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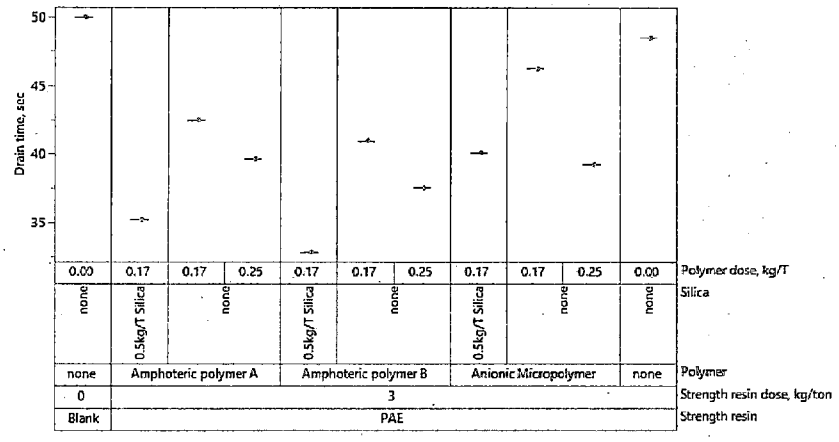


FIG 1

(57) Abstract: The present invention generally relates to methods and compositions for manufacture of tissue, paper, or board and for enhancing retention and drainage thereof. In particular, the disclosure provides methods for enhancing retention and drainage by addition of a retention and drainage aid comprising reactive cationic polymers (e.g., cationic strength resins), water-soluble amphoteric terpolymers, and optionally anionic organic or inorganic microparticles. Preparation of paper sheets under these conditions provides improved retention, drainage time, STFI and burst strength, and improved hydrophobic particle control.

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— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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USE OF AMPHOTERIC EMULSION POLYMERS WITH STRENGTH RESINS AS RETENTION AND DRAINAGE AIDS

RELATED APPLICATIONS

[0001] The present application claims benefit of priority to US Provisional Application No.: 63/510,759, filed on June 28, 2023, and to Finnish Application Number 20236130 filed on October 12, 2023, the contents of both of which are incorporated by reference in their entireties.

FIELD OF THE INVENTION

[0002] The present invention generally relates to methods and compositions for manufacture of tissue, paper, or board and for enhancing retention and drainage thereof. In particular, the disclosure provides methods for enhancing retention and drainage by addition of a retention and drainage aid comprising reactive cationic polymers (e.g., cationic strength resins), water-soluble amphoteric terpolymers, and optionally anionic organic or inorganic microparticles. Preparation of paper sheets under these conditions provides improved retention, drainage time, STFI and burst strength, and improved hydrophobic particle control.

BACKGROUND OF THE INVENTION

[0003] Glyoxylated polyacrylamide (GPAM) is generally used in a variety of paper grades to enhance the dry and temporary wet strength. It is used for example to increase the initial wet strength of many household tissues which come in contact with water in use. Glyoxylated polyacrylamide is also applied to increase the compression strength and the dimensional stability of many board-grade paper products.

[0004] In the production of paper or paperboard, a dilute aqueous composition known as "furnish" or "stock" is sprayed onto a moving mesh known as a "wire" or "wire screen". Solid components of this composition, such as cellulosic fibers, fines, and inorganic particulate mineral fillers are drained or filtered by the wire to form a paper sheet. The percentage of solid material retained on the wire is known as the "first pass retention" of the papermaking process.

[0005] Paper and board manufacturers require chemical additives that will effectively provide enhanced on-machine retention and drainage while also providing additional benefits, such as improved paper strength and wet pressability. These requirements are especially challenging for papermaking operations in mills with high recycled content.

[0006] Retention is a function of different mechanisms, such as filtration by mechanical entrainment, electrostatic attraction, and bridging between the fibers and the fillers in the furnish. Because both the cellulosic fibers and many common filler materials are negatively charged, they are mutually repellent. Generally, the only factor tending to enhance retention is mechanical entrainment. Therefore, a retention aid is generally used to improve retention of the fibers and fillers on the wire.

[0007] Drainage relates to the rate of removal of water from the furnish as the paper sheet is formed. Drainage usually refers to only water removal which takes place in the "drainage zone" (gravity and vacuum sections) of the paper machine primarily before any pressing of the wet paper web subsequent to formation of the web. Thus, drainage aids are used to improve the overall efficiency of dewatering in the production of paper or paperboard.

[0008] Improvements in retention and drainage of the final paper or paperboard sheet are particularly desirable for several reasons, the most significant of which is productivity. Good retention and good drainage enable a paper machine to run faster and to increase production.

[0009] These improvements are realized by the use of retention and drainage aids. These retention and drainage aids are generally added to the furnish as the furnish approaches the headbox of the paper machine and may comprise a coagulant/flocculant system used in conjunction with one or more shearing stages.

[0010] A coagulant is typically a low molecular weight cationic synthetic polymer that reduces the negative surface charges on the fiber, fines, and/or filler particles to accomplish agglomeration of such particles. The flocculant, which generally is a high molecular weight cationic, nonionic, or anionic synthetic polymer, bridges the particles and/or agglomerates, from one surface to another, thereby binding the particles into larger flocs. The larger flocs increase retention of the particles; however, as they are filtered out of the water onto the fiber web, the pores of the flocs are covered, thereby reducing the drainage efficiency of the fiber web. The larger flocs can be broken down by shearing which is provided by one or more of the cleaning, mixing and pumping stages of the papermaking process.

[0011] Greater retention of fines and fillers permits a reduction in the content of cellulosic fiber. As pulps of inferior quality are employed to reduce papermaking costs, the retention aspect of papermaking becomes even more important. This is due to the higher level of fines found in lower quality pulps, such as recycled fiber and coated broke. Greater retention of fines, fillers, and other slurry components also reduces the amount of such substances lost to the white water. This reduces the amount of material wastes, the cost of waste disposal, and the adverse environmental effects therefrom.

[0012] There is a need in the art to provide an improved coagulant/flocculant system which replaces the cationic coagulant/high molecular weight anionic flocculant system of the prior art resulting in a substantial improvement of the retention and drainage properties of the paper furnish and the physical properties of the formed paper product such as formation and brightness. This is particularly true for paper furnishes containing recycled deinked fiber, groundwood, bleached fiber linerboard and/or coated broke and either treated or untreated fillers, higher levels of stickies, calcium ions, and conductivity.

[0013] Recycled fiber material is commonly used as raw material for paper or board. The recycled fiber material comprises in addition to the fibers a number of other substances. Particulate foreign material is separated from the pulp in the pulper or at the screening. Some substances are naturally retained on the fibers and do not disturb the process. Other substances, such as stickies, may be separated from the pulp at the screening and at least partly removed from the process.

