2006.01)

U.S. Cl. ................. 162/164.6; 162/158; 162/164.1; 162/175

ABSTRACT
Compositions and methods of producing paper-based materials are disclosed. The techniques can utilize an amine-containing polymer, such as chitosan, to functionalize one or more components of a mixture used to form materials such as paper-based materials. Such components can include the fibers of a pulp and/or filler particles. Techniques and compositions are also described to further improve the qualities of a paper material by utilizing a complementary polymer which can couple with the amine-containing polymer. Other compositions and methods are directed to forming paper-based materials that are expandable.
EXPANSION AGENTS FOR PAPER-BASED MATERIALS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation-in-part application that claims the benefit of a U.S. patent application bearing Ser. No. 12/184,308, filed Aug. 1, 2008, entitled "Functionalization of Paper Components;" which is a continuation of PCT Application No. PCT/US07/05159, filed Feb. 5, 2007; which claims the benefit of a U.S. Provisional Patent Application filed on Feb. 3, 2006 and bearing serial number 60/765,119, and also claims the benefit of another U.S. Provisional Patent Application filed on Nov. 7, 2006 and bearing Ser. No. 60/864,783. All applications are hereby incorporated by reference herein in their entirety.

FIELD OF THE APPLICATION

[0002] The technical field of the present application relates to compositions and methods for enhancing the properties of materials such as paper-related products.

BACKGROUND

[0003] Paper manufacturing is an important industrial process, resulting in the production of a vast variety of products. Paper products oftentimes include the use of filler materials, which allow products to be produced more cheaply. The use of fillers, however, can decrease the quality of the product in terms of strength, appearance, and other features. Though additives have been derived for further improving the quality of manufactured paper, a need persists for processes and compositions that further improve the quality of paper. Indeed, the development of additives which result in improved efficiency and lower cost production is desirable.

SUMMARY

[0004] Some embodiments are directed to expandable paper products. The product can include paper pulp having fibers, which can optionally bear a net negative charge. The expandable paper product can also include expansion particles, which can be configured to increase the volume of the product. Linker agents can be configured to be attached to the expansion particles, which can interact with the fibers to increase retention of expansion particles in the expanded paper product. Linker agents can be covalently, or non-covalently, attached to one or more expansion particles.

[0005] Examples of expansion particles can include one or more of blowing agents, encapsulated propellants, and elastomer-based particles. Encapsulated propellants can include a polymeric shell encapsulating an expandable material. Expansion particles can also be embodied by particles that exhibit hydrophobicity.

[0006] Linker agents can be configured to impart a net positive charge to a surface of the plurality of expansion particles. Linker agents can include any combination of entities such as a coupling agent, a crosslinking agent, and a polymer. In some instances, a multifunctional silane coupling agent can be used as a linker agent. Crosslinking agents, which can covalently link an expansion particle with a pulp fiber, can include any combination of functional groups such as an aldehyde, an isocyanate, and an epoxide. Polymers or linker agents can include any combination of a cationic polymer, a polymer exhibiting lower critical solution temperature behavior, a pH sensitive polymer, and an amphiphilic polymer. Amine-containing polymers, such as polyetheramine, chitosan, polyvinyl amine, polyalkyleneimine, polyallyl amine, and polydiallyl amine, can be used as linker agents.

DETAILED DESCRIPTION

[0007] Other embodiments are directed to methods for producing an expandable paper product. A linker agent can be used to attach expansion particles to fibers of a paper pulp, which can act to increase retention of the expansion particles. The linker agent can be covalently or non-covalently attached. Linker agents can be used to impart a net positive charge to a surface of at least some of the expansion particles, which can be attracted to a net negatively charged fiber in the paper pulp. The expansion particles can be activated, either before or after the linker agent is attached to the particles and/or inserted into a paper making formulation, to produce the expandable paper product. Activation can be embodiment by elevating the temperature of the expansion particles to cause an increase in volume in the expandable paper product.

[0008] In some instances, hydroxyl groups can be introduced on a surface of the expansion particles. The expansion particles can be exposed to a silane-containing fluid (e.g., gas and/or liquid), which can result in at least a portion of the silane-containing fluid attaching to at least some of the hydroxyl groups. In other instances, a polymer can be provided to act as a linker agent, which can exhibit a lower critical solution temperature. The expansion particles can be contacted with the polymer at a sufficiently high temperature to cause precipitation of the polymer onto the surface at least some of the expansion particles. In another instance, the expansion particles can be contacted with a polymer (e.g., chitosan or some other amine-containing polymer) at a sufficiently high pH to cause precipitation of the polymer onto a surface of at least some expansion particles. The expansion particles can also be crosslinked with the fibers of the paper pulp.

[0009] As utilized in the present application, the term "functionalization" and "functionalize" refer to a change in one or more aspects of the physicochemical nature of an entity. For example, with respect to a particle, functionalization of a particle surface refers to a change in one or more aspects of the particle surface, which result in some physicochemical change in how the particle surface interacts with other entities. Consistent with some embodiments described herein, functionalization of an entity can result in a change in some macroscopic property (e.g., tensile strength) when the functionalized entity is used to produce a product due to the associations of the functionalized entity with other components, or even with other functionalized entities. Functionalization can also alter the types of chemical reactions that an entity can be subjected to relative to when the entity is not functionalized.

[0010] The term "polymer" refers to a molecule comprising a plurality of repeat units or monomers. A polymer can comprise one or more distinct repeat units. For example, a "copolymer" refers to a polymer having two or more distinct repeat units. Repeat units can be arranged in a variety of manners. For example, a homopolymer refers to a polymer with one type of repeat unit where the repeat units are adjacent connected. In another example, a plurality of different repeat units can be assembled as a copolymer. If A represents one repeat unit and B represents another repeat unit, copolymers can be represented as blocks of joined units (e.g., A-A-
interstitially spaced units (e.g., A-B-A-B-A-B-A-B-A-B . . . A.A-A-A . . . B-B-B-B-B-B . . . ) or randomly arranged units. Of course, these representations can be made with 3 or more types of repeat units as well. In general, polymers (e.g., homopolymers or copolymers) include macromolecules in a broad range of configurations (e.g., cross-linked, linear, and/or branched).

[0011] The term "segments," and the phrase "polymer segments," which can be used interchangeably, refer to a portion of a polymer that includes one or more units. A segment can include one or more types of units (e.g., A-A-A-A or A-B-C-A-C).

