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STRENGTH****Publication Classification**(71) Applicant: **Buckman Laboratories International,
Inc.**, Memphis, TN (US)(51) **Int. Cl.**
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USPC **162/164.3**; 162/168.2; 162/168.3(73) Assignee: **Buckman Laboratories International,
Inc.**, Memphis, TN (US)(57) **ABSTRACT**(21) Appl. No.: **14/023,483**(22) Filed: **Sep. 11, 2013****Related U.S. Application Data**(60) Provisional application No. 61/712,030, filed on Oct.
10, 2012.

Methods of making paper or paperboard having enhanced dry strength are provided. An enzyme and a polymer including at least one of a cationic water-soluble polymer and an amphoteric water-soluble polymer can be added to a papermaking pulp to yield a treated pulp. The treated pulp can then be formed into paper or paperboard having a dry strength greater than paper or paperboard formed from papermaking pulp without the addition of the enzyme and polymer. Any suitable enzyme can be used, for example, a laccase or a cellulase. Any suitable polymer can be used. For example, at least one of a glyoxylated polyacrylamide (gPAM), a polyvinylamine, a decarboxylated polyacrylamide, and a dimethylamine-epichlorohydrin (epi-DMA).

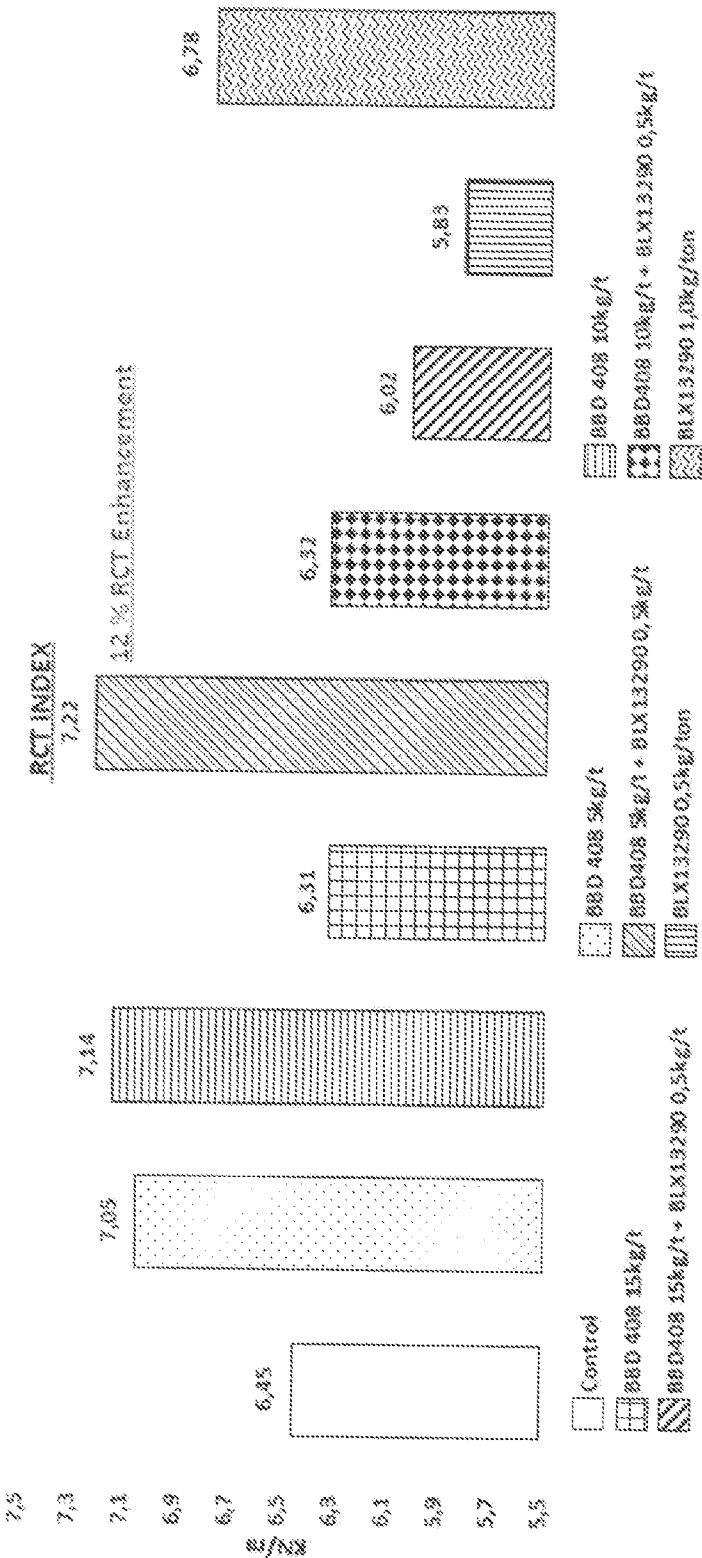


FIG. 1

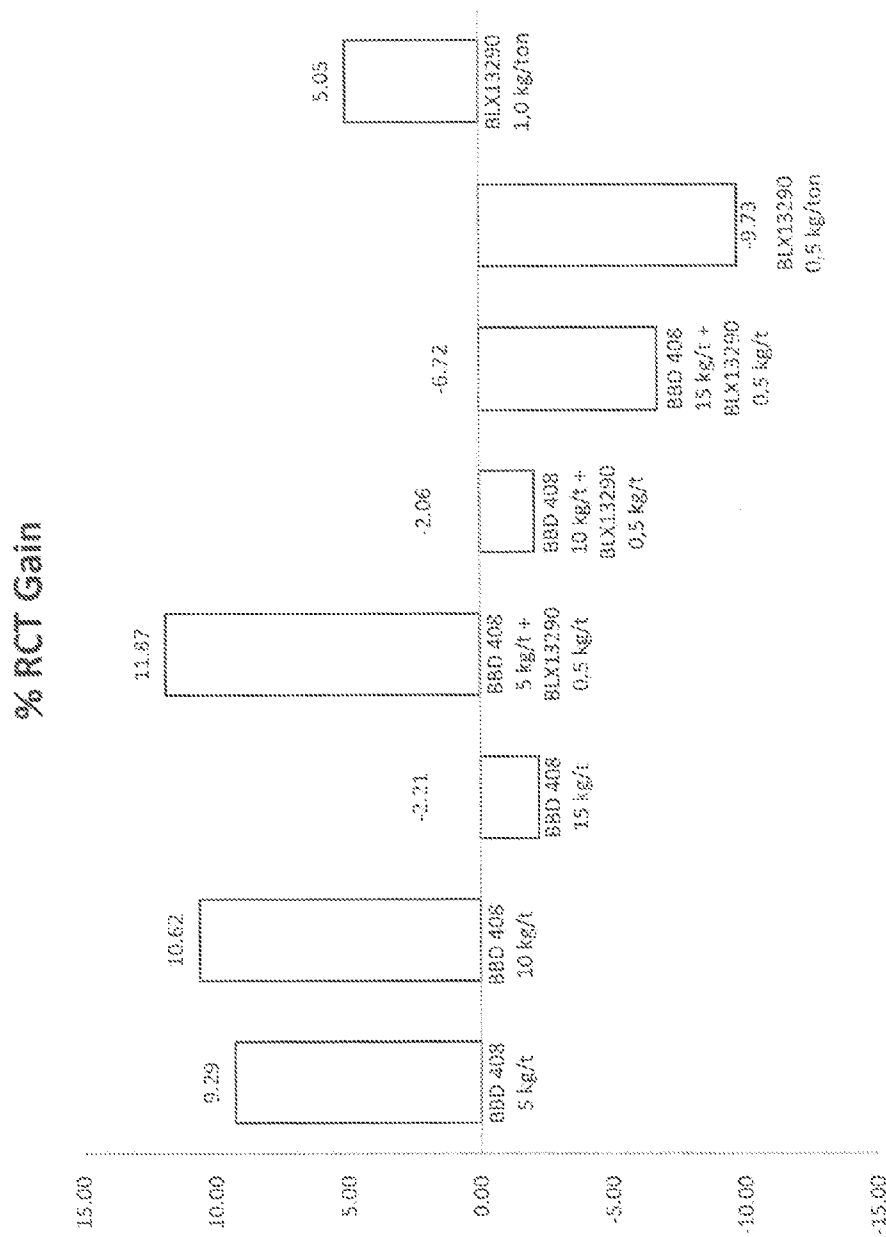


FIG. 2

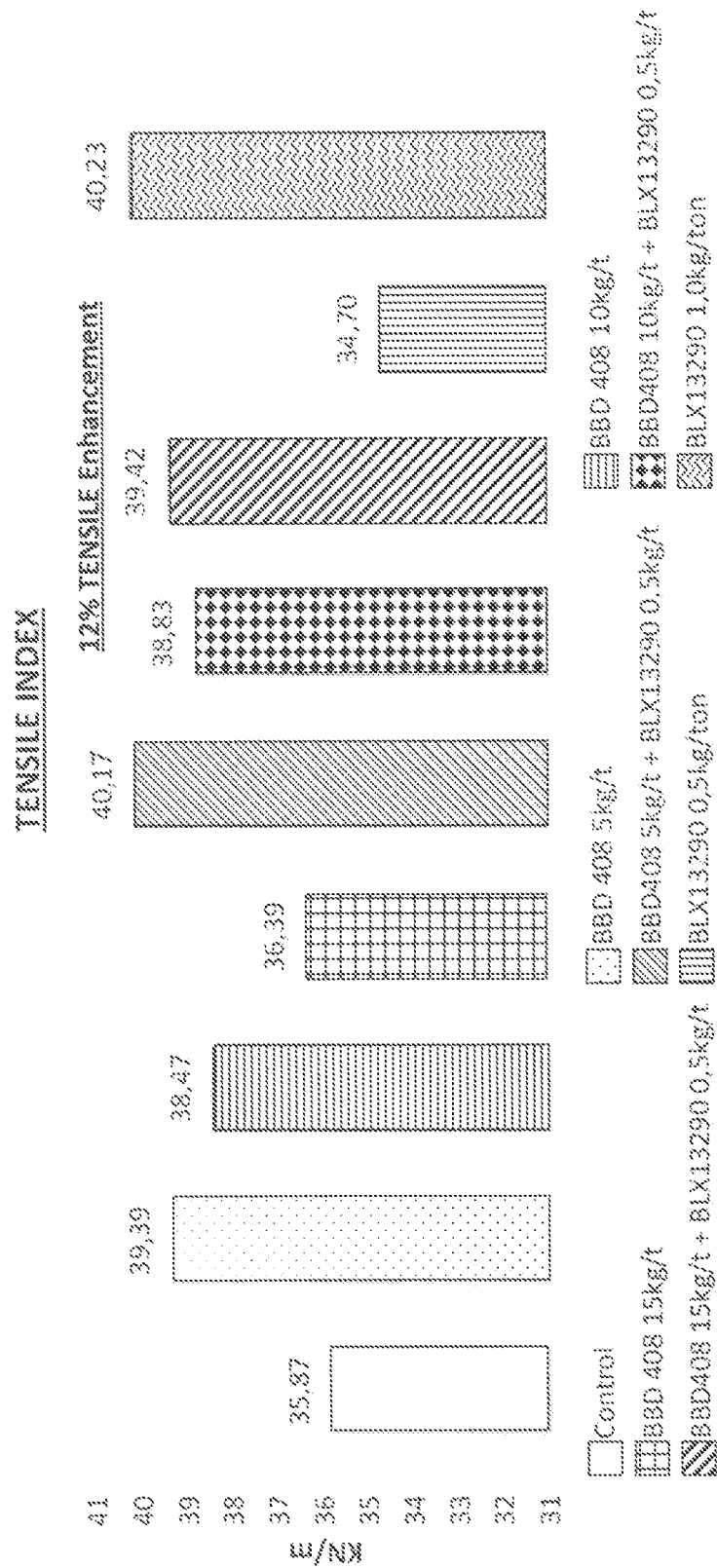


FIG. 3

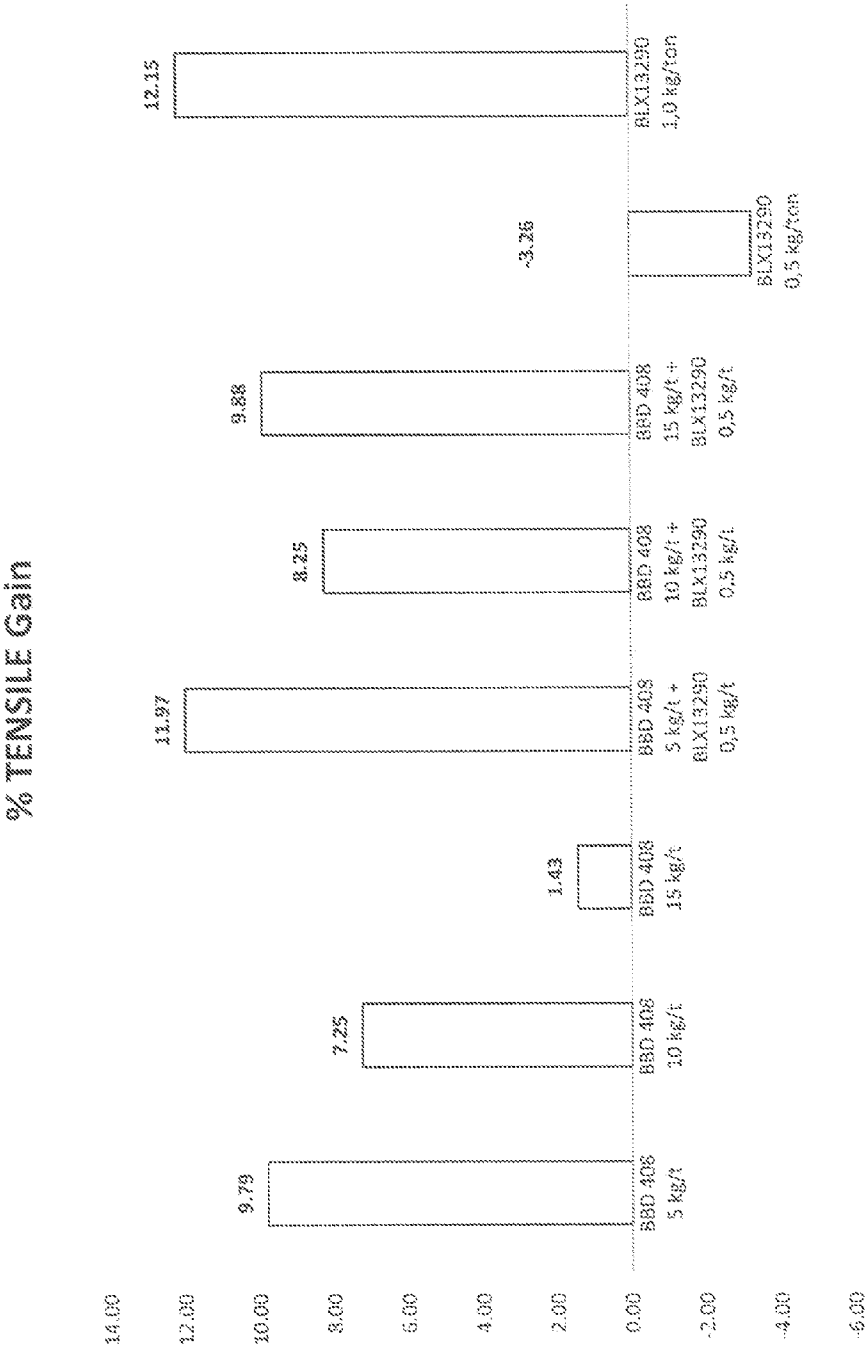


FIG. 4

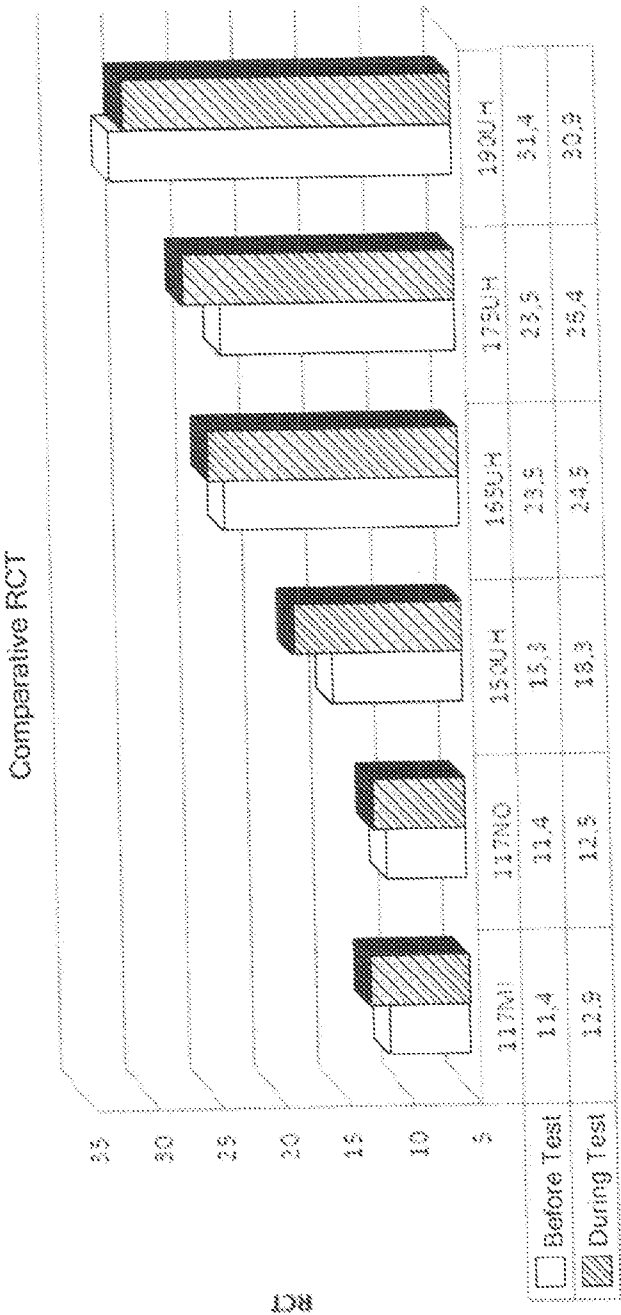


FIG. 5

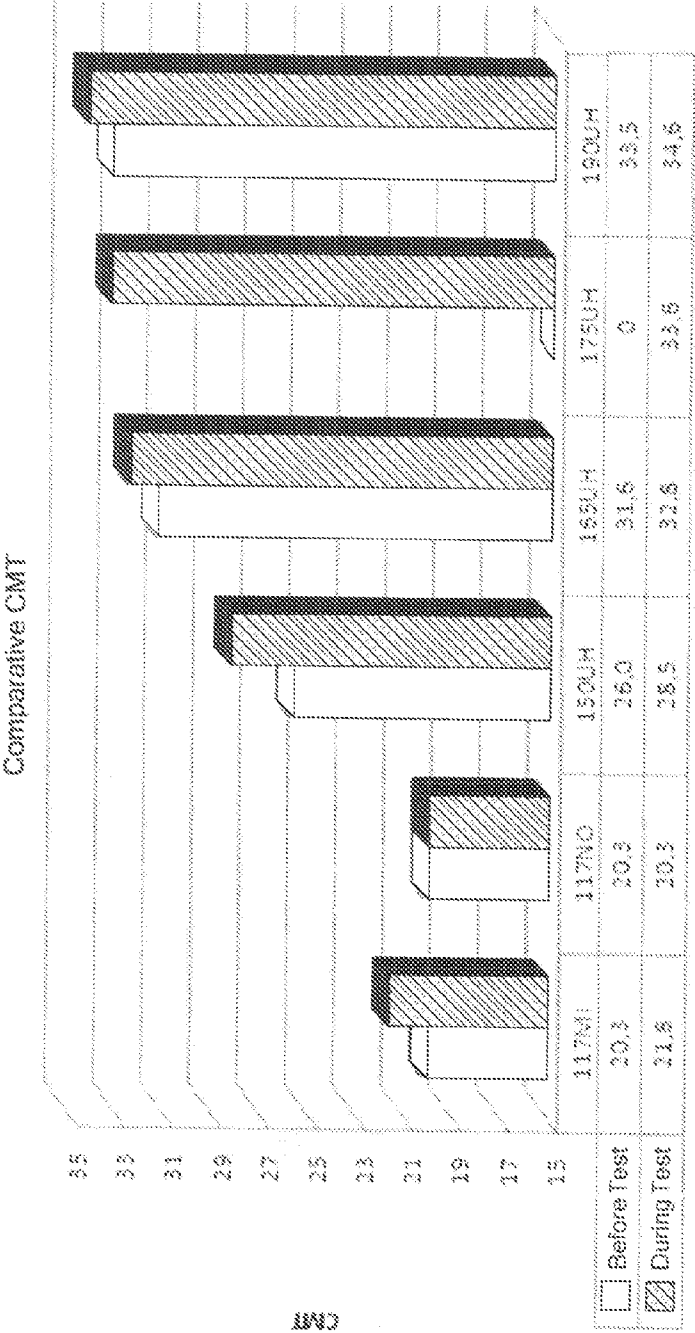


FIG. 6

METHODS FOR ENHANCING PAPER STRENGTH

[0001] This application claims the benefit under 35 U.S.C. §119(e) of prior U.S. Provisional Patent Application No. 61/712,030, filed Oct. 10, 2012, which is incorporated in its entirety by reference herein.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to papermaking processes. More particularly, the present invention relates to a papermaking process and using at least one enzyme and at least one polymer to enhance the dry strength of paper and paperboard.

[0003] Papermaking generally includes forming an aqueous pulp composition and then sheeting and drying the pulp to form a desired paper product. Enzymes can be added to the pulp to make the papermaking process more efficient and/or to yield paper products having desired characteristics. While enzymes can appreciably increase the rate of chemical reactions, finding the right conditions to realize enzyme optimization has proved to be difficult. As a consequence, when enzymes are used, they are used in a manner that yields sub-optimal enzymatic activity. That inefficiency can require the use of additional, often costly, enzymes, as well as longer production times and additional energy inputs. Even with the use of enzymes, the resulting paper products can have insufficient dry strength. Accordingly, there exists a need for enhancing the activity of enzymes to provide more efficient processes and stronger paper products.

SUMMARY OF THE INVENTION

[0004] A feature of the present invention is to provide a papermaking method yielding paper or paperboard with enhanced dry strength.