[0014] Use of recycled fiber material as raw material is the main source of hydrophobic substances, so called stickies, in paper and board making. While some or even most of these hydrophobic substances are removed during the pulping of recycled fiber raw materials, substantial amounts are still carried over during the paper or board making process. Hydrophobic substances, which have not been removed in de-inking or other recycled fiber processing stages, e.g., which are not trapped by the screens, enter the paper or board machine and circulate in the process waters. Due to the increased environmental awareness and regulations, papermaking processes have become more and more closed and use less fresh water. This results in heavy accumulation of interfering substances, including hydrophobic substances, in the fiber suspension and process waters. These

substances may agglomerate into bigger hydrophobic particles, which are capable of forming deposits. Additionally, accumulation of dissolved salts renders traditional CPAMs less effective. Traditional CPAMs are not effectively reactive with dissolved salts because traditional CPAMs are too big in molecular size and too low in polymer cationic charge.

[0015] In addition to the recycled fiber material, recycle of coated broke can also cause similar problems as described above for the recycled fiber material. Coated broke contaminant deposition in papermaking systems can cause serious operational problems if left uncontrolled. Coated broke is repulped and used as a furnish source at most coated fine paper mills. The most difficult problem involved with recycling coated broke is derived from the binder materials, sometimes in combination with pigments or fillers, since these polymers and the materials to which they have been attached, are the origin of sticky deposits. These sticky deposits cause difficulties when recycled back to the paper machine operation. Formed deposits may cause web breakages, so as a precautionary measure the most affected surfaces, such as drying cylinders, calendars, wires and felts, are being regularly washed and cleaned, which leads to downtime and loss of production.

[0016] Considerable effort has been directed toward developing improved retention and drainage aids. PCT/US99/29135 discloses a polyampholyte coagulant, which is used as a retention/drainage/formation aid in a papermaking process. However, commercially available retention and drainage aids remain inadequate for manufacture of paper and board with a high percentage of recycled fiber content.

[0017] High molecular weight polymeric additives and retention aid polymers added tend to hold water during the first passes in the press section, which dramatically increases drain time and reduces wet pressability of the fibrous web. A retention and drainage aid that would allow for more efficient dewatering in the press section and faster drying of the paper web in the dryer section would lead to significant steam savings and faster productivity for the paper manufacturer.

[0018] Based on the foregoing there is a need for improved polymer additives for use in the manufacturing of paper, tissue, towel, and/or board from recycled materials, which provide retention and drainage enhancement, while also controlling hydrophobic particles and agglomerates ("stickies") in the furnish. Therefore, it is an object of the present invention to provide methods and compositions for enhancing retention and drainage (i.e., retention and drainage aids) which provide improved retention, drainage time, paper strength, and improved hydrophobic particle control.

SUMMARY OF THE INVENTION

[0019] The present invention generally relates to methods and compositions for manufacture of tissue, paper, or board and for enhancing retention and drainage thereof. In particular, the disclosure provides methods for enhancing retention and drainage by addition of a retention and drainage aid comprising reactive cationic polymers (e.g., cationic strength resins), water-soluble amphoteric terpolymers, and optionally anionic organic or inorganic microparticles. Preparation of paper sheets under these conditions provides improved retention, drainage time, STFI and burst strength, and improved hydrophobic particle control.

[0020] In one aspect, the present invention provides a method for manufacture of tissue, paper, or board, the method comprising:

[0021] (a) forming or providing an aqueous suspension comprising cellulosic fibers;

[0022] (b) optionally diluting the aqueous suspension;

[0023] (c) flocculating the aqueous suspension to form a flocculated fiber suspension;

[0024] (d) removing sufficient water from the flocculated fiber suspension to form a wet fibrous web, preferably by introducing the flocculated fiber suspension into a headbox and draining the flocculated fiber suspension on a wire screen; and

[0025] (e) pressing and drying the wet fibrous web to obtain a tissue, paper, or board;

[0026] wherein the method further comprises prior to step (c) treating the aqueous suspension comprising cellulosic fibers with a retention and drainage aid comprising:

[0027] (i) one or more reactive cationic polymers; and

[0028] (ii) one or more water-soluble amphoteric polymers.

[0029] In some exemplary embodiments of the method said retention and drainage aid optionally further comprises one or more anionic organic or inorganic microparticles.

[0030] In some exemplary embodiments of the method (i) said one or more reactive cationic polymers, (ii) said one or more water-soluble amphoteric polymers, and optionally (iii) said one or more anionic organic or inorganic microparticles:

[0031] (a) are added sequentially in any order, simultaneously, or premixed prior to addition; or

[0032] (b) are added sequentially in the order of (i), (ii), and then optionally (iii), wherein a mixing time is allowed after each addition and said mixing time ranges from 0.01-10 min, 0.1-5 min, or 1-2 min.

[0033] In some exemplary embodiments of the method said one or more reactive cationic polymers comprise:

[0034] (a) functional groups that are reactive to cellulosic or lignocellulosic fiber surfaces; and

[0035] (b) a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

[0036] and further comprise one of the following;

[0037] (c) one or more cationic glyoxalated polyacrylamides (GPAMs);

[0038] (d) one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or

[0039] (e) a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55, wherein said one or more cationic PAE resins and said one or more cationic GPAMs are added sequentially in any order, simultaneously, or premixed prior to addition to said aqueous suspension comprising cellulosic fibers.

[0040] In some exemplary embodiments of the method said one or more cationic GPAMs:

[0041] (a) are suitable for use as a dry and/or wet strengthening agent;

[0042] (b) are synthesized by reacting glyoxal with a base polymer, wherein said base polymer comprises a weight average molecular weight ranging from 5-5000 kDa, 50-2500 kDa, 80-2000 kDa, or 100-1000 kDa and comprises nonionic monomers, cationic monomers, and optional anionic monomers, wherein

[0043] (i) said nonionic monomers are selected from the group of primary amide-containing monomers comprising acrylamide, methacrylamide, ethyl acrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, N-ethyl methacrylamide, and any combination thereof;

[0044] (ii) said cationic monomers are selected from acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof; and

[0045] (iii) said optional anionic monomers contain functional groups selected from carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof;

[0046] (c) comprise a glyoxal:base polymer weight ratio ranging from 0.1:99.9 to 50:50, 5:95 to 20:80, or 5:95 to 10:90;

[0047] (d) comprise a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

[0048] (e) comprise a percent cationic monomer content ranging from 3-60% by weight, a percent anionic monomer content ranging from 0-50% by weight, wherein the remainder of the monomer content comprises nonionic monomers;

[0049] (f) are formulated optionally as a dry powder or as an aqueous composition comprising a GPAM solids percentage ranging from about 0.5% to about 20%, optionally from greater than about 2% to about 10%, further optionally from about greater than 4% to about 8%.

[0050] In some exemplary embodiments of the method said one or more cationic PAE resins:

[0051] (a) are suitable for use as a wet strengthening agent;

[0052] (b) are synthesized by reacting one or more polyamidoamine backbones with epichlorohydrin, wherein said one or more polyamidoamine backbones are synthesized by reacting a carboxylic acid and/or a carboxylic acid derivative with an amine, wherein said one or more polyamidoamine backbones comprise a molar ratio of the amine to the carboxylic acid and/or carboxylic acid derivative ranging from 1:1 to 2:1, 1.05:1 to 2:1, or 1.5:1 to 2:1;

[0053] (c) comprise a molar ratio of epichlorohydrin to secondary amine groups of the polyamidoamine backbone ranging from about 0.15 to about 1.7.