[0012] Some embodiments are directed to compositions and methods for producing materials such as paper-based materials. Such embodiments can utilize an amine-containing polymer, which can be a polycation. The amine-containing polymer can associate with one or more components of a mixture (e.g., a paper-making mixture). Components can include pulp fibers, the surfaces of a particle filler, and other elements or portions of the elements. In general, the association of the amine-containing polymer with any particular component can functionalize that component, potentially increasing the strength, or improving one or more other qualities, of a paper product produced with compositions consistent with such embodiments.

[0013] Accordingly, some exemplary embodiments are directed to compositions that can be used to produce various materials, such as paper-based materials. Though such mixtures can include any number of typical components utilized in commercial paper making, some embodiments include a solution medium (e.g., an aqueous solution), a pulp material, and filler particles. The mixtures can include an amine-containing polymer, which can associate and/or interact with one or more components of the mixture. For example, the amine-containing polymer can functionalize the component of the mixture with which the polymer interacts. In one aspect, the amine-containing polymer can functionalize the particle filler component (e.g., the surface of the filler particles), but does not substantially functionalize the pulp. In another aspect, the amine-containing polymer can functionalize the pulp (e.g., the fibers of the pulp), but does not substantially functionalize the filler component. In still another aspect, the amine-containing polymer functionalizes both the filler component and the pulp. Functionalization can and cannot also optionally occur with other components in a selective manner.

[0014] Functionalization of one or more components of a paper-making mixture with an amine-containing polymer can result in the enhancement of one or more properties of the mixture or a paper product formed from the mixture, relative to the properties when functionalization of the component is absent. For instance, functionalization of one or more components can lead to an enhancement of mechanical properties of a paper product, e.g., tensile strength.

[0015] With respect to the pulp and the filler particles in a mixture, though some embodiments can utilize functionalization of both components, some particular embodiments only functionalize one of the two components, while leaving the other component substantially unfunctionalized, i.e., either the pulp or the filler particles are functionalized, but not both. It has surprisingly been found that in some instances, only functionalizing the pulp or the filler particles, but not both components, can lead to paper products that are stronger, or about as strong, relative to both components being functionalized.

[0016] The following text describes some features of the components of mixtures consistent with embodiments of the present invention. Unless specifically delineated in particular embodiments, it is understood that one or more of the described features, or specific components, can be utilized with any of the embodiments within the scope of the present application. For instance, any of the specific types of amine-containing polymers can be used in any mixture type (e.g., chitosan or polyalkyleneimines or a combination of the two can be used to functionalize any one or more of pulp, filler particles, and other components of a mixture). It is also understood that features of components can be utilized any combination with the embodiments consistent herein. For instance, in describing the average molecular weight of an amine-containing polymer, it is understood that such average molecular weights can be applied to any described polymer (e.g., homopolymers or copolymers of any particular type of polymer such as branched polyethyleneimine or polyvinylamine). It is further understood that those skilled in the art will appreciate variations and combinations of the described features that are also within the scope of the present disclosure.

[0017] With respect to various embodiments disclosed herein, an amine-containing polymer can be any homopolymer or copolymer that has at least a portion of its repeat units containing an amine (e.g., quaternary, tertiary, secondary or primary). Advantageously, the amine-containing polymer can contain repeat units with primary amines due to the reactivity of the primary amine. In particular embodiments, the amine-containing polymer is a polycation. Polycations can be advantageously utilized, for example, when the components sought to be functionalized have a net negative charge. In such instances, the use of electrostatic interactions with pulp fibers and/or filler can be effective in certain embodiments when the pulp fibers and/or filler have an inherent negative charge that can interact with the polycation.

[0018] A variety of amine-containing polymers can be utilized with various embodiments that include one or more different types of amine-containing polymers. Amine-containing polymers can be naturally occurring macromolecules with amine groups such as chitosan. Also, various types of synthetic polymers bearing amine groups such as polyalkyleneamines, polyvinylamine, polyallylamine, and polydiallylamine can be utilized. Of course, copolymers comprising any combination of amine-containing homopolymer units can also be used.

[0019] In some instances, it can be advantageous to utilize amine-containing polymers that are relatively inexpensive because of the scale and relative costs of paper manufacturing. Chitosan is an aminopolysaccharide typically prepared by deacetylation of chitin (poly-beta(1,4)-N-acetyl-D-glucosamine) obtained from marine organisms such as shrimp, crabs, lobsters, squid, and the like. Accordingly, it can be prepared with relative ease. Branched polyethyleneimine (herein "BPEI") is an easily manufactured synthetic polymer that is also readily available at moderate cost. Thus, some embodiments utilize chitosan, polyethyleneimine (such as BPEI), or a combination of the two polymers as separate homopolymers or as one or more copolymers. Though many specific instances herein discuss the use of chitosan with particular embodiments and examples, it is understood that such descriptions are merely illustrative of features of the present invention, and not intended to limit the practice of the present invention.
Though the average molecular weight of an amine-containing polymer is not necessarily limited, in some embodiments the average molecular weight of the amine-containing polymer can range from about 1,000 daltons to about 10,000,000 daltons; or from about 10,000 daltons to about 500,000 daltons. Such ranges can advantageously utilize amine-containing polymers which can be large enough to functionalize one or more components effectively, while not being so large as to effect the paper-making process.

Measurement of the average molecular weights for any polymer discussed herein can be with respect to a number of bases. For example, can be number averaged, weight averaged, or averaged based on some other weighting factors. As well, the techniques utilized to determine molecular weight can include the range of those known to those skilled in the art. Examples include gel permeation chromatography and light-scattering.

For certain amine-containing polymers, the average molecular weight can be difficult to ascertain. Chitosan is an example of such an amine-containing polymer. In such instances, the average molecular weight can be defined by some alternative parameter such as viscosity. Accordingly, in some embodiments the chitosan has an average molecular weight defined by a viscosity range between about 10 centipoise and about 800 centipoise. The viscosity can optionally be further defined by a set of conditions, such as being measured for a 1% solution of chitosan in pH 4 (or 0.1M) aqueous acetic acid at 25°C.

The pulp utilized in some embodiments disclosed herein can comprise fibers such as cellulose-based fibers, and can also include components typically found in pulps used to make paper products. Accordingly, the fibers of the pulp can have a net negative charge. Such charge can be utilized advantageously in some embodiments to cause electrostatic attraction of an amine-containing polymer that is, or is partially, a polycation. In some embodiments, the fibers of a pulp exclude the presence of synthetic fibers such as polymer-based fibers (e.g., aromatic amide fibers). Thus, some embodiments utilize pulps that include substantially naturally-occurring fibers.