[0005] A further feature is to provide methods and/or techniques to increase dry strength in paper or paperboard (either in the wet stage or after being dried).

[0006] Another feature of the present invention is to provide a method for papermaking requiring lower amounts of additives and correspondingly lower product volumes while maintaining product quality.

[0007] Yet another feature of the present invention is to provide a method for paper production featuring both economic and environmental benefits including lower toxicity, recycling, use of renewable resources, and lower energy requirements.

[0008] Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and obtained by means of the elements and combinations particularly pointed out in the written description and appended claims.

[0009] To achieve these and other advantages and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to a method of making paper or paperboard having enhanced dry strength. An enzyme and a polymer that is or includes at least one cationic water-soluble polymer and/or at least one amphoteric water-soluble polymer can be added to a papermaking pulp to yield a treated pulp. The treated pulp can then be formed into paper or paperboard having a dry strength

greater than paper or paperboard formed from papermaking pulp without the addition of the enzyme and polymer. The dry strength can be measured using any suitable strength test, for example, a ring crush test (RCT) and/or a corrugating medium test (CMT). Any suitable enzyme can be used, for example, a laccase or a cellulase. Any number, combination, or kind of enzyme(s) can be used. Any suitable polymer can be used. For example, a glyoxylated polyacrylamide (gPAM), a polyvinylamine, a decarboxylated polyacrylamide, or a dimethylamine-epichlorohydrin (epi-DMA), or any combinations thereof. The enzyme(s) and polymer(s) can be added stepwise. The enzyme and the polymer can be added as a composition. Whether added stepwise or together as a composition, the enzyme and the polymer can be added in synergistic amounts, wherein the paper or paperboard has a dry strength greater than if either the enzyme or polymer alone were added and/or greater than the expected additive effect.

[0010] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are only intended to provide a further explanation of the present invention, as claimed.

[0011] The accompanying drawings, which are incorporated in and constitute a part of this application, illustrate several aspects of the present invention and together with the description, serve to explain the principles of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a bar graph shows results of using enzyme and polymer to increase dry strength based on the ring crush test (RCT).

[0013] FIG. 2 is a bar graph showing the percentage gain in dry strength based on RCT using polymer, enzyme, or a combination thereof.

[0014] FIG. 3 is a bar graph showing the results of using enzyme and polymer to increase dry strength based on tensile index.

[0015] FIG. 4 is a bar graph showing the percentage gain in dry strength based on tensile index using polymer, enzyme, or a combination thereof.

[0016] FIG. 5 is a bar graph showing a comparison of RCT results before (without) addition of enzyme and polymer and during (after) addition of enzyme and polymer.

[0017] FIG. 6 is a bar graph showing a comparison of corrugating medium test (CMT) results before (without) addition of enzyme and polymer and during (after) addition of enzyme and polymer.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0018] The present invention provides methods of making paper or paperboard. The invention further relates to methods to increase strength in paper or paperboard, either at the wet stage or once dried. For example, the present invention relates to a method of making paper or paperboard having enhanced dry strength. At least one enzyme and at least one polymer that is or includes at least one cationic water-soluble polymer and/or at least one amphoteric water-soluble polymer can be added to a papermaking pulp to yield a treated pulp. The treated pulp can then be formed into paper or paperboard having a dry strength greater than paper or paperboard formed from papermaking pulp without the addition of the enzyme and polymer.

[0019] The enzyme and polymer can be applied to a papermaking pulp at the same time or sequentially within a period of time (e.g., within 1.0 second to 10 minutes) to permit the components to interact in combination with the pulp. The enzyme and polymer can be pre-combined as a pre-mixture, and then added together in a common composition to the pulp. The enzyme and polymer can be co-mixed in an addition pipeline or other feedline that feeds the resulting co-mixture to an introduction port, such as a port on a pulp processing unit. The enzyme and polymer can be added separately and simultaneously to the pulp from different introduction ports on the same processing unit. The enzyme and polymer can be introduced sequentially, that is, separately at separate times, from the same or different introduction ports or locations on the papermaking system within a short period of time. In sequential addition, the enzyme and polymer components can be separately added in time with both components brought into contact in the pulp within a short period of time, for example, within about 5 minutes of each other, or within about 4 minutes of each other, or within about 2 minutes of each other, or within about 1 minute of each other, or within about 30 seconds of each other, or within shorter periods of time. After contacting the pulp with the enzyme and polymer, the resulting pulp can be further processed and formed into a paper or paperboard.

[0020] The method of the present invention can be practiced on conventional papermaking machines with modifications that can be easily made in view of the present invention. The method of the present invention can be practiced, for example, on a wet end assembly of a conventional papermaking machine with modifications that can be easily made in view of the present invention. The method can employ many different types of papermaking pulp or combinations thereof.

[0021] The methods, formulations, and systems of the present invention can use any suitable enzyme or combination of two or more enzymes. One or more enzymes classified by The International Union of Biochemistry and Molecular Biology can be used, including oxidoreductases (EC1) for catalyzing oxidation/reduction reactions, transferases (EC2) for catalyzing transfer of a functional group, hydrolases (EC3) for catalyzing the hydrolysis of various bonds, lyases (EC4) for catalyzing the cleavage of various bonds by means other than hydrolysis and oxidation, isomerases (EC5) for catalyzing the isomerization changes within a single molecule, and ligases (EC6) for catalyzing the joinder of two molecules with covalent bonds. Enzymes can be from any source, can be produced recombinantly, or extracted from naturally occurring sources. An enzyme can be a wildtype or a mutant form of the enzyme can be used. The enzyme can be modified any manner, for example, in vivo post-transcriptionally and/or processed after extraction.

[0022] Laccases and/or cellulases can be used as enzymes in accordance with the present invention. Any suitable laccase and/or cellulase can be used. Laccase is a polyphenol oxidase (EC 1.10.3.2; p-benzenediol:oxygen oxidoreductase) that catalyzes the oxidation of a variety of inorganic and aromatic compounds, particularly phenols, with the reduction of molecular oxygen to water. Laccases are widely distributed enzymes in higher plants, fungi, insects, and bacteria. For example, laccases are known to be produced by a variety of fungi, including species of the following genera: *Aspergillus*, *Neurospora*, *Podospora*, *Botrytis*, *Pleurotus*, *Fomes*, *Phlebia*, *Trametes*, *Polyporus*, *Stachybotrys*, *Rhizoctonia*, *Bipolaris*, *Curvularia*, *Amerosporium*, and *Lentinus*. For example,

a laccase produced by a genetically modified *Aspergillus oryzae* can be used. BLX-13290, available from Buckman Laboratories International, Inc., Memphis, Tenn., can be used.

[0023] The enzyme or the formulation containing the enzyme (for example, a pre-formed formulation containing the enzyme and polymer of the present invention) can have an enzymatic activity of at least 10 units/g. For example, the enzyme or the composition containing the enzyme can have an enzymatic activity of at least 15 units/g, at least 20 units/g, at least 25 units/g, at least 100 units/g, or at least 500 units/g, for instance, from 10 units/g to 1,500 units/g or higher. An enzyme pre-formulated in a composition (formulation) can be used as the source of the enzyme combined with the polymer. An enzyme composition can contain, for example, from about 1.0 wt. % to about 99 wt. %, from about 1.0 wt. % to about 10 wt. %, from about 10 wt. % to about 90 wt. %, from about 25 wt. % to about 75 wt. %, or from about 40 wt. % to about 60 wt. % enzyme based on the total weight of the composition. The enzyme can be present in any suitable amount or concentration based on the target substrate or substrate composition. When a given amount of water is present in the enzyme formulation, these percentages are reduced proportionally by a dilution factor. Once the enzyme formulation is added to the substrate composition, the percentages are again reduced by a dilution factor. These enzyme compositions can further contain, for example, polyethylene glycol, hexylene glycol, polyvinylpyrrolidone, tetrahydrofuryl alcohol, glycerine, water, and other conventional enzyme composition additives, as for example, described in U.S. Pat. No. 5,356,800, which is incorporated herein in its entirety by reference.