[0054] In some exemplary embodiments of the method said one or more water-soluble amphoteric polymers:

[0055] (a) are comprised of acrylamide (AM) monomers, one or more anionic monomers, and one or more cationic monomers, wherein,

[0056] (i) said one or more anionic monomers contain functional groups selected from the group consisting of carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof; and

[0057] (ii) said one or more cationic monomers are selected from the group consisting of acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt,

dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof;

[0058] (b) comprise an inverse phase emulsion, a dry polymer, or an aqueous polymer solution, preferably an inverse phase emulsion;

[0059] (c) comprise a polymer standard viscosity (SV) ranging from <3.5 cPs, 1-3.5 cPs, 2-3.5 cPs, or 2.5-3.5 cPs;

[0060] (d) comprise a molecular weight ranging from 1.5-9 million Daltons, 1.5-8 million Daltons, 2-8 million Daltons, 4-8 million Daltons, or preferably 2-5 million Daltons;

[0061] (e) comprise an acrylamide (AM) monomer content ranging from 77-100 wt%, 78-100 wt%, 80-100 wt%, 90-100 wt%, or 95-100 wt%;

[0062] (f) comprise an anionic monomer content ranging from ≤3 wt%, ≤2 wt%, 0.01-3 wt%, 0.5-2 wt%, 1-2 wt%, 1.5-2 wt%, or 1.8-2 wt%;

[0063] (g) comprise a cationic monomer content ranging from ≤20 wt%, 1-20 wt%, 2-16 wt%, 4-12 wt%, or 7-9 wt%; or

[0064] (h) any combination of the foregoing.

[0065] In some exemplary embodiments of the method said one or more anionic organic or inorganic microparticles are selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides.

[0066] In some exemplary embodiments of the method:

[0067] (a) said one or more reactive cationic polymers comprises said one or more cationic GPAMs and/or said one or more cationic PAE resins in aqueous form;

[0068] (b) said one or more cationic GPAMs comprise said base polymer comprising cationic monomers selected from DADMAC, AETAC, and combinations thereof; nonionic monomers selected from acrylamide, methacrylamide, and combinations thereof; and optionally anionic monomers selected from acrylic acid and/or corresponding water soluble salts, water dispersible alkali metal salts, alkaline earth metal salts, ammonium salts, and combinations thereof, or said base polymer comprises (i) acrylamide and DADMAC, (ii) acrylamide and AETAC, or (iii) acrylamide, DADMAC, and AETAC,

[0069] (c) said one or more water-soluble amphoteric polymers

[0070] (i) comprises an inverse emulsion of acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers;

[0071] (ii) preferably comprises an acrylic acid (AA) monomer content of no more than 2 wt %; and

[0072] (iii) preferably comprises a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7; and

[0073] (d) said one or more anionic organic or inorganic microparticles comprise colloidal silica.

[0074] In some exemplary embodiments of the method, when added to said aqueous suspension comprising cellulosic fibers:

[0075] (a) said one or more reactive cationic polymers are added at a dosage ranging from 0.1-15 g/kg, 0.5-5 g/kg, or 0.5-4 g/kg;

[0076] (b) said one or more water-soluble amphoteric polymers are added at a dosage ranging from 0.05-5 g/kg, 0.1-4 g/kg, or 0.3-1 g/kg;

[0077] (c) said one or more anionic organic or inorganic microparticles are added at a dosage ranging from 0.1-1 g/kg, 0.2-0.8 g/kg, or 0.4-0.6 g/kg.

[0078] In some exemplary embodiments of the method, said aqueous suspension comprising cellulosic fibers comprises a pH ranging from 4-8, 4-7.5, 4-7, 4.5-7, or 5-7 and further comprises:

[0079] (a) cellulosic fibers optionally obtained from sources selected from softwood fiber, hardwood fiber, recycled fiber, recycled old corrugated cardboard (OCC), recycled mixed office waste (MOW), recycled mixed office paper, refined fiber, mill broke fibers, coated broke, non-wood fibers, including but not limited to straw and wheat pulp, and a mixture of any of the foregoing;

[0080] (b) pulp selected from Kraft pulp, unbleached Kraft pulp, bleached pulp, unbleached pulp, process water from pulp, paper, and/or board production, neutral sulfite semi chemical (NSSC) pulp, mechanical pulp, non-wood pulp, and a mixture of any of the foregoing; or

[0081] (c) a stock selected from a thick stock, a thick stock diluted with chemical water, synthetic water, white water, and/or process water, and a thin stock, and a mixture of any of the foregoing.

[0082] In some exemplary embodiments of the method, when used for manufacture of tissue, paper, or board, the method results in:

[0083] (a) improved retention of said cellulosic fibers; a

[0084] (b) improved drainage of said flocculated fiber suspension;

[0085] (c) improved STFI and/or burst strength;

[0086] (d) a reduced hydrophobic particle and/or hydrophobic agglomerate count;

[0087] (e) an improved dry tensile, immediate wet tensile, and/or soaked wet tensile strength; or

[0088] (f) any combination of (a)-(e)

[0089] compared to a tissue, paper, or board prepared by an identical method in the absence of (i) addition of said one or more reactive cationic polymers or (ii) addition of said one or more water-soluble amphoteric polymers.

[0090] In another aspect, the present invention provides a method for manufacture of tissue, paper, or board, the method comprising:

[0091] (a) forming or providing an aqueous suspension comprising cellulosic fibers;

[0092] (b) optionally diluting the aqueous suspension;

[0093] (c) flocculating the aqueous suspension to form a flocculated fiber suspension;

[0094] (d) removing sufficient water from the flocculated fiber suspension to form a wet fibrous web, preferably by introducing the flocculated fiber suspension into a headbox and draining the flocculated fiber suspension on a wire screen;; and

[0095] (e) pressing and drying the wet fibrous web to obtain a tissue, paper, or board;

[0096] wherein the method further comprises prior to step (c) treating the aqueous suspension comprising cellulosic fibers with a retention and drainage aid comprising:

[0097] (i) one or more reactive cationic polymers comprising functional groups that are reactive to cellulosic or lignocellulosic fiber surfaces and a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7, wherein said one or more reactive cationic polymers comprise one or more cationic glyoxalated polyacrylamides (GPAMs); one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55, wherein said one or more cationic PAE resins and said one or more cationic GPAMs are added sequentially in any order, simultaneously, or premixed prior to addition to said aqueous suspension comprising cellulosic fibers;

[0098] (ii) one or more water-soluble amphoteric polymers comprising an inverse emulsion of acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers; preferably comprising an acrylic acid (AA) monomer content of no more than 2 wt %; and preferably comprising a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7; and

[0099] (iii) optionally one or more anionic organic or inorganic microparticles comprising silica.

[0100] In another aspect, the present invention provides a fiber stock composition comprising:

[0101] (a) an aqueous suspension comprising cellulosic fibers; and

[0102] (b) a retention and drainage aid comprising

[0103] (i) one or more reactive cationic polymers;

[0104] (ii) one or more water-soluble amphoteric polymers; and

[0105] (iii) optionally one or more anionic organic or inorganic microparticles;

[0106] obtainable by a method according to any of the foregoing claims.