Fillers utilized in some embodiments disclosed herein can include particulates that are typically utilized as fillers in paper manufacturing applications. For instance, the fillers can have a surface that is, at least partially, substantially inorganic in nature. Thus, non-limiting examples of filler particles can include particles constructed from calcium carbonate, kaolin, titanium dioxide, and other inorganic materials. Fillers can also be a composite of inorganic and organic particles. In some embodiments, the surface of the fillers can have a net negative charge, which can tend to attract amine-containing polymers that are polycationic in nature.

In some embodiments, functionalization of one or more components (e.g., pulp and/or filler) can be achieved by some type of coupling interaction between an amine-containing polymer and the component. Such coupling can be achieved using either a coupling agent or through electrostatic interactions that permit the polycation to self-assemble onto the surface of the component. The use of electrostatic interactions with pulp fibers and filler can be effective in certain embodiments because both pulp fibers and filler have an inherent negative charge that can interact with the polycation. Coupling agents, such as multifunctional crosslinking agents described herein, can be used to increase the amount of amine-containing polymer that can adhere to a surface, such as a surface of the filler particles.

For the compositions and methods disclosed herein, multifunctional crosslinking agents can be used as a coupling agent. Such agents can react with at least one of the amine-containing polymer and the component to be coupled. For example, in some embodiments the multifunctional coupling agent can include a silicon containing coupling agent and at least one of the following functional groups: an epoxy group, a hydroxyl group, a carboxyl group, and/or an isocyanate group. In one embodiment, the multifunctional coupling agent is a silane coupling agent. In another embodiment, the coupling agent does not include silicon (e.g., in embodiments in which silicon is not used). In certain embodiments, the multifunctional coupling agent includes an isocyanosilane, for example, a trialkoxy isocyanosilane, such as trimethoxy isocyanosilane, triethoxy isocyanosilane, and/or triisoproxy isocyanosilane. In certain embodiments, the multifunctional coupling agent includes an epoxy siloxane. The multifunctional coupling agent can include triethoxy methacryloxypropyl silane. Other agents can also be employed as would be understood by those skilled in the art.

In some embodiments, functionalization of a paper making component can be achieved without the use of a coupling agent. For instance, the amine-containing polymer can be added directly to a pulp stream, a filler stream, or to both, resulting in the association of the amine-containing polymer and the pulp, filler, or both. If chitosan is used as the amine-containing polymer, the component can be functionalized by precipitating chitosan onto the surface of the component using, for example, a shift in pH. Since chitosan is only soluble in acidic conditions, the polymer can be made to precipitate when the pH is raised by adding a base to the solution after adding chitosan (e.g., to a pH of at least about 6). Accordingly, it can be advantageous to prepare mixtures of one or more components (e.g., one or more of fillers and pulp) with chitosan having a pH close to the precipitation point of the amine-containing polymer to reduce the amount of base needed to induce precipitation and functionalize the component. Thus, the pH of the mixture can be in the range from about 4 to about 8, or from about 5 to about 8, or from about 6 to about 8. In some instances, it can be advantageous to utilize a multivalent acid to enhance the dissolution of chitosan into a pulp furnish or other paper-making mixture. Accordingly, some embodiments can utilize a mixture with one or more multivalent acids; non-limiting examples include citric, tartaric, aldaric (any in the family), oxalic, malonic, malic, succinic, glutaric, and adipic acid.

Alternatively, precipitation can occur spontaneously when a chitosan solution is added to a basic environment like a calcium carbonate solution. In some embodiments, the amount of chitosan to be added can be from about 0.01% to about 5.0% (based on weight of the component), or from about 0.1% to about 2%.

In some embodiments, a complementary polymer can be added to a paper-making mixture. In general, the complementary polymer can be capable of coupling with an amine-containing polymer (e.g., the complementary polymer can react or nonreactively interact with the amine-containing polymer). Such a complementary polymer can be used to enhance the properties of the mixture, or a resulting paper product produced from the mixture, relative to not using the complementary polymer. The complementary polymer can
be utilized when an amine-containing polymer is intended to functionalize pulp (e.g., fibers), filler particles, or both pulp and filler particles, among other paper-making mixture components.

[0030] In a mixture, the complementary polymer can be coupled with the amine-containing polymer, or can be free but will eventually couple with the amine-containing polymer. As well, the complementary polymer can be added to a process after an amine-containing polymer has functionalized one or more mixture components, or before functionalization has occurred such as in an emulsion technique described herein.

[0031] Some embodiments can utilize any complementary polymer (e.g., homopolymers, copolymers, and combinations of different polymers) which can interact nonreactively with an amine-containing polymer or which can react with the amine-containing polymer (e.g., reacting with an amine group). If the complementary polymer nonreactively interacts rather than reacts with the amine-containing polymer, the interaction may involve electrostatic forces, hydrogen bonds, or any other secondary interaction forces or association mechanisms. For example, the nonreactive interaction can be an electrostatic interaction when a polyanion is used as a portion or the entirety of the complementary polymer. Accordingly, an appropriate polymer can also be used that includes repeat units with anionic charge. Advantageously, the polyanion can include one or more carboxylic acid groups. Non-limiting examples of suitable polyanion, polyanion segments, include biopolymers such as pectin, xanthan gum, and carboxymethyl cellulose, and synthetic polymers such as polycrylic acid or poly(meth)acrylic acid. Other types of complementary polymers, such as polyanions or polymers with polyanionic segments, can also be used consistent with the embodiments disclosed herein.

[0032] In embodiments when the complementary polymer can react with the amine-containing polymer, the complementary polymer can contain repeat units that include one or more groups which can react with a portion of the amine-containing polymer. In particular embodiments, the groups can be selected to react with an amine functionality (primary, secondary, tertiary, or quaternary). Such groups include but are not limited to epoxides, anhydrides (e.g., maleic anhydride), carboxylic acids, and isocyanates. When copolymers are utilized as a complementary polymer, such copolymers can also contain some repeat units with these reactive groups. The molecular weight of the complementary polymer can be between about 1,000 daltons and about 10,000,000 daltons; or between about 10,000 daltons and about 500,000 daltons.

[0033] As previously mentioned, a complementary polymer can be used to enhance the properties of a mixture, or a resulting paper product produced from the mixture. For example, the complementary polymer can be used to provide additional strength to a resulting paper-based product, whether an amine-containing polymer is used to functionalize pulp, filler particles, or both pulp and filler. Without being bound by theory, it is believed that the complementary polymer can act to bridge components that have been functionalized with the amine-containing polymer. As an example, if only the pulp fibers are functionalized, the polymer bridges different fibers. However, if both the pulp and filler have been functionalized, the filler can also be bound to the pulp for enhancing mechanical properties of the paper making mixture or a resulting paper product.