[0024] The enzyme can be added to the pulp in an amount, for example, of from about 0.01% by weight to about 10% by weight enzyme based on the dry weight of the pulp, or from about 0.05% by weight to about 5.0% by weight, or from about 0.1 by weight to about 2.5% by weight, or from about 0.2 by weight to about 1.5% by weight enzyme based on the dry weight of the pulp, though other amounts can be used. These additional amounts of the enzyme relative to pulp can apply to use of pre-mixtures of the enzyme and polymer in a common composition, and also the other addition options indicated herein for introducing the enzyme and the polymer separately to pulp (simultaneously or sequentially). Any amount, percentage, or proportion of enzyme described herein can be on an active enzyme basis. For example, an enzyme amount referred to as 1.0% by weight enzyme can refer to 1.0% by weight active enzyme.

[0025] The amount of polymer used can vary depending on the specific polymer used, and generally can be added to the pulp in an amount, for example, of from about 0.5 pound polymer per ton paperstock, based on dried solids of the pulp, or in an amount from about 0.5 pound to about 8 pounds per ton of paperstock, or from about 1 pound to about 6 pounds per ton of paperstock, or from about 1.5 pounds to about 4 pounds per ton of paperstock, or from about 2 pounds to about 3 pounds polymer per ton of paperstock, based on the dried solids of the pulp, though other amounts can be used. These additional amounts of the polymer relative to pulp can apply to use of pre-mixtures of the enzyme and the polymer in a common composition, and other suitable addition options for introducing the enzyme and the polymer separately to pulp.

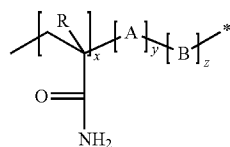
[0026] The amount of the polymer used can be, for example, from about 1.0 wt. % to about 99 wt. %, from about

10 wt. % to about 90 wt. %, from about 25 wt. % to about 75 wt. %, or from about 40 wt. % to about 60 wt. % polymer based on the total weight of composition. The polymer can be present, for example, in an amount of at least 0.1% by weight, at least 0.5 wt. %, at least 1.0 wt. %, at least 5.0 wt. %, or at least 10 wt. %, based on the total dry weight of the papermaking pulp. The enzyme and the polymer can be present in a weight ratio of enzyme to polymer of from about 0.1:10 to about 10:0.1, from about 0.5:5.0 to about 5.0:0.5, or from about 1.0:2.0 to about 2.0:1.0. The weight ratio of polymer to enzyme can be less than about 5:1, from about 5:1 to about 50:1, from about 8:1 to about 40:1, from about 10:1 to about 30:1, from about 12:1 to about 20:1, about 10:1, about 15:1, about 20:1, about 30:1, or greater than about 50:1.

[0027] For the present invention, the polymer can be or refer to the presence of one or more polymers. The polymer can be at least one cationic water-soluble polymer and/or at least one amphoteric water-soluble polymer. For example, the polymer can be or include one or more of the following: a glyoxylated polyacrylamide (gPAM), a polyvinylamine, a decarboxylated polyacrylamide, and a dimethylamine-epichlorohydrin (epi-DMA). Bubond® 408, available from Buckman Laboratories International, Inc., Memphis, Tenn., can be used. Any suitable glyoxylated polyacrylamide can be used, for example, those described in U.S. Pat. Nos. 3,556, 932, 4,603,176, 4,605,702, 4,954,538, 5,723,022, 7,034,087, and 7,119,148, and U.S. Patent Application Publication Nos. 2008/0308242 and 2010/0326615, which are incorporated herein in their entireties by reference. A glyoxalated polyacrylamide, in an aqueous solution at about 4.0% active, at about 8.0% active, at about 12% active, at about 16% active, about 20 active, or any other suitable percent active can be used. Decarboxylated polyacrylamides include, for example, a polymer or copolymer formed using acrylamide monomer, after which a "Hoffman degradation" reaction has been performed to remove a carbonyl group from at least some of the acrylamide monomers in the polymer and converting the amide groups into primary amine groups.

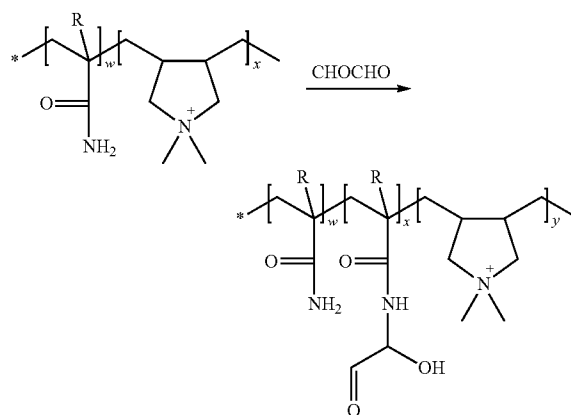
[0028] A glyoxalated polyacrylamide can contain, for example, from about 75% to about 10%, by weight, acrylamide monomer and from about 25% to about 90%, by weight, cationic monomer copolymerizable with the acrylamide monomer, based on the total weight of the polymer, and have sufficient glyoxal-reactive amide substituents and —CHOHCHO substituents to be thermosetting. The glyoxalated acrylamide polymer can contain, for example, from about 70% to about 30%, by weight, acrylamide monomer and from about 30% to about 70%, by weight, cationic monomer, or, for example, from about 65% to about 50%, by weight, acrylamide monomer and from about 35% to about 50%, by weight, cationic monomer, or, for example, from about 62% to about 55%, by weight, acrylamide monomer and from about 38% to about 45%, by weight, cationic monomer. A suitable glyoxylated polyacrylamide can be created by forming a copolymer of acrylamide and dimethyldiallylammonium chloride and then reacting that copolymer with glyoxal.

[0029] A glyoxalated polyacrylamide can incorporate a base polymer resin having the following exemplary formula



wherein R is H, C₁ alkyl, C₂ alkyl, C₃ alkyl, C₄ alkyl, or halogen; A is a cationic unit which imparts a charge to the resin polymer; B is an optional non-nucleophilic unit which does not react with glyoxal under aqueous condition; wherein the weight percent of x is from 75% to about 10%; the weight percent of y is from 25% to about 90%; the weight percent of z is from 0% to 65%; and the molecular weight of the base polymer resin is from 500 Daltons to 100,000 Daltons, or, for example, 3,000 Daltons to 20,000 Daltons, or, for example, 3,000 Daltons to 13,000 Daltons, or, for example, 5,000 Daltons to 9,000 Daltons.

[0030] The glyoxalation of polyacrylamide according to an exemplary illustration is schematically indicated below.



[0031] Glyoxal reacts with amide groups to form a pendant glyoxalated group. In addition, glyoxal cross-links the base polymer molecules at glyoxal-reactive amide substituents of the acrylamide units (not shown), leading to a thermosetting interpolymer and an associated increase of solution viscosity. The presence of high cationic monomer content in the resulting glyoxalated polyacrylamide polymers reduces the amide content and/or the cross-linking rate. Thus, the product can be prepared at a higher solid content but with longer shelf life. This higher charged glyoxalated polyacrylamide resin also gives comparable wet/dry strength in paper as commercially available 7.5% glyoxalated polyacrylamide products.