[0107] In another aspect, the present invention provides a composition for use as a retention and drainage aid in manufacture of tissue, paper, or board, the composition comprising:

[0108] (a) one or more reactive cationic polymers comprising a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7, wherein said one or more reactive cationic polymers comprise

[0109] (i) one or more cationic glyoxalated polyacrylamides (GPAMs) synthesized by reacting glyoxal with a base polymer, wherein said base polymer comprises a weight average molecular weight ranging from 5-5000 kDa, 50-2500 kDa, 80-2000 kDa, or 100-1000 kDa; (i) acrylamide and DADMAC, (ii) acrylamide and AETAC, or (iii) acrylamide, DADMAC, and AETAC and further wherein said one or more GPAMs comprises a glyoxal:base polymer weight ratio ranging from 0.1:99.9 to 50:50, 5:95 to 20:80, or 5:95 to 10:90; and a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

[0110] (ii) one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or

[0111] (iii) a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55;

[0112] (b) one or more water-soluble amphoteric polymers comprising acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers; wherein said one or more water-soluble amphoteric emulsion polymers preferably comprise an acrylic acid (AA) monomer content of no more than 2 wt % and a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7, wherein said one or more water-soluble amphoteric polymers is a an inverse emulsion, a dry polymer, an aqueous solution, preferably an inverse phase emulsion; and

[0113] (c) optionally one or more anionic organic or inorganic microparticles selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides.

BRIEF DESCRIPTION OF THE DRAWINGS

[0114] The invention will be described in more detail with reference to appended drawings, described in detail below.

DETAILED DESCRIPTION OF THE INVENTION

[0115] Before describing the invention, the following definitions are provided. Unless stated otherwise all terms are to be construed as they would be by a person skilled in the art.

[0116] **FIG 1** provides an exemplary variability chart showing DDA drain time (sec) for recycled towels prepared from 100% OCC furnish treated with PAE and amphoteric emulsion polymers with or without silica according to **Example 1**.

[0117] **FIG 2** provides an exemplary variability chart showing filtrate turbidity (NTU) for recycled towels prepared from 100% OCC furnish treated with PAE and amphoteric emulsion polymer with or without silica according to **Example 1**.

[0118] **FIG 3** provides an exemplary variability chart showing DDA drain time (sec) for recycled towels prepared from 100% OCC furnish treated with GPAM and amphoteric emulsion polymer with or without silica according to **Example 1**.

[0119] **FIG 4** provides an exemplary variability chart showing filtrate turbidity (NTU) for recycled towels prepared from 100% OCC furnish treated with GPAM and amphoteric emulsion polymer with or without silica according to **Example 1**.

[0120] **FIG 5** provides an exemplary graph of DDA drain time (sec) vs. polymer dosage for a packaging grade furnish with conductivity 3.84 mS/cm treated with reference cationic polyacrylamide (CPAM, solid line) + GPAM and an amphoteric emulsion polyacrylamide (amPAM, dashed line) + GPAM according to **Example 3**.

[0121] **FIG 6** provides an exemplary graph of DDA drain time (sec) vs. polymer dosage for a packaging grade furnish with conductivity 5.09 mS/cm treated with reference cationic polyacrylamide (CPAM, solid line) + GPAM and an amphoteric emulsion polyacrylamide (amPAM, dashed line) + GPAM according to **Example 3**.

[0122] **FIG 7** provides an exemplary bar graph of filtrate turbidity (NTU) vs. polymer dosage for a reference cationic polyacrylamide (CPAM) and an amphoteric emulsion polyacrylamide (amPAM) for packaging grade liner sheets at three conductivity levels according to **Example 3**.

[0123] **FIG 8** provides an exemplary graph of strength (GM STFI) vs. GPAM dosage for packaging grade liner sheets prepared with amphoteric emulsion polyacrylamide or dry amphoteric polyacrylamide according to **Example 4**.

[0124] **FIG 9** provides an exemplary bar graph of strength properties (STFI and Burst strength) of handsheets prepared according to **Example 5**.

[0125] **FIG 10** provides an exemplary variability chart showing DDA drain time (sec) for towels prepared from 100% recycled mixed office paper according to **Example 6**.

[0126] **FIG 11** provides an exemplary variability chart showing filtrate turbidity (NTU) for towels prepared from 100% recycled mixed office paper according to **Example 6**.

DEFINITIONS

[0127] As used herein the singular forms "a", "and", and "the" include plural referents unless the context clearly dictates otherwise.

[0128] As used herein, the singular forms "a," "an," and "the" may mean "one" but also include plural referents such as "one or more" and "at least one" unless the context clearly dictates otherwise. All technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention belongs unless clearly indicated otherwise.

[0129] As used herein, the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or."

[0130] As used herein the term "or combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term unless stated otherwise.

[0131] PAPERMAKING

[0132] As used herein, the term "paper" includes products comprising a cellulosic sheet material including paper sheet, paperboard, and the like.

[0133] As used herein, the terms "papermaking process" and "papermaking application" generally refers to any process in which any form of paper and/or paperboard product may be produced. For example, such processes include making paper products from pulp, such as methods comprising forming an aqueous cellulosic papermaking furnish, draining the furnish to form a sheet, and drying the sheet. The steps of forming the papermaking furnish, draining and drying may be carried out in any conventional manner generally known in the art.

[0134] As used herein, the terms "wet end of a paper machine" or "wet end" generally refer to the parts of a papermaking process between pulping (or bleaching) and wet-pressing of the paper.

[0135] As used herein, the term "fiber" refers to the basic structural unit of paper or board.

[0136] As used herein, the terms "recycled fiber" and "recovered fiber", refer to paper, paperboard, and fibrous wastes from retail stores, office buildings, homes, manufacturing plants, and so forth, after they have passed through their end-usage as a consumer item. Manufacturing wastes include: dry paper and paperboard waste generated after completion of the papermaking process including by way of example: envelope cuttings, bindery trimmings, and other paper and paperboard waste resulting from printing, cutting, forming, and other converting operations; bag, box, and carton manufacturing wastes; mill wrappers, and rejected unused stock; and repulped finished paper and

paperboard from obsolete inventories of paper and paperboard manufacturers, merchants, wholesalers, dealers, printers, converters, or others. In particular the term "recycled fibers" includes recycled fibers derived by processing of paper and other consumer cellulosic materials, e.g., paper, old corrugated containerboard (OCC), mixed office waste (MOW), old magazine (OMG), unbleached kraft pulp, neutral sulphite semi chemical (NCCS) pulp and/or mechanical pulp. Source materials for recycled fibers may be selected from old corrugated containerboard, mixed office waste, old newsprint, old magazines, double liner kraft, and any mixtures thereof. Mixed waste (MXW) denotes recycled mixture of recycled board, such as OCC, white lined chipboard and/or folding boxboard, and recycled paper, such as old newsprint, old magazines and/or office waste papers. Mixed office waste denotes recycled fiber material mainly containing copying papers, printer papers and offset papers. Double lined kraft denotes recycled fiber material comprising clean sorted unprinted corrugated cardboard cartons, boxes, sheet or trimmings, e.g., of kraft or jute liner. White lined chipboard (WLC) denotes multiply board comprising deinked fiber material and/or un-deinked recycled fiber material originating e.g., from OCC, mixed office waste or old newspapers (ONP) in or more of the layers. Presence of any of these recycled fiber materials in the fiber suspension usually decreases drainage and paper strength and provides a substantial load of starch, hydrophobic, and colloidal substances to the process.