[0034] In some embodiments, the complementary polymer can contain one or more components that can impart additional or alternative properties to a resulting paper product besides strength enhancement. As an example, elastic homopolymers or copolymers can be used to change the resulting paper's stiffness or wear resistance, or hydrophobic homopolymers or copolymers can be used to change the water contact angle (e.g., the tendency to resist water penetration). Combinations of various types of complementary polymers can also be used to provide multiple property enhancement (e.g., strength, elasticity, and water resistance).

[0035] In other embodiments, the complementary polymer can be emulsified by the amine-containing polymer. This combination can be mixed with a portion of a pulp furnish, i.e., delivered in one addition versus in sequential steps. In this case, one or a combination of the type of amine-containing polymers discussed previously can be used, along with one or more complementary polymers which are not soluble in water. The complementary polymer can interact nonreactively with the amine-containing polymer. Besides being substantially hydrophobic, the complementary polymer can have any of the properties previously disclosed herein. The complementary polymer can either be emulsified using the amine-containing polymer alone (e.g., if it is in liquid form) or dissolved in a water-immiscible solvent to form a “water-in-oil” emulsion. This emulsion can then be added to either the fiber and/or filler stream so that the amine-containing polymer can interact with the filler and/or fiber. For example, upon drying, the micelle can open up to allow the emulsified polymer to interact or bind between multiple fillers and/or fibers.

[0036] Some exemplary embodiments are drawn to methods of producing materials such as paper-based materials, which are optionally consistent with one or more of the compositions disclosed herein. One exemplary method includes functionalizing fibers of a pulp using an amine-containing polymer. Filler particles can be combined with the functionalized pulp fibers to produce at least a portion of a paper-forming mixture such as a pulp furnish. A paper-based material can then be produced from the paper-forming mixture. In some instances, it can be advantageous for the method not to substantially functionalize the filler particles, though the pulp components can be functionalized. The method can be practiced as a batch process or in continuous fashion using flowing streams of components.

[0037] In alternative embodiments, the methods of producing materials functionalize filler particles (e.g., the surface of filler particles) using the amine-containing polymer. Fibers of a pulp can be combined with the functionalized filler particles to produce a portion or the entirety of a paper-making mixture, which can be subsequently used to produce a paper-based material. In this embodiment, it can be advantageous in some instances to not substantially functionalize the fibers of the pulp. In still other embodiments, both the pulp and the filler particles can be functionalized.

[0038] The types of amine-containing polymers, filler particles, and pulps that can be used with these methods include all the types disclosed in the present application. As well, specific techniques for functionalizing the pulp, filler particle, or both pulp and filler particles can follow the techniques disclosed herein (e.g., addition of coupling agents to aid coupling of an amine-containing polymer to a component). In one particular example, chitosan can be combined with either pulp or filler particles to form a functionalizing mixture. The
pH of the mixture can be raised to a level of at least about 6 to cause the chitosan to associate with the pulp fibers or filler particles, thereby functionalizing the component. It is also understood that paper-forming mixtures utilized in the various methods can include any of the other components of mixtures disclosed herein (e.g., complementary polymers).

The step of producing a paper-based material from the paper-forming mixture can utilize any set of paper forming techniques including those known to ones skilled in the art. For example, the paper-forming mixture can be set on a screen to form a sheet. The sheet can be subsequently dried to form the paper product. Modifications of this technique and others to accommodate embodiments disclosed herein are also contemplated by the present application.

For example, in methods that utilize a complementary polymer, the complementary polymer can be added to a paper-making mixture before a sheet is formed from the mixture, or after the sheet has been formed (e.g., applied onto the sheet). When the complementary polymer is added to the process before sheet formation, it can be of sufficient quantity to produce a desired enhancement in some property (e.g., mechanical properties of the end paper product), but not enough to cause problems with sheet formation. In some embodiments, this addition level can be from about 0.01% to about 5.0% (based on sheet dry weight), or between about 0.1% and about 2%.

When the complementary polymer is added after sheet formation, it can be added prior to drying the sheet (e.g., while the sheet is still on the paper machine), or it may be added after drying the sheet (e.g., in a coating or other dry end process). The polymer can be added in solution form which can either be aqueous or non-aqueous. Aqueous solutions can be used when addition is done prior to drying the sheet, but non-aqueous solutions can be advantageous after drying due to energy usage in eliminating the solvent. When the complementary polymer is reactive, the reaction can occur anytime in the process after introduction of the complementary polymer, i.e., the reaction between the complementary polymer and the amine-containing polymer can occur either immediately after addition or anytime thereafter.

In alternative embodiments connected with the use of a complementary polymer, the methods described herein can include emulsifying a complementary polymer (e.g., a substantially hydrophobic polymer) with the amine-containing polymer in an aqueous solution. The emulsion formed from the complementary polymer and amine-containing polymer can be added to the pulp fibers, the filler particles, or both to cause the amine-containing polymer to functionalize one or more components. In instances where both pulp fibers and filler particles are functionalized, the amine-containing polymer can couple a portion of the pulp and a portion of the filler particles.

Some embodiments are directed to compositions and methods for forming paper-based materials that are expandable such as paper-based materials that exhibit high bending stiffness. High bending stiffness is desirable in many paper and paperboard applications. Bending stiffness relates to the amount of force required to bend a paper product through a designated angle. Stiffness can be important for packaging materials, box boards, corrugated paper products, and the like. At the same time, it is desirable that packaging materials, while stiff, be lightweight and economically produced.

The use of expansion agents in a paper pulp formulation can create an expandable paper material (e.g., high bending stiffness material) by creating void spaces in a paper product upon activation. These agents, however, are often hydrophobic in nature, and usually lack the surface functionalities necessary to attach themselves to the pulp fibers during the papermaking process. Their hydrophobicity also makes their dispersion in aqueous slurries difficult and thereby reduces the effectiveness of use of such agents in papermaking.

Accordingly, some embodiments are drawn to techniques and compositions involving expandable paper products that incorporate the use of linker agents. The linker agents can be configured to be attached to expansion particles, which can be activated to increase the volume of the expandable paper product. The linker agents can also interact with the fibers of a paper pulp to increase retention of the expansion particles, relative to not using a linker agent, during the paper making process. Any of the paper pulps, and associated fibers, disclosed in the present application can be utilized with the expandable paper product embodiments described herein.