[0032] Cationic monomers include, for example, 2-vinylpyridine, 2-vinyl-N-methylpyridinium chloride, (p-vinylphenyl)trimethyl ammonium chloride, diallyldimethylammonium chloride, 2-(dimethylamino)ethyl acrylate, trimethyl(p-vinylbenzyl)ammonium chloride, p-dimethylaminoethylstyrene, dimethylaminopropyl acrylamide, 2-methylacryloyloxyethyltrimethyl ammonium methylsulfate, and 3-acrylamido-3-methylbutyl trimethyl ammonium chloride.

[0033] The acrylamide can be replaced by other primary amide-containing monomers such as methacrylamide, ethylacrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, N-ethyl methacrylamide and the like. Thus, polyacrylamides, which by definition are polymers made from acrylamide monomers, include repeating units from at least one or more of these various compounds. The acrylamide monomer provides the primary reaction sites on the base polymer backbone to which the glyoxal substituents are attached. The base polymer has a sufficient number of base acrylamide monomers in its structure (pendant amide groups)

so that, once functionalized with glyoxal, the resulting polymer is thermosetting. As used herein, "thermosetting" and "crosslinking," and similar terms are intended to embrace the structural and/or morphological change that occurs, for example, by covalent chemical reaction or ionic interaction between separate molecules in a composition. Generally, the amount of base acrylamide monomer can be at least about 10 weight percent of the base polymer. The base acrylamide monomer can be provided in an amount of at least about 50 weight percent and sometimes in excess of 60 weight percent of the total weight of vinyl monomers from which the base polyacrylamide is prepared.

[0034] The base polymer optionally can also contain a non-nucleophilic monomer to reduce amide-glyoxal cross-linking reaction. The suitable non-nucleophilic monomers include vinyl acetate, N-vinylpyrrolidone, N,N-dimethylacrylamide, acrylonitrile, styrene, hydroxyl alkyl(meth)acrylates and the like. The weight percent of this non-nucleophilic unit can range from zero to 65 (e.g., 1.0 wt. % to 80 wt. %, 5.0 wt. % to 70 wt. %, 10 wt. % to 60 wt. %, 15 wt. % to 50 wt. %, 20 wt. % to 40 wt. % and the like based on the total weight of the molecule).

[0035] The base polymer product of the copolymerization of the acrylamide monomer and cationic monomer, or polyacrylamide base polymer, can be prepared by free radical polymerization in an aqueous system. Methods for making base polyacrylamide can be suitably modified. To prepare a polyacrylamide base polymer of a desired chemical composition and monomer distribution, the full complement of the cationic monomer(s) and the non-nucleophilic monomer(s) can be added all at once at the beginning of the polyacrylamide polymerization reaction. Alternatively, the cationic monomer(s) and the non-nucleophilic monomer(s) can be added continuously along with acrylamide monomer over the time course of the polymerization reaction. Still other options for reacting the cationic monomers and the non-nucleophilic monomers with the acrylamide monomer such as sequentially, batch, semi-batch, and the like, can be used. Commonly used free radical initiators that can be used include various peroxide, azo compounds, potassium, and ammonium persulfates, and a redox initiator system. The polyacrylamide base polymer has a molecular weight ranging, for example, from 500 Daltons to 100,000 Daltons, from 3,000 Daltons to 20,000 Daltons, from 3,000 Daltons to 13,000 Daltons, or from 5,000 Daltons to 9,000 Daltons. The molecular weight can be influenced by changing the reaction temperature, the level of solids in the reaction, the amount of initiator, the amount of chain transfer agent, and by other methods used by those skilled in the art. The suitable chain transfer agents include isopropyl alcohol, mercaptans, sodium formate, and sodium acetate.

[0036] The so-prepared base polymer can then be reacted with glyoxal, for instance, at a pH of 7.0 to 10. The weight ratio of the glyoxal to the base polymer ranges, for example, from about 0.01 to about 0.60:1, and for example, from about 0.10 to about 0.30:1, respectively. The reaction temperature can be maintained in the range of 15° C. to 50° C. A buffer can be added to control solution pH throughout the reaction. Suitable buffers include sodium phosphates, sodium pyrophosphate, borax, and Tris. Once the solution reaches a desired viscosity, dilute acid can be added to quench the reaction. The final pH of the solution can range from about 2.0 to about 5.0. Alternatively, either the glyoxal solution or the base polymer solution can be added to the reaction mixture

slowly over time, or both the glyoxal and the base polymer solution can be added to the reaction mixture slowly over time. Still other options for reacting glyoxal and base polymer are recognized by those skilled in the art.

[0037] When prepared as a pre-mixture, the composition (formulation) containing the enzyme(s) and the polymer(s) can be formulated by sequentially or simultaneously combining the components in a fluid medium, such as water. The order of addition of the components is not limited. The various ingredients that form the enzyme and polymer compositions of the present invention can be mixed together using conventional mixing techniques, such as a mixer, blender, stirrer, and/or an open vessel. Before and/or following aqueous dispersion of the enzyme and the polymer, the pH of the resulting combination generally can be controlled, for example, to a defined level of a pH of from about 3.0 to about 10, or a pH of from about 4.0 to about 10, or a pH of from about 7.0 to about 10.0, and more suitably from about 8.0 to about 9.0. These pH ranges can apply to the composition and/or to the composition in an aqueous solution. Adjustment of the pH of the composition can be accomplished, for example, through the addition of either sodium hydroxide or ammonium hydroxide (aqueous ammonia).

[0038] The enzyme and polymer composition can include one or more additives, such as dyes, pigments, defoamers, biocides, pH adjusting agents, and/or cationic starch, and/or other conventional paper making or processing additives. Anionic components, for example, can cause deposits (gels) in the pulp or white water. The enzyme and cationic polymer composition can contain, for example, less than about 3.0 wt. %, less than 2.0 wt. %, or less than 1.0 wt. %, or less than 0.5 wt. %, based on the total weight of the composition, of anionic components that cause deposits or gels. The presence of reducing agents, for example, sulfite or sulfide, can interfere with the activities of certain enzymes, for example, laccases, as certain polymers, for example, glyoxylated polyacrylamides.

[0039] The enzyme and polymer composition, as a pre-mixture, can be prepared as a physically stable aqueous dispersion, which can be more stable, for example, from about 10 wt. % to about 60 wt. %, from about 25 wt. % to about 50 wt. %, or from about 35 wt. % based on the total weight of solids. At about 45 wt. %, the viscosity can tend to stay in a pourable range. Higher solids levels can tend to gradually thicken during any storage before use.

[0040] The enzyme and polymer compositions, when prepared as pre-mixtures of these components, can be prepared as masterbatches for dilution at a later time or the desirable concentration can be made at the same time that the composition is prepared. The enzyme and polymer composition can be prepared on-site or off-site or parts or components of the composition can be prepared or pre-mixed off-site or on-site prior to the ultimate formation of the composition. The compositions containing the pre-mixtures of enzyme and polymer can be formed immediately prior to their introduction into the papermaking process or sheet making process, or the compositions can be prepared beforehand, such as before use, minutes before use, hours before use, or days or weeks or months before use, for example, within about 2 to 3 weeks of usage. When the compositions are introduced as a pre-mixture of the enzyme and the polymer, the pre-mixture can be made from about 1.0 to about 100 seconds before their introduction into the papermaking process, or from about 1.0 hour to about 5 hours, from about 1.0 hour to about 10 hours, from about 1.0

hour to about 24 hours before use, from about 1.0 day to about 7.0 days, from about 1.0 day to about 30 days, from about 1.0 day to about 60 days, or from about 1 day to about 180 days, before use.