[0137] As used herein, the term "OCC" refers to old corrugated cardboard and/or containerboard. Corrugated refers to those boxes where the materials are made from three separate layers of paper, two liners and a corrugated, or wavy, layer sandwiched between them. Brown paper bags are commonly accepted with OCC for recycling. The term OCC denotes recycled fiber material which have liners of test liner, jute or kraft, and may cover also double sorted corrugated containerboard (DS OCC).

[0138] As used herein, the terms "broke" or "mill broke" refer to paper, which during the paper making process becomes suitable only for repulping e.g., trimmings or paper that is out of specification. Broke is re-used material which never left the mill is not regarded as recycled or recovered. Broke is a valuable source of fiber and is recycled internally at the mill.

[0139] As used herein, the term "coated broke" refers to broke that contains coatings that are applied to the base sheet of paper as it is being manufactured. When the broke contains these coatings, it presents special problems in recycling to recover fiber values because the coatings introduce materials which would not normally be present in the original stock of fiber used to manufacture the base paper sheet. The coated broke may also contain dyes and/or other additives. In the present application coated broke includes surface-sized, dyed, and/or creped broke.

[0140] As used herein, the term "recycled fiber composition" generally refers to a composition comprising recycled cellulosic fibers, typically a composition wherein most or all are recycled fibers, e.g., at least 20, 40, 50, 60, 70, 80, 90 or 100%.

[0141] As used herein, the term "fiber suspension" is understood as an aqueous suspension, which comprises fibers, preferably recycled fibers, and optionally fillers. For example, the fiber suspension may comprise at least 5 %, preferably 10-30 %, more preferably 11 - 19 % of mineral filler. Mineral filler may be any filler conventionally used in paper and board manufacturing, such as ground calcium carbonate, precipitated calcium carbonate, clay, talc, gypsum, titanium dioxide, synthetic silicate, aluminum trihydrate, barium sulphate, magnesium oxide or their any of mixtures.

[0142] As used herein the term "headbox" refers a receptacle in a papermaking machine that holds suspended aqueous cellulosic solids and which regulates the flow thereof onto a wire or screen that provides for the draining of water therefrom.

[0143] As used herein the term "lignocellulosic substrate" refers to a paper and/or paperboard product formed from plant dry matter from any source, virgin or recycled, which may be coated, printed, and/or formed into a packaging product. For example, such substrates include paper products made from pulp, such as by methods comprising forming an aqueous cellulosic papermaking furnish, draining the furnish to form a sheet, and drying the sheet. The steps of forming the papermaking furnish, draining and drying may be carried out in any conventional manner generally known in the art. The substrates may contain polymeric strengthening agents, such as wet strength and dry strength agents.

[0144] As used herein, the term "slurry" generally refers to a mixture of water, dissolved paper pulp, and optionally other soluble or insoluble components produced or added during the stock preparation phase of papermaking.

[0145] As used herein, the terms "furnish" or "papermaking furnish" generally refers to a mixture of cellulosic fibers, pulp, optional fillers, dyes, and water from which paper or board is made.

[0146] As used herein, the term "thick stock" generally refers to mixture of papermaking pulp and other materials with a consistency of about 1 to 5%.

[0147] As used herein, the term "thin stock" generally refers to a mixture of papermaking pulp and other materials, after having been diluted to a consistency below 1% with whitewater or other process water at a fan pump.

[0148] As used herein, the term "white water" generally refers to process water within a paper machine system, especially referring to water that is drained from paper as the sheet is being formed.

[0149] As used herein, the terms "fixation", "fixing" and "fix" means that a substance is associated or attached onto the fibers at least temporarily or permanently.

[0150] As used herein, the term "flocculation" generally refers to the tendency for fibers to collect together in bunches in the presence of flow, and especially in the presence of retention aids; the same word also refers to the action of high-mass polymers in forming bridges between suspended colloidal particles, causing strong, relatively irreversible agglomeration.

[0151] The term "flocculant" may generally refer to a reagent that may bridge neutralized or facilitate coagulation of particles into larger agglomerates, typically resulting in more efficient settling. Flocculation process generally involves addition of a flocculant followed by mixing to facilitate collisions between particles, allowing for the destabilized particles to agglomerate into larger particles that can be removed by gravity through sedimentation or by other means, e.g., centrifugation, filtration.

[0152] As used herein the term "dry strength" generally refers to the force or energy required to break a paper sample, by one of various procedures, after equilibration in a standard atmosphere.

[0153] As used herein the term "wet strength" generally refers to the strength of a sheet of paper after it has been exposed to a standard solution for a standard length of time, but often expressed as a ratio vs. the dry strength.

[0154] Polymer molecular weights may be measured by various methods known to persons of skill in the art. For example, weight average molecular weight may be measured using gel permeation chromatography (GPC). Additionally, polymer molecular weights may be measured by GPC/Light Scattering/Viscometry also known as Triple Detection GPC which employs Refractive Index Detector (with or without UV Detector), Dilute Solution Viscometry and Light Scattering all in series to determine molecular weights, distribution and related solution parameters.

[0155] RETENTION AND DRAINAGE AID

[0156] As used herein, the terms "polymer" or "polymeric additives" and similar terms are used in their ordinary sense as understood by one skilled in the art, and thus may be used herein to refer to or describe a large molecule (or group of such molecules) that may comprise recurring units. Polymers may be formed in various ways, including by polymerizing monomers and/or by chemically modifying one or more recurring units of a precursor polymer. Unless otherwise specified, a polymer may comprise a "homopolymer" that may comprise substantially identical recurring units that may be formed by, for example, polymerizing a particular monomer. Unless otherwise specified, a polymer may also comprise a "copolymer" that may comprise two or more different recurring units that may be formed by, for example, copolymerizing, two or more different monomers, and/or by chemically modifying one or more recurring units of a precursor polymer. Unless otherwise specified, a polymer or copolymer may also comprise a "terpolymer" or a "tetrapolymer" which generally refer to polymers that comprise three, four, or more different recurring monomer units. The term "polymer" as used herein is intended to include both the acid form of the polymer as well as its various salts. Polymers may be amphoteric in nature, that is, containing both anionic and cationic substituents, although not necessarily in the same proportions.

[0157] As used herein, the terms "polyacrylamide" or "PAM" generally refer to polymers and co-polymers comprising acrylamide moieties, and the terms encompass any polymers or copolymers, including terpolymers, comprising acrylamide moieties, e.g., one or more acrylamide (co)polymers of acrylamide and additional monomers capable of copolymerizing with acrylamide. Furthermore, PAMs may comprise any of the polymers or copolymers discussed herein. Additionally, the PAMs described herein, e.g., one or more acrylamide (co)polymers, may be produced in one of various forms, including, for example, dry (powder) form (e.g., DPAM), emulsion polyacrylamide (EPAM), or liquid polyacrylamide. Amphoteric polyacrylamides (AmPAM) may be formulated in dry (powder) form (e.g., AmDPAM), or emulsion form (AmEPAM) .