The term “attach” refers to a coupling between entities. Such coupling can either be direct, such as a polymer sharing a covalent chemical bond with a surface site of a particle together, or can be indirect, such as coupling a polymer and a surface site together using an intermediary agent which is directly coupled to the polymer and the surface site (e.g., a bifunctional coupling agent). Attachment between entities can occur by any feasible mechanism consistent with an embodiment of the invention. Accordingly, non-limiting mechanisms by which chemical entities can be bound together include covalent bonding, non-covalent bonding, electrostatic (or ionic) forces, Van der Waals forces, hydrogen bonding, other intermolecular forces, and combinations of the listed mechanisms.

Some embodiments utilize linker agents that are covalently attached to the expansion particles, while other embodiments utilize linker agents that are not covalently attached to the expansion particles.

Since many expansion particles are hydrophobic in nature, the particles often do not inherently possess surface functionalities readily available for chemical modification. Accordingly, linker agents can act to modify the surfaces of the expansion particles, which can improve the particulate retention and dispersion during the paper making process. For example, many paper pulps are formed from fibers that carry a net negative charge. Accordingly, some embodiments utilize linker agents capable of imparting a net positive charge to the surfaces of the expansion particles. The modified particles can then have some electrical charge affinity for the fibers, and thus exhibit improved expansion particle retention in the papermaking pulp and/or paper product. It is understood, however, that linker agent affinity for a pulp fiber can be through any type of molecular force, and is not limited to electrostatic interactions. Indeed, in some embodiments, the linker agent can be covalently bonded to a fiber and/or attracted by other forces such as van der Waals, hydrogen bonding, polymer/fiber entanglement and/or other molecular forces.

A variety of expansion particle types can be utilized with the embodiments disclosed herein, including combinations of different types of particles. Some non-limiting examples include blowing agents, encapsulated propellants,
and elastomer-based particles. Activation of the expansion particle can be through any suitable mechanism such as chemical reaction and/or exposure to a selected temperature range. For example, an expansion particle can be formed in a chemical reaction during the papermaking process to provide the expanded qualities of the final product.

[0050] Blowing agents in the pre-blown state can be added into the fiber slurry before a sheet of paper is formed. The blowing agents can include any particles that release gas upon being exposed to a sufficiently high temperature to cause void formation that result in a foamed sheet being formed. Non-limiting examples of materials that can act as blowing agents include structures that can comprise sodium bicarbonate, azodicarbonamide-based blowing agents, and p,p'-oxbis (benzenesulfonfonylhydrazide).

[0051] Encapsulated propellants can be made of polymeric materials, which encapsulate a propellant (e.g., gas or liquid or other expandable material). When heated to above its softening temperature, the polymer shell softens and the gas/liquid or other material contained within the shell expands thereby irreversibly expanding the polymer shell. When such particles are incorporated into paper making process, they can expand during the drying stage of the papermaking, or later resulting in creation of void spaces in the interior of the paper leading to increased stiffness while reducing the basis weight of such a paper. Some potential encapsulated propellants include styrene particles encapsulating organic solvents such as chlorinated hydrocarbons, toluene, etc.; or particles made of styrene-maleic anhydride copolymers which trap acetone within the particle’s interior.

[0052] For compressible articles, expansion particles made with elastomers can be effective as dampeners in sensitive packaging applications. Elastomeric expandable particles can be prepared by a mixture of polymers such as styrene and butadiene polymers, or their copolymers. The elastomer component and thereby compressibility of the particles could be controlled by the content of the butadiene part. In another example, styrene maleic anhydride could be mixed (in acetone) with isobutylene-maleic anhydride copolymers in different ratios to change the elastomeric content of the resulting particle. In such embodiments, the elastomeric particles can regain their shape upon removal of force absorbing shock imposed on the paperboard. Such expandable particles are commonly available and can also be made in the laboratory using a variety of polymers using spraying or spray drying equipment.

[0053] Linker agents for use with some embodiments include any combination of materials capable of attaching with expansion particles and interacting with the fibers of a paper pulp. Examples of linker agents include coupling agents, crosslinking agents, and a variety of polymers.

[0054] Coupling agents include multifunctional coupling agents such as multifunctional silane coupling agents, and others as described earlier in the present application. Application of the coupling agents can be performed in a variety of manners. In some particular embodiments, the expansion particles can be exposed to a silane-containing fluid (e.g., vapors or a dilute solution) such as aminopropyltrimethoxysilane. To enable silane attachment, hydroxyl groups can be introduced on the surface of the expansion particles using mild oxidizing agents, or corona treatment, or radio frequency plasma treatment. Such silane modified particles would then have amine functionality, and can associate with anionic pulp fibers.

[0055] Crosslinking agents include entities capable of covalently linking fibers with expansion particles. This can lead to stronger retention of expansion particles in the paper and paperboard articles, and can reduce the possibility of particles coming off the paperboard and reducing its effectiveness. Potential crosslinking agents include molecules with one or more suitable functional groups such as aldehydes (e.g., glyoxal and glutaraldehyde), epoxides, and isocyanates.

[0056] A variety of polymers can be used as linking agents. For example, the polymers include polycations for imparting a net positive charge to an expansion particle surface. In some embodiments, the polycations are amine-containing polymers such as chitosan and others as described within the present application. Attachment of the polymers to an expansion particle (e.g., chitosan to a blowing agent) can be provided through a variety of mechanisms.

[0057] In some embodiments, linker agents are utilized that include polymers that exhibit a lower critical solution temperature (herein “LCST”) phenomena. That is, the polymer tends to phase separate at elevated temperatures. For instance, polymers such as polyetheramines (e.g., Jeffamine compounds from Huntsman Corporation, Woodlands, Tex.) can be used to modify surfaces of expansion particles. Polyetheramines containing either ethylenediamine or propylenediamine monomers exhibit LCST behavior. By contacting expansion particles in mixtures containing polyetheramines at temperatures below their LCST, and slowly warming the solution to above LCST, the precipitation of the polyetheramines onto the surfaces of particles is induced. This can immobilize cationic groups (e.g., amines) on particle surfaces, which can be useful in attractive association with anionic pulp fibers.

[0058] In some embodiments, amphiphilic block copolymers can be utilized as linker agents. The amphiphilic block copolymers can have hydrophobic and hydrophilic polymer segments. The hydrophilic segments can include cationic groups for potential interaction with pulp fibers. The hydrophobic segments can interact with an expansion particle surface, resulting in the attachment of the block copolymer to the expansion particle. Accordingly, the hydrophilic segments with cationic groups can act to impart a net positive charge to the expansion particle surface.