[0041] The pulp or stock can be treated with the composition including both the enzyme and polymer as a pre-mixture at any location in the papermaking system before formation of the paperweb on the wire, e.g., an addition point prior to the headbox in the system. The separate additions of these components to the pulp according to other indicated options also can be done at any of these locations in the papermaking system. The methods of the present invention can be practiced on any pulp related applications, including, for example, where pulps are treated and dewatered. The methods can be practiced, for example, on conventional paper making machines (such as a Fourdrinier type paper machine), for example, on wet end assemblies of paper making machines, with modifications that can be made in view of the present invention. On the wet end, a paper machine can include, for example, a pulp tank, a blend chest, a stuff box, a white water silo, a fan pump, a screen, and a head box. The paper machine can optionally include one or more refiners. The enzyme and/or polymer can be added to the pulp at or between any of these machine components. The enzyme can be added to the pulp at a suitable point that allows sufficient time for the enzyme to act on the pulp fiber. Polymer addition can be added at a location that minimizes contact time with the pulp fiber near the end of the wet end and approaching the dry end of the paper machine, such as proximal the head box. For example, the polymer can be added at the fan pump suction, the stuff box, before the screen, after the screen, or any combination thereof.

[0042] The enzyme and polymer composition containing a pre-mixture of these components can be added to paperstock, for example, in an amount of at least about 0.5 pound per ton of paperstock, based on dried solids of the pulp, at least about 1.0 pound per ton of paperstock, from about 0.5 to about 10 pounds per ton of paperstock, from about 0.75 to about 7.5 pounds per ton of paperstock, from about 1.0 to about 5.0 pounds per ton of paperstock, or from about 1.25 to about 4.0 pounds per ton of paperstock, from about 1.5 to about 3 pounds per ton of paperstock, or from about 0.5 to about 1.5 pounds per ton of paperstock, based on dried solids of the pulp in the paperstock, or other amount. Where separate additions of the enzyme and polymer to the pulp are used according to other indicated options herein, the combined amounts of these components relative to the pulp also can be within one or more of these above-indicated ranges.

[0043] The enzyme and polymer, as part of a single pre-mixed composition or as separate components, can be added to many different types of papermaking pulp, stock, or combinations of pulps or stocks. For example, the pulp can contain virgin pulp and/or recycled pulp, such as virgin sulfite pulp, broke pulp, Kraft pulp, soda pulp, thermomechanical pulp (TMP), alkaline peroxide mechanical pulp (APMP), chemithermomechanical pulp (CTMP), chemimechanical pulp (CMP), groundwood pulp (GP), mixtures of such pulps, and the like. The Kraft pulp can be, for example, a hardwood kraft pulp, a softwood kraft pulp, or combinations thereof. The recycled pulp can be or include waste paper, old corrugated containers (OCC), and other used paper products and materials. For example, there are a variety of mechanical pulping methods to which this invention can be applied. Thermomechanical pulp (TMP) uses a combination of heated

wood chips and mechanical processes. Stone Groundwood (SGW) grinds or macerates the wood chips. Chemithermomechanical pulp (CTMP) uses a variety of chemicals, heat, and grinding techniques to produce pulp. Different types of pulp involve different types of paper although many papers can use a combination or "blend" of several different types of pulp and recycled/recovered paper. The papermaking pulp or stock can contain cellulose fibers in an aqueous medium at a concentration, for example, of at least about 50% by weight of the total dried solids content in the pulp or stock, though other concentrations may be used. These pulp formulations can be referred to as fiber furnishes.

[0044] The pulps or stocks of the present invention can be treated with one or more optional additives within the papermaking system. These additives can be added before, during, or after introduction of the enzyme and the polymer. These optional additives can include, for example, additional polymers such as cationic, anionic and/or non-ionic polymers, clays, other fillers, dyes, pigments, defoamers, pH adjusting agents such as alum, sodium aluminate, and/or inorganic acids, such as sulfuric acid, microbiocides, supplemental water retention aids such as cationic colloidal alumina micro-particles, coagulants, supplemental flocculants, leveling agents, lubricants, defoamers, wetting agents, optical brighteners, pigment-dispersing agents, cross-linkers, viscosity modifiers or thickeners, or any combinations thereof, and/or other conventional and non-conventional papermaking or processing additives. The pH of the (treated) pulp generally, but not exclusively, can be controlled to a defined level of from about 2.0 to about 12, from about 4.0 to about 8.0, or from about 5.5 to about 6.5, or about 6.0. The temperature of the papermaking pulp can be from about 5.0° C. to about 75° C., from about 15° C. to about 60° C., or from about 25° C. to about 50° C. Temperature and pH can be varied based on the particular enzyme(s) and polymer(s) used.

[0045] Any desired paper product can be produced, for example, 130, 165, and 190 g/m² Kraft UM paper. 117MI, 117NO, 150UH, 165UH, 175UH, and 190UH papers can be produced. Paper and paperboard made using the methods of the present invention are marked by their enhanced dry strength. Dry strength can be measured using any suitable technique and apparatus. For example, a ring crush test (RCT) and/or a corrugating medium test (CMT) can be employed. Industry protocols that can be used include, for example, Ring Crush of Paperboard (TAPPI T818 cm-97), Ring Crush of Paperboard (Rigid Support Method (TAPPI T822), Short Span Compressive Strength of Paperboard (TAPPI T826), and Flat Crush of Corrugating Medium (CMT test) (T809 om-93). Examples of other strength tests include, for example, an internal bond test (Scott bond test), a burst test (Mullen test), a dry or wet tensile test, and the like. The use of enzyme and polymer can increase dry strength by at least 1.0%, at least 5.0%, at least 8.0%, at least 10%, at least 12%, at least 15%, at least 20%, at least 25%, or at least 50% compared to enzyme alone, polymer alone, or in the absence of both enzyme and polymer. Whether added stepwise or together as a composition, the enzyme and the polymer can be added in synergistic amounts, wherein the paper or paperboard has a dry strength greater than if either the enzyme or polymer alone were added. Dry strength enhancement can be additive or super-additive. The synergism achieved in obtained dry strength can be greater than the expected additive effect of using the enzyme and polymer.

[0046] The present invention includes the following aspects/embodiments/features in any order and/or in any combination:

1. A method of making paper or paperboard having enhanced dry strength comprising: adding at least one enzyme and at least one polymer comprising at least one cationic water-soluble polymer or at least one amphoteric water-soluble polymer, or both, to a papermaking pulp to yield a treated pulp; and forming the treated pulp into paper or paperboard having a dry strength greater than paper or paperboard formed from papermaking pulp without the addition of the enzyme and polymer.

2. The method of any preceding or following embodiment/feature/aspect, wherein the dry strength is measured using a strength test that is a ring crush test (RCT) or a corrugating medium test (CMT).

3. The method of any preceding or following embodiment/feature/aspect, wherein the enzyme comprises at least one cellulase, or at least one laccase, or both.

4. The method of any preceding or following embodiment/feature/aspect, wherein the enzyme is laccase.

5. The method of any preceding or following embodiment/feature/aspect, wherein the polymer comprises a glyoxylated polyacrylamide (gPAM), a polyvinylamine, a decarboxylated polyacrylamide, or a dimethylamine-epichlorohydrin (epi-DMA), or any combination thereof.

6. The method of any preceding or following embodiment/feature/aspect, wherein the enzyme is laccase and the polymer is gPAM.

7. The method of any preceding or following embodiment/feature/aspect, wherein the enzyme and polymer are added stepwise.

8. The method of any preceding or following embodiment/feature/aspect, wherein the enzyme and the polymer are added as a composition.

9. The method of any preceding or following embodiment/feature/aspect, wherein the composition comprises from about 1.0 wt. % to about 99 wt. % enzyme and from about 99 wt. % to about 1.0 wt. % polymer, based on the total dry solids weight of the composition.