[0158] As used herein, the term "amphoteric polymer" refers to polymers containing both anionic and cationic groups on the macromolecular chain. These polymers exhibit both attraction and repulsion in their electrostatic intermolecular interactions (resulting in anti-polyelectrolyte association called "Amphoteric Effect") and they exhibit excellent salt tolerance, especially in high Ca+2 aqueous compositions.

[0159] As used herein, the term "emulsion polymer" generally refers to inverse emulsions (water-in-oil) in which water droplets containing the polymer are suspended in an oil phase, also termed a hydrophobic phase.

[0160] As used herein, the term "inverse phase emulsion" refers to a liquid polymer composition of polymer dissolved in an aqueous solution which is dispersed into an oil phase (e.g., hydrophobic liquid) to form an oil-continuous phase, which is then mixed with an aqueous solution so that the dispersed polymer phase of the liquid polymer composition becomes a substantially aqueous-continuous phase, and the hydrophobic liquid phase becomes a dispersed, discontinuous phase. The

inversion point can be characterized as the point at which the viscosity of the inverted polymer solution has substantially reached its maximum under a given set of conditions. In practice, this may be determined for example by measuring viscosity of the composition periodically over time and when three consecutive measurements are within the standard of error for the measurement, then the solution is considered inverted.

[0161] As used herein, the term "liquid polymer" refers to a combination of at least one polymer and a liquid, typically an aqueous liquid. The polymer in a may be thoroughly dissolved or may be a partially dissolved suspension, dispersion, or slurry. An "aqueous polymer mixture" or "hydrated polymer composition" refers to a combination of at least one polymer and an aqueous liquid. When a dry polymer is combined with an aqueous liquid, the polymer is initially partially hydrated at the polymer–water interface. Polymers do not dissolve instantaneously in aqueous or non-aqueous solvents. Dissolution is controlled by either the disentanglement of the polymer chains or by the diffusion of the chains through a boundary layer adjacent to the polymer–solvent interface. After thorough mixing, the polymer may become fully hydrated, at which point the wetting process is complete and the polymer may be either partially dissolved or fully dissolved, depending on the nature and composition of the polymer and solvent.

[0162] The term "water-soluble polymer" generally refers to any polymer that may dissolve and/or disperse in water. Said polymers may modify the physical properties of aqueous systems undergoing gelation, thickening, viscosification, or emulsification/stabilization. Said polymers may perform a variety of functions, including but not limited to use as dispersing and suspending agents, stabilizers, thickeners, viscosifiers, gellants, flocculants and coagulants, film-formers, humectants, binders, and lubricants.

[0163] As used herein, the term "monomer" generally refers to nonionic monomers, anionic monomers, cationic monomers, zwitterionic monomers, betaine monomers, and amphoteric ion pair monomers.

[0164] As used here "Q9 monomer" refers to 2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) which has a molecular formula of C8H16ClNO2 and a molecular weight of 193.67 g/mol.

[0165] As used herein acrylamide or "AM" refers to a neutral monomer of molecular formula: C3H5NO and a molecular weight of 71.08 g/mol.

[0166] As used herein acrylic acid or "AA" refers to an anionic monomer of molecular formula: CH2CHCOOH and a molecular weight of 72.06 g/mol.

[0167] As used herein, the term "cationic monomer" generally refers to a monomer that possesses a positive charge. Examples thereof include acryloyloxy ethyl trimethylammonium chloride (Q9) monomers. Cationic monomers may also be selected from acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate

methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof.

[0168] As used herein the term "nonionic monomer" generally refers to a monomer that possesses a neutral charge. Exemplary nonionic monomers may comprise but are not limited to comprising monomers selected from the group consisting of acrylamide ("AMD"), methacrylamido, vinyl, allyl, ethyl, and the like, all of which may be substituted with a side chain selected from, for example, an alkyl, arylalkyl, dialkyl, ethoxyl, and/or hydrophobic group. In an exemplary embodiment, a nonionic monomer may comprise AMD. In some embodiments, nonionic monomers may comprise but are not limited to comprising vinyl amide (e.g., acrylamide, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide), 4-acryloylmorpholine, maleic anhydride, N-vinylpyrrolidone, vinyl acetate, N-vinyl formamide and their derivatives, such as hydroxyethyl(methyl(acrylate CH2=CR-COO-CH2CH2OH (I) and CH2=CR-CO-N(Z1)(Z2) (2) N-substituted (methyl) acrylamide (II), R=H or Me; Z1=5-15C alkyl; 1-3C alkyl substituted by 1-3 phenyl , phenyl or 6-12C cycloalkyl (both optionally substituted) and Z2=H; or Z1 and Z2 are each 3-10C alkyl; (II) is N-tert. hexyl, tert. octyl, methylundecyl, cyclohexyl, benzyl, diphenylmethyl or triphenyl acrylamide. Nonionic monomers include N-isopropylacrylamide, N-vinyl formamide, methacrylamide; N-alkylacrylamides, including but not limited to, N-methylacrylamide, N-ethylacrylamide, N-propylacrylamide, and N-butylacrylamide; N,N-dialkylacrylamides, including, but not limited to, N,N-dimethylacrylamide and N,N-diethylacrylamide; N-alkyl methacrylamides; alkyl acrylates; hydroxyalkyl acrylates and methacrylates, including but not limited to, hydroxymethyl acrylate, 2-hydroxyethyl acrylate, 3-hydroxypropyl acrylate, 4-hydroxybutyl acrylate, hydroxymethyl methacrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, and 4-hydroxybutyl methacrylate; dihydroxyalkyl acrylates and methacrylates, including but not limited to, 2,3-dihydroxypropyl acrylate, 3,4-dihydroxybutyl acrylate, 2,3-dihydroxypropyl methacrylate (DHPMA), and 3,4-dihydroxybutyl methacrylate; alkyl acrylates, including but not limited to, methyl methacrylate; acrylonitrile; N-vinylmethylacetamide, N-vinylmethylformamide; N-vinyl acetate, glyoxalated acrylamides, and vinyl pyrrolidone. Nonionic monomers can be combined for example to form copolymers with acrylamide.

[0169] As used herein, the term "anionic monomers" may refer to either anionic monomers that are substantially anionic in whole or (in equilibrium) in part, at a pH in the range of about 1.0 to about 10.0. The "anionic monomers" may be neutral at low pH (e.g., from a pH of about 0-1, 0-2, or 0-3) depending on the pKa values of acidic protons contained therein. Some anionic monomers are obtained in anionic form as alkali metal salts, alkaline earth metal salts, and ammonium salts, e.g., sodium acetate and sodium 2-acrylamido-2-methylpropane sulfonic acid (AMPS).