[0059] In some embodiments, expansion particles are attached to polymers having a pH sensitivity. For instance, chitosan solutions are prepared by dissolving the chitosan polymer slowly in acidic aqueous solution. Once soluble, chitosan can be precipitated out of the solution by raising the pH of this solution using a base such as NaOH. If there are particles present in the solution, the precipitate will coat their surface resulting in amine functionalized particles. Accordingly, expansion particles can be mixed in an acidic chitosan solution. The pH of the solution can be increased incrementally until chitosan is precipitated onto the particles resulting in a surface coating of chitosan. The precipitation can lead to high particle surface coverage with chitosan. The amount of surface coverage by chitosan can be controlled by varying the ratio of chitosan to particles in the mixture.

[0060] In some embodiments, a mixture of different polymers can be utilized. The polymers are preferably soluble in a common solvent and can be deposited onto the surface of the expansion particles, or can be formed into an expansion particle, with at least one of the polymers acting as the linker agent. For instance, at least one of the polymers can be present
in higher proportion, which can form the bulk of a particle shell. The minority polymer component can have amine functionality, or other cationic functionality, either in the backbone or as a side group. An example is chitosan. The minority polymer component can become part of the shell of the expansion particle and can act as a linker agent, providing cationic surface functionality to enable attachment between the particle and anionic surfaces such as pulp fibers.

In a particular embodiment, mixtures of polymers such as styrene maleic anhydride (herein “SMA”) and styrene maleimide (herein “SMAI”) copolymers can be used to create expansion particles which have cationic maleimide functional groups from SMAI on their surface. SMA and SMAI can be mixed together in common solvents such as acetone or other expandable fluid. The mixture can be spray dried to produce expansion particles encapsulating acetone with maleimide surface functional groups. The density of maleimide surface functionality and thereby the surface charge density can be controlled by varying the amount of SMAI in the mixture.

In some embodiments, chitosan analogues polymers can be utilized as linker agents. The chitosan analogues can be designed by taking polymers with amine functionalities such as polyvinylamine or polyallylamine or polyethyleneimine and modifying them with side groups that are hydrophobic in nature. Examples of such side groups can include hydrocarbon-based chains (e.g., linear or branched carbon/hydrogen molecules, either aromatic or aliphatic, such as those having between 2 and 20 carbons in the backbone), which can be unsubstituted or substituted with water-repellent functionalities such as fluoro functionalities and/or heteroaromatics. The hydrophobic groups can render the water soluble amine polymers less water soluble at selected pHs, resulting in precipitation of the modified polymer. Such chitosan analogues can be used to functionalize expansion particles to increase their retention onto to negatively charged surfaces.

In other embodiments, side groups attached to an amine-containing polymer can include polymer segments or monomers exhibiting LCST behavior. Association and precipitation of the amine-containing polymer with these side groups can be controlled by temperature manipulation.

Other embodiments are drawn to paper-based materials that can be produced from any of the mixtures or methods described in the present application.

EXAMPLES

The following examples are provided to illustrate some aspects of the present application. The examples, however, are not intended to limit the scope of any embodiment of the invention.

Example 1
Control Pulp Synthesis

A 5% pulp slurry was prepared by blending 17.5 g of pine furnish (dry weight) with 32.5 g of birch (dry weight) in 1 L of water. This thick slurry was then diluted to 0.5% by adding 9.5 L of water to the 1 L of thick stock slurry. To this 0.5% slurry, 12.5 mL of a 2.0% CG110 chitosan solution (Primex, Iceland) was slowly added.

Example 3
Chitosan on Pulp (with Addition of NaOH)

A 5% pulp slurry was prepared by blending 17.5 g of pine furnish (dry weight) with 32.5 g of birch (dry weight) in 1 L of water. This thick slurry was then diluted to 0.5% by adding 9.5 L of water to the 1 L of thick stock slurry. To this 0.5% slurry, 12.5 mL of a 2.0% CG110 chitosan solution was slowly added. A solution of 0.1 M NaOH was then titrated into the pulp slurry until the pH reached 8.0 (the original pH was approximately 6.5—example 2).

Example 4
Control Precipitated Calcium Carbonate (PCC)

A 10% PCC slurry was made by stirring 10 g of PCC into 1 L of water.

Example 5
Chitosan Coated PCC

A 10% PCC slurry was made by stirring 10 g of PCC into 100 mL of water. To this slurry, 2.5 mL of a 2.0% CG110 chitosan solution was slowly added. The high pH of the PCC solution caused the chitosan to precipitate onto the PCC particles. This was verified by taking a sample and attaching a reactive intense blue dye that turned the PCC blue. The dye did not react with PCC that was not functionalized with chitosan.

Example 6
Handsheets Preparation

Handsheets were prepared using a handsheet maker, model Mark V Dynamic Handsheet Mold/Paper Chemistry Jar from Paper Chemistry Laboratory Inc. (Larchmont, N.Y.). The appropriate volume of 0.5% pulp slurry (functionalized or unfunctionalized) was combined with the appropriate volume of the 10% filler slurry (functionalized or unfunctionalized). This combined slurry was diluted with water up to 2 L and added to the handsheet maker. The overhead stirrer was then powered on and set to stir at 1100 RPM for 5 seconds, 700 RPM for 5 seconds, 400 RPM for 5 seconds, and then raised out of the slurry. The water was then drained off. The subsequent sheet was then transferred off of the wire and pressed and dried. Each test condition was repeated to make two handsheets for each trial point. Three 1" wide strips were then cut out from each handsheet for tensile testing on an Instron Single Column Testing System Model #3343 (Norwood, Mass.). The reported values are the averages of the six strips (three from each handsheet).

Example 7
Control 100% Pulp

Two handsheets were produced using the above procedure. In the process, 500 mL of pulp from example 1 was used along with no filler. These were control sheets that had an average max load/width of 9.9 lb/in. When normalized by
the basis weight (i.e., the density of each sheet on a mass per unit area basis), the result was 0.11 lb*in²/lb.

Example 8

100% Pulp (w/Chitosan, no Base)

[0073] Two handsheets were produced using the above procedure. In the process, 500 mL of pulp from example 2 was used with no filler. These sheets had an average max load/width of 10.1 lb/in. When normalized by the basis weight, the result was 0.12 lb*in²/lb.

Example 9

Control 90% Pulp/10% PCC

[0074] Two handsheets were produced using the above procedure. In the process, 450 mL of pulp from example 1 was used with 12.5 mL of filler from example 4. The retention of the filler from example 4 with pulp from example 1 was previously tested to be approximately 20%, so these handsheets would be approximately 10% by weight PCC. These 90% fiber/10% PCC sheets had an average max load/width of 5.9 lb/in. When normalized by the basis weight, the result was 0.068 lb*in²/lb.