10. The method of any preceding or following embodiment/feature/aspect, wherein the enzyme and polymer are added in synergistic amounts, wherein the paper or paperboard has a dry strength greater than if either the enzyme or polymer alone were added.

11. A method of making paper or paperboard having enhanced dry strength comprising: adding a laccase and a glyoxylated polyacrylamide to a papermaking pulp to yield a treated pulp; and forming the treated pulp into paper or paperboard having a dry strength greater than paper or paperboard formed from papermaking pulp without the addition of the laccase and the glyoxylated polyacrylamide.

[0047] The present invention can include any combination of these various aspects, features, or embodiments above and/or below as set forth in sentences and/or paragraphs. Any combination of disclosed features herein is considered part of the present invention and no limitation is intended with respect to combinable features.

[0048] The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the present invention, in which parts and percentages are proportions by weight unless otherwise specified.

EXAMPLES

Example 1

[0049] This example demonstrates the surprising and unexpected results achieved by the methods of the present invention. 110 g/m² paper was produced on a laboratory scale consistent with the methods of the present invention. Differ-

ing amounts of enzyme (BLX 13290) and polymer (Bubond® 408) were used to produce the paper. A ring crush test (RCT) and a tensile strength test were performed on the resulting paper. FIG. 1 is a bar graph and shows results of using enzyme and polymer to increase dry strength based on the RCT. The RCT index is shown in kN/m for the various treatments. FIG. 2 is a bar graph showing the percentage gain in dry strength based on RCT using polymer, enzyme, or a combination thereof. FIG. 3 is a bar graph showing the results of using enzyme and polymer to increase dry strength based on tensile index (kN/m) for the different treatments. FIG. 4 is a bar graph showing the percentage gain in dry strength based on tensile index using polymer, enzyme, or a combination thereof for the different treatments. Unexpectedly, a combination of enzyme and polymer was able to significantly increase the dry strength of the paper, whether measured by RCT or by tensile strength. These results establish that the present invention can yield surprisingly strong paper with positive ramifications for both the environment and production costs.

Example 2

[0050] This example demonstrates the surprising and unexpected results achieved by the methods of the present invention. A trial was conducted to determine if an existing program could be replaced with a new program in order to increase dry strength increase at lower cost while maintaining or improving other desirable properties. The existing program involved use of cationic polyvinylamine (0.85 kg/metric ton on a dry basis) plus anionic polyvinylamine (0.9 kg/metric ton on a dry basis). The new program involved use of cationic glyoxal polyacrylamide (0.50 kg/metric ton on a dry basis) plus laccase product (0.5 kg/metric ton on a wet basis). BLX 13290 was used as the enzyme (laccase product) and Bubond® 408 was used as the polymer application for strength enhancement. The grade was corrugated medium and testliner, including 117MI, 117NO, 150UH, 165UH, 175UH, and 190UH. The furnish was 100% recycled unbleached fiber paper Paper was produced using a Fourdrinier one ply, two press section machine.

[0051] Enzyme was applied in a first pulp tank after repulping at pH 6.9, a temperature of 40° C., 4.0 wt. % solids by total weight of the pulp composition, and a contact time of two hours upstream of the paper machine head box. Polymer was applied at the suction of the fan pump close to the paper machine head box. The enzyme product should be given enough time to act on the fiber, for example, 40 minutes, at a pH range of 6.5 to 8.0, and a temperature range of 40° C. to 60° C. The polymer can be applied at the paper machine dry end approach flow with minimum contact time with the fiber such as at the fan pump suction, stuff box accept, pre-screen, or post-screen.

[0052] The papers produced were tested for dry strength using the ring crush test (RCT) and the corrugating medium test (CMT). Results are shown in Tables 1 and 2, as well as in FIGS. 5 and 6. FIG. 5 is a bar graph showing a comparison of RCT results (Kgf/cm²) before (without) addition of enzyme and polymer and during (after) addition of enzyme and polymer. FIG. 6 is a bar graph showing a comparison of corrugating medium test (CMT) results (Kgf/cm²) before (without) addition of enzyme and polymer and during (after) addition of enzyme and polymer.

TABLE 1

RING CRUSH TEST (Kgf/cm ²)							
Grade	Month 1	Month 2	Month 3	Average Before Trial	Average During Trial	Gain	Observation
117MI	11.4	11.3	11.5	11.4	12.9	13.30%	Improved
117NO	11.4	11.3	11.5	11.4	12.5	9.30%	Improved
150UH	14.7	16.3	15.5	15.3	18.3	19.60%	Improved
165UH	23.6	23.3	23.8	23.5	24.5	4.10%	Improved
175UH	—	23.5	—	23.5	26.4	12.10%	Improved
190UH	31.1	31.5	31.5	31.4	30.9	-1.70%	Lost

TABLE 2

CORRUGATING MEDIUM TEST (Kgf/cm ²)							
Grade	Month 1	Month 2	Month 3	Average Before Trial	Average During Trial	Gain	Observation
117MI	19.8	19.9	20.9	20.3	21.8	7.20%	Improved
117NO	19.8	19.9	20.9	20.3	20.3	0.10%	Improved
150UH	24.1	26.8	26.8	26	28.5	9.70%	Improved
165UH	30.8	30.6	33.6	31.6	32.8	3.80%	Improved
175UH	—	—	—	—	33.6	—	No Data
190UH	33.2	32.8	35	33.5	34.6	3.50%	Improved

[0053] Applicants specifically incorporate the entire contents of all cited references in this disclosure. Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range, or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0054] It will be apparent to those skilled in the art that various modifications and variations can be made to the embodiments of the present invention without departing from the spirit or scope of the present invention. Thus, it is intended that the present invention covers other modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A method of making paper or paperboard having enhanced dry strength comprising:

adding at least one enzyme and at least one polymer comprising at least one cationic water-soluble polymer or at least one amphoteric water-soluble polymer, or both, to a papermaking pulp to yield a treated pulp; and

forming the treated pulp into paper or paperboard having a dry strength greater than paper or paperboard formed from papermaking pulp without the addition of the enzyme and polymer.

2. The method of claim 1, wherein the dry strength is measured using a strength test that is a ring crush test (RCT) or a corrugating medium test (CMT).

3. The method of claim 1, wherein the enzyme comprises at least one cellulose, or at least one laccase, or both.

4. The method of claim 3, wherein the enzyme is laccase.

5. The method of claim 1, wherein the polymer comprises a glyoxylated polyacrylamide (gPAM), a polyvinylamine, a decarboxylated polyacrylamide, or a dimethylamine-epichlorohydrin (epi-DMA), or any combination thereof.

6. The method of claim 1, wherein the enzyme is laccase and the polymer is gPAM.

7. The method of claim 1, wherein the enzyme and polymer are added stepwise.

8. The method of claim 1, wherein the enzyme and the polymer are added as a composition.

9. The method of claim 8, wherein the composition comprises from about 1.0 wt. % to about 99 wt. % enzyme and from about 99 wt. % to about 1.0 wt. % polymer, based on the total dry solids weight of the composition.

10. The method of claim 1, wherein the enzyme and polymer are added in synergistic amounts, wherein the paper or paperboard has a dry strength greater than if either the enzyme or polymer alone were added.

11. A method of making paper or paperboard having enhanced dry strength comprising:

adding a laccase and a glyoxylated polyacrylamide to a papermaking pulp to yield a treated pulp; and

forming the treated pulp into paper or paperboard having a dry strength greater than paper or paperboard formed from papermaking pulp without the addition of the laccase and the glyoxylated polyacrylamide.

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