[0170] Examples of anionic monomers which may be used herein include but are not limited to those comprising acrylic, methacrylic, maleic monomers and the like, sodium acrylate, calcium

diacrylate, and/or any monomer substituted with a carboxylic acid group or salt thereof. In some embodiments, anionic monomers may be substituted with a carboxylic acid group and include, for example, acrylic acid, and methacrylic acid. In some embodiments, an anionic monomer which may be used herein may be a (meth)acrylamide monomer wherein the amide group has been hydrolyzed to a carboxyl group. Said monomer may be a derivative or salt of a monomer according to other embodiments. Additional examples of anionic monomers comprise but are not limited to those comprising sulfonic acids or a sulfonic acid group, or both. In some embodiments, the anionic monomers which may be used herein may comprise a sulfonic function that may comprise, for example, 2-acrylamido-2-methylpropane sulfonic acid (acrylamido tertiary butyl sulfonic acid or "ATBS"). In some embodiments, anionic monomers may comprise organic acids. In some embodiments, anionic monomers may comprise acrylic acid, methacrylic acid, maleic acid, itaconic acid, acrylamido methylpropane sulfonic acid, vinylphosphonic acid, styrene sulfonic acid and their salts such as sodium, ammonium and potassium. In other embodiments, anionic monomers may comprise acrylic acid, methacrylic acid; sulfonic acids, phosphonic acids, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, vinyl phosphonic acid, and alkali metal salts, alkaline earth metal salts, and ammonium salts thereof. Anionic monomers can be combined for example to form a terpolymer of acrylamide , acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AMPS). In an exemplary embodiment, one or more acrylamide (co)polymers may comprise at least one monoethylenically unsaturated monomer comprising acid groups, for example monomers that comprise at least one group selected from -COOH, SO3H, or -PO3H2. Examples of such monomers may include , but are not limited to, acrylic acid, methacrylic acid, vinyl sulfonic acid, allyl sulfonic acid or 2-acrylamido -2-methylpropane sulfonic acid, particularly preferably acrylic acid and/or 2-acrylamido-2–methylpropane sulfonic acid, and most preferred acrylic acid or the salts thereof. In an exemplary embodiment, one or more acrylamide (co)polymers, or each of the one or more acrylamide (co)polymers, may comprise acrylic acid and/or 2-acrylamido-2-methylpropanesulfonic acid or salts thereof.

[0171] RETENTION AND DRAINAGE AID

[0172] As used herein, the term "reactive cationic polymers" refers to polymers that contain reactive moieties (e.g., azetidinium rings, aldehydes, hemiacetals, and the like), which react with carboxylate and -OH moieties on cellulosic and lignocellulosic fibers to form covalent bonds. Exemplary reactive cationic polymers, including but not limited to, cationic glyoxalated polyacrylamides (GPAMs) and cationic polyamidoamine-epichlorohydrin (PAE) resins are typically used as wet and/or dry strength additives in papermaking. Herein, GPAMs and PAE resins are used in combination with amphoteric emulsion and dry polyacrylamides as retention and drainage aids.

[0173] As used herein, the term "cationic glyoxalated polyacrylamides (GPAMs)" or "GPAM" generally refers to a polymer obtained by reacting glyoxal and a polyacrylamide base polymer. Methods for producing glyoxalated polyacrylamides are known in the art. (*See* e.g., U.S. Pat. No. 3,556,932 which first disclosed the synthesis of a GPAM composition prepared by reacting glyoxal with a cationic polyacrylamide). In some instances, the polyacrylamide backbone of the GPAM can incorporate a small amount of a cationic monomer, rendering the polymer self-retaining on fibers. In general, GPAM comprises a reactive polymer that can covalently bind with cellulose upon dehydration.

[0174] In some embodiments, cationic glyoxalated polyacrylamides (GPAMs) refers to an aldehyde containing polymer, preferably cationic glyoxalated polyacrylamide ("GPAM") suitable for use as a dry and/or wet strengthening agent, wherein said cationic GPAM comprises: A.) a base polymer comprising a cationic monomer, optionally wherein the cationic monomer comprises DADMAC and/or acryloyloxyethyltrimethyl ammonium chloride ; B.) the base polymer comprises a weight average molecular weight of at least 5,000 Da, preferably at least 80,000 Da, more preferably 100-1000 kDa; C.) the cationic GPAM comprises a glyoxal:base polymer weight ratio of at least about 5:95, optionally from about 10:90; and D.) the GPAM optionally comprises a solids percentage of from about 0.5% to about 20%, optionally from greater than about 2% to about 10%, further optionally from about greater than 4% to about 8%;

[0175] In some embodiments, cationic monomers may be selected from the group consisting of acryloyloxy ethyl trimethylammonium chloride, methacryloyloxyethyltrimethylammonium chloride, methacrylamidopropyltrimethylammonium chloride, acrylamidopropyltrimethylammonium chloride, methacryloyloxyethyldimethylammonium sulfate, dimethylaminoethyl acrylate, dimethylaminopropylmethacrylamide, diallyldimethylammonium chloride (DADMAC); dialkylaminoalkyl acrylates and methacrylates and their quaternary or acid salts, including, but not limited to, dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethyaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate, methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt, dialkylaminoalkylacrylamides or methacrylamides and their quaternary or acid salts such as acrylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate and diallyldialkylammonium halides such as diallyldiethylammonium chloride and diallyldimethyl ammonium chloride. In some embodiments, said one or more cationic monomers may comprise DADMAC. In some embodiments, said one or more cationic monomers may comprise acryloyloxyethyltrimethyl ammonium chloride. In some embodiments, said one or more cationic monomers may comprise DADMAC and/or acryloyloxyethyltrimethyl ammonium chloride. In some embodiments, said one or more cationic monomers may be selected from the group consisting of methacryloyloxyethyltrimethyl ammonium chloride, acryloyloxyethyltrimethyl ammonium chloride, 3- (methacrylamido) propyltrimethyl ammonium chloride, 3-(acryloylamido) propyltrimethyl ammonium chloride, diallyldimethyl ammonium chloride, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, and dimethylaminopropylacrylamide, dimethylaminopropylmethacrylamide.

[0176] In some embodiments, the backbone polymer may comprise one or more primary amide-containing monomers. In some embodiments, the backbone polymer may comprise one or more monomers selected from the group consisting of acrylamide, methacrylamide, ethylacrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, N-ethyl methacrylamide, and any

combination thereof. In some embodiments, the backbone polymer may comprise one or more acrylamide monomers.

[0177] In some embodiments, the backbone polymer may comprise one or more anionic monomers. Preferably the anionic monomers are selected from the group consisting of monomers containing a carboxylic acid functional group, a sulfonic acid functional group, phosphonic acid functional group, their corresponding water soluble or dispersible salts, and any combinations thereof; preferably the anionic monomers are selected from the group consisting of acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methane sulfonic acid, acrylamido ethane sulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding water soluble or dispersible alkali metal, alkaline earth metal, and ammonium salts, and any combinations thereof; more preferably the anionic monomers are selected from acrylic acid, its water soluble or dispersible alkali metal, alkaline earth metal, or ammonium salts, and any combinations thereof.

[0178] As used herein, the term "glyoxylation percentage" refers to the percentage of acrylamide-based monomers which are glyoxalated in a polymer of the cationic GPAM composition, e.g., the first base polymer and/or the second base polymer.