Example 10

90% Pulp (with Chitosan, No Base)/10% PCC

[0075] Two handsheets were produced using the above procedure. In the process, 450 mL of pulp from example 2 was used with 3.0 mL of filler from example 4. The retention of the filler from example 4 with pulp from example 2 was previously tested to be approximately 83%, so these handsheets would be approximately 10% by weight PCC. These 90% fiber/10% PCC sheets had an average max load/width of 9.1 lb/in. When normalized by the basis weight, the result was 0.095 lb*in²/lb.

Example 11

90% Pulp (with Chitosan, NaOH added)/10% PCC

[0076] Two handsheets were produced using the above procedure. In the process, 450 mL of pulp from example 3 was used with 3.0 mL of filler from example 4. The retention of the filler from example 4 with pulp from example 3 was previously tested to be approximately 83%, so these handsheets would be approximately 10% by weight PCC. These 90% fiber/10% PCC sheets had an average max load/width of 10.1 lb/in. When normalized by the basis weight, the result was 0.11 lb*in²/lb; a substantially similar result to the control sample of 100% pulp.

Example 12

90% Pulp/10% PCC (with Chitosan)

[0077] Two handsheets were produced using the above procedure. In the process, 450 mL of pulp from example 1 was used with 2.5 mL of filler from example 5. The retention of the filler from example 5 with pulp from example 1 was previously tested to be approximately 99%, so these handsheets would be approximately 10% by weight PCC. These 90% fiber/10% PCC sheets had an average max load/width of 8.2 lb/in. When normalized by the basis weight, the result was 0.087 lb*in²/lb.

Example 13

90% Pulp (with Chitosan, NaOH added)/10% PCC (with Chitosan)

[0078] Two handsheets were produced using the above procedure. In the process, 450 mL of pulp from example 3 was used with 2.5 mL of filler from example 5. The retention of the filler from example 5 with pulp from example 1 was previously tested to be approximately 99%, so these handsheets would be approximately 10% by weight PCC. These 90% fiber/10% PCC sheets had an average max load/width of 7.2 lb/in. When normalized by the basis weight, the result was 0.080 lb*in²/lb. Accordingly, example 13 shows that functionalizing the pulp and PCC with chitosan unexpectedly results in a sheet that is less strong than just functionalizing the pulp (example 11) or just functionalizing the PCC (example 12).

Example 14

Addition of a Complementary Polymer

[0079] Handsheets were created using the above procedures. After drying the handsheet, approximately 6.5 mL of a 0.2% aqueous poly[(isobutylene-alt-maleic acid), ammonium salt]-co-(isobutylene-alt-maleic anhydride) solution was applied to the handsheet. Each test condition was repeated to make two handsheets for each trial point. Three 1" wide strips were then cut out of each handsheet for tensile testing on the Instron 3343. The reported values are the averages of the six strips (three from each handsheet).

Example 14a

Poly[(Isobutylene-Alt-Maleic Acid), Ammonium Salt]-Co-(Isobutylene-Alt-Maleic Anhydride) added to 100% Pulp

[0080] Two handsheets were made using the procedure described in example 7 (100% pulp). Then, the sheets were treated with the Poly[(isobutylene-alt-maleic acid), ammonium salt]-co-(isobutylene-alt-maleic anhydride) solution using the above procedure. These sheets had an average max load/width of 13.2 lb/in. When normalized by the basis weight, the result was 0.14 lb*in²/lb.

Example 14b

Poly[(Isobutylene-Alt-Maleic Acid), Ammonium Salt]-Co-(Isobutylene-Alt-Maleic Anhydride) added to 100% Pulp with Chitosan

[0081] Two handsheets were made using the procedure described in example 8 (100% pulp with chitosan). Then, the sheets were treated with the Poly[(isobutylene-alt-maleic acid), ammonium salt]-co-(isobutylene-alt-maleic anhydride) solution using the above procedure. These sheets had an average max load/width of 14.2 lb/in. When normalized by the basis weight, the result was 0.15 lb*in²/lb.

[0082] In example 14a, the second polymer addition produced a sheet approximately 35% stronger than the control
sheet (example 7). In example 14b, a sheet was produced that was approximately 50% stronger than the sheet with chitosan on pulp (example 8).

Example 15
Preparation of Control Long Fiber Pulp

[0083] A 5% slurry was prepared by blending 20 g refurbished long fibers in 400 ml of water. The slurry was diluted to 0.5% pulp by adding 3.6 L of water.

Example 16
Handsheet Preparation

[0084] Handsheets were prepared using a Mark V Dynamic Paper Chemistry Jar and Hand-Sheet Mold from Paper Chemistry Laboratory, Inc. (Larchmont, N.Y.). To form a handsheet, the appropriate volume of a selected 0.5% pulp slurry prepared according to example 15 was functionalized with up to 2% the of the appropriate polymer(s) (based on dry weight), as disclosed in the Examples below. Polymer additions were done at 10 minute intervals. The functionalized pulp slurry was diluted with water up to 2 L and added to the handsheet maker. The slurry was then mixed at a rate of 1100 RPM for 5 seconds, 700 RPM for 5 seconds, and 400 RPM for 5 seconds. The water was removed from the slurry by draining to form the handsheet. The handsheet was then transferred off of the wire, pressed, and dried.

Example 17
Control Handsheets

[0085] Handsheets were produced according to the method in example 16, using 400 ml of the material produced according to example 15. There was some fluctuation of pulp concentration from run to run, producing some slight variability in basis weights for these samples. The final paper weight was approximately 2 g for the control sheets. The maximum load-width for these sheets, when subjected to the tensile test of example 6, ranged from 10.3 lb/in to 11.4 lb/in.

Example 18
Expandable Particles

[0086] Expandable particles were made with Styrene maleic anhydride copolymers using a paint spray gun such as Preval. A 10% solution of Styrene maleic anhydride in different styrene to maleic anhydride ratios of 1:1, 2:1, 3:1, 4:1 were made in acetone. The solution was sprayed onto a large enclosed chamber by using a pressurized paint dispenser atomizer such as Preval (make). The chamber was closed for 10 minutes and the particles were collected from the bottom of the box and used for papermaking.

Example 19
Expandable Particles Coated with Chitosan

[0087] Handsheets were produced according to the method of example 16, using 400 ml of the pulp slurry from example 15 and 20% SMA particles based on dry weight. A 2% chitosan solution was then added to the pulp-starch slurry, with concentrations of chitosan ranging from 0.5% to 8% of the final weight of the handsheet. As an alternative, chitosan can be precipitated onto the expandable particles by using NaOH to titrate the mixture of particles and chitosan to a pH of 6.5 before adding the expandable particles to the pulp slurry. Using varying concentrations of chitosan, the retention of expandable particles in the pulp slurry can be increased.

Example 20
Expandable Particles with Polyvinylamine

[0088] Handsheets were produced according to the method of example 16, using 400 ml of the pulp slurry from example 15 to which was added various percentages of expandable particles based on dry weight. A 2% polyvinylamine (PVAm) solution was then added to the slurry, with concentrations of PVAm ranging from 0.5% to 8% of the final weight of the handsheet.

Example 21
Expandable Particles with Poly Dialkylamidomethyl Ammonium Chloride (DADMAC)

[0089] Handsheets were produced according to the method of example 16, using 400 ml of the pulp slurry from example 15 to which was added varying amounts of expandable particles based on dry weight of the pulp. DADMAC was then added to the expandable particles-pulp slurry, with concentrations of DADMAC ranging from about 0.25% to 2% of the final paper weight.

Example 22
Preparation of Retention Aids

[0090] Polyvinylamine was modified with hydrophobic side groups by the use of monoepoxy functionalized alkyl chains of varying length by dissolving various amounts of the epoxy functionalized compound with polyvinylamine in a common solvent such as acetone. The stoichiometry of substitution of the alkyl chain onto the polyvinylamine backbone can be controlled by the amount of the epoxy functionalized alkyl chain in the reaction mixture.

Example 23
Characterization of Retention Aid

[0091] The modified polyvinylamine was dissolved in water and the pH was incrementally lowered till the solution became cloudy. The pH at which the polymer precipitated out of solution was recorded.

Example 24
Elastomeric Expandable Fillers

[0092] Expandable elastomeric particles were made with isobutylene maleic anhydride copolymers using a paint spray gun such as Preval. A 10% solution of isobutylene maleic anhydride was made in acetone. The solution was sprayed onto a large enclosed chamber by using a pressurized paint disperser atomizer such as Preval (make). The chamber was closed for 10 minutes and the particles were collected from the bottom of the box and coated with chitosan as in example 19.

EQUIVALENTS

[0093] While the present invention has been described in terms of specific methods, structures, and compositions it is understood that variations and modifications will occur to
those skilled in the art upon consideration of the present invention. For example, the methods and compositions discussed herein can be utilized beyond the preparation of the paper compositions in some embodiments. As well, the features illustrated or described in connection with one embodiment can be combined with the features of other embodiments. Such modifications and variations are intended to be included within the scope of the present invention. Those skilled in the art will appreciate, or be able to ascertain using no more than routine experimentation, further features and advantages of the invention based on the above-described embodiments. Accordingly, the invention is not to be limited by what has been particularly shown and described, except as indicated by the appended claims.

[0094] All publications and references are herein expressly incorporated by reference in their entirety. The terms “a” and “an” can be used interchangeably, and are equivalent to the phrase “one or more” as utilized in the present application. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

What is claimed is:

1. An expandable paper product, comprising: paper pulp comprising fibers; a plurality of expansion particles configured to increase the volume of the expanded paper product; and a plurality of linker agents configured to be attached to the plurality of expansion particles, and to interact with the fibers to increase retention of the plurality of expansion particles in the expanded paper product.

2. The expandable paper product of claim 1, wherein the expansion particles comprise at least one of blowing agents, encapsulated propellants, and elastomer-based particles.

3. The expandable paper product of claim 2, wherein the expansion particles are encapsulated propellants, the encapsulated propellants comprising a polymeric shell encapsulating an expandable material.

4. The expandable paper product of claim 1, wherein the expansion particles comprise hydrophobic particles.

5. The expandable paper product of claim 1, wherein the plurality of linker agents impart a net positive charge to a surface of the plurality of expansion particles.

6. The expandable paper product of claim 1, wherein the fibers exhibit a net negative charge.

7. The expandable paper product of claim 1, wherein the plurality of linker agents comprise at least one of a coupling agent, a crosslinking agent, and a polymer.

8. The expandable paper product of claim 7, wherein the plurality of linker agents are polymers, the polymers comprising at least one of a cationic polymer, a polymer exhibiting lower critical solution temperature behavior, a pH sensitive polymer, and an amphiphilic polymer.

9. The expandable paper product of claim 8, wherein the polymers are amine-containing polymers.

10. The expandable paper product of claim 9, wherein the amine-containing polymers comprise at least one of polyetheramine, chitosan, polyvinyl amine, polyalkyleneimine, polyallyl amine, and polydiallyl amine.

11. The expandable paper product of claim 7, wherein the crosslinking agent comprises functional groups, the functional groups comprising at least one of an aldehyde, an isocyanate, and an epoxide.

12. The expandable paper product of claim 11, wherein the coupling agent is a multifunctional silane coupling agent.

13. The expandable paper product of claim 11, wherein the plurality of linker agents are covalently attached to the plurality of expansion particles.

14. The expandable paper product of claim 11, wherein the plurality of linker agents are non-covalently attached to the plurality of expansion particles.

15. A method for producing an expandable paper product, comprising:

using a linker agent to attach expansion particles to fibers of a paper pulp to thereby increasing retention of the expansion particles; and activating the expansion particles to produce the expandable paper product.

16. The method of claim 15, wherein the step of activating the expansion particles comprises elevating the temperature of the expansion particles to cause an increase in volume in the expandable paper product.

17. The method of claim 15, wherein the step of using the linker agent comprises using the linker agent to impart a net positive charge to a surface of at least a portion of the expansion particles.

18. The method of claim 17, wherein the at least a portion of the expansion particles are attracted to a net negatively charged fiber in the paper pulp.

19. The method of claim 15, wherein the step of using the linker agent comprises:

introducing hydroxyl groups on a surface of the expansion particles; and exposing the expansion particles to a silane-containing fluid, the silane-containing fluid attaching to at least a portion of the hydroxyl groups.

20. The method of claim 15, wherein the step of using the linker agent comprises:

providing a polymer exhibiting a lower critical solution temperature as the linker agent; and contacting the expansion particles with the polymer at a high enough temperature to cause precipitation of the polymer onto a surface of the expansion particles.

21. The method of claim 15, wherein the step of using the linker agent comprises:

contacting the expansion particles with a polymer at a high enough pH to cause precipitation of the polymer onto a surface of the expansion particles.

22. The method of claim 15, wherein the step of using the linker agent comprises:

crosslinking the expansion particles with the fibers of the paper pulp.

23. The method of claim 15, wherein the step of using the linker agent comprises:

at least one of covalently attaching and non-covalently attaching the expansion particles to the linker agent.