[0179] As used herein, the terms "cationic polyamidoamine-epichlorohydrin (PAE) resins", "PAE resin", or "PAE", generally refer to reactive cationic polymers generally synthesized by reacting one or more polyamidoamine backbones comprising an acid value of between about 35 to about 40 with epichlorohydrin. In some embodiments, the molar ratio of epichlorohydrin: secondary amine groups of the polyamidoamine backbone may be between about 0.15 to about 1.7. In some embodiments, said method may comprise a low-temperature hold time of less than 24 hours under a 30-35°C temperature range at the beginning of the synthesis reaction. In some embodiments, said method may include the addition of a strong acid and a weak acid. In some embodiments, said method may comprise the addition of a weight ratio of weak acid: strong acid of about 0.25 or more, 1.2 or more, 1.6 or more, e.g., wherein said strong acid comprises sulfuric acid and/or said weak acid comprises formic acid. In some embodiments, said method may further comprise sequential addition of formic acid and sulfuric acid. In some embodiments, said method may comprise one or more additions of formic acid and/or one or more additions of sulfuric acid. In some embodiments, said method may result in a stable PAE resin comprising a solids percentage ranging about 10-30%, 20-27% or about 25%. In some embodiments, said method may result in a stable PAE resin comprising final resin pH of about 2.5 to about 3.8. In some embodiments, said stable PAE resin may comprise about 10,500 ppm or more, about 10,500 ppm or less, about 5,000 ppm or less, about 1,000 ppm or less of epichlorohydrin byproducts following synthesis of said stable PAE resin.

[0180] Polyamidoamine epichlorohydrin resins (PAE resins) have been applied in the manufacture of paper for a variety of applications. For example, PAE resins are widely used as strength additives to increase the paper wet strength. PAE resins are also the most common adhesives used in the creping process for producing tissue and towel products. Conventional PAE resins are typically produced in a two-step reaction. In the first step, a polyamidoamine is prepared by condensation of near equimolar amounts of a polyamine and a polycarboxylic acid or polycarboxylic acid derivative. The polyamidoamine that is formed is then reacted with epichlorohydrin in an aqueous solution to produce the PAE resin. The detailed synthesis is well known and is documented in numerous patents, e.g., US Pat. Nos., 2,926,116, and 7,175,740.

[0181] As used herein, the term "water-soluble amphoteric polymers" or "water-soluble amphoteric terpolymers" generally refers to polymers comprised of acrylamide (AM) monomers, one or more anionic monomers, and one or more cationic monomers. Such polymers may be utilized in the inventive retention and drainage aids as amphoteric dry polymers (AmDPAM). Exemplary water-soluble amphoteric dry terpolymers (AmDPAM) are documented in EP3250752B1. Water-soluble amphoteric polymers may also be utilized in the inventive retention and drainage aids as amphoteric emulsion polymers (AmEPAM).

[0182] Exemplary water-soluble amphoteric polymers comprise one or more anionic monomers containing functional groups selected from the group consisting of carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof.

[0183] Exemplary water-soluble amphoteric polymers comprise one or more cationic monomers selected from the group consisting of acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof.

[0184] Preferred embodiments of water-soluble amphoteric polymers are synthesized from three different monomers, i.e., acrylamide (AM) (nonionic), acrylic acid (AA) (anionic at higher pH levels), Q9 (cationic). In exemplary embodiments the inventive emulsion amphoteric polymers: are synthesized by inverse emulsion; comprise an acrylic acid anionic monomer content < 2 wt% and up to 20 wt% Q9, > 78 wt% acrylamide (AM) monomers; in more preferred exemplary embodiments comprise the following composition: AM: AA: Q9- 89:2:9; possess a low SV value (<3.5 cPs) or

preferably from 2.5 to 3.5 cPs; and possess a MW – of at least 1.5 million Daltons to 9 million Daltons, typically from 2 to 5 million Daltons.

[0185] As used herein, the terms "anionic microparticles", "anionic organic or inorganic microparticles", or "anionic additives" generally refers to anionic materials added to papermaking furnish as part of drainage-aid programs. Exemplary anionic organic or inorganic microparticles are selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides. Preferred anionic organic or inorganic microparticles may include silica or colloidal silica. The function of the colloidal silica appears to involve (a) release of water from polyelectrolyte bridges, causing them to contract, and (b) acting as a link in bridges that involve macromolecules adsorbed on different fibers or fine particles. These effects create more streamlined paths for water to flow around the fibers. The tendency of microparticles to boost first-pass retention also will tend to have a positive effect on initial dewatering rates. It has been reported that paper produced by means of a microparticle retention and drainage program has a more open, porous structure, though the effect may become obscured by subsequent wet-pressing and calendering operations.

[0186] TERMS AND UNITS

[0187] As used herein, the term "aqueous solution" or "solution" generally refers to a mixture of water and a water-soluble solute or solutes which are completely dissolved with little to no residual undissolved polymer gel. The solution may be homogenous. When mixed with excess of water, the polymer product is preferably fully dissolved and the obtained polymer solution is preferably free from discrete polymer particles or granules or residual gel.

[0188] As used herein, the term "aqueous suspension", "aqueous slurry", or "slurry" generally refer to a heterogeneous mixture of a fluid that contains insoluble or sparingly soluble solid particles sufficiently large for sedimentation. Suspensions and slurries of the present invention may also comprise some amount of solid particles, often termed colloidal particles, which do not completely settle or take a long time to settle completely.

[0189] As used herein, the term "consistency" generally refers to percent oven dry mass in the stock, slurry, or furnish (i.e., 100% * oven dry mass/total mass).

[0190] The terms, "total solids" or "total suspended solids" are used interchangeably herein and generally refer the total amount or weight of suspended solids contained in oil sands or other sands comprising dispersion. "Total solids" or "total suspended solids" generally does not include dissolved solids.

[0191] As used herein, the term "ppm" refers to parts per million on the basis of milligrams of solute per liter of aqueous solution or slurry (e.g., mg/L).

[0192] As used herein, the terms "lbs/ton" or "#/T" denote pounds of dry mass of added material (e.g., additive, solute, and/or particle) per ton of suspended solids (e.g., weight of AKD per total dry ton of suspended solids).

[0193] As used herein, the terms "kg/T" or "kg/ton" denote kilograms of dry mass (additive, solute, and/or particle) per ton of slurry, stock, and/or furnish.

[0194] As used herein, the phrases "% by wt." denotes pounds of dry mass of additive per dry mass of solids in the formulation, solution, or slurry, multiplied by 100%.

DESCRIPTION OF THE INVENTION

[0195] A recently discovered synergy between a novel amphoteric emulsion polymer and reactive resins such as PAE and GPAM in paper furnish containing high amounts of recycled content shows unexpected performance efficiency for retention and drainage and potentially as a pressing aid. In mills with high recycled content with higher levels of calcium ions and high conductivity, North American paper manufacturers are looking for effective chemistry that will provide on-machine retention and drainage while maintaining strength properties.

[0196] Glyoxalated polyacrylamide (GPAM) products are widely used in the paper industry, often to increase paper wet and dry strength. Additional benefit is to increase the drainage of fiber slurry. GPAM is typically prepared through the reaction between glyoxal and a cationic polyacrylamide base polymer. The original GPAM was reported in US Pat. No. 3556932. The cationic polyacrylamide base polymer has a molecular weight below 25,000 Da and a molar ratio of acrylamide to diallyldimethyl ammonium chloride of 99:1 to 75:1.

[0197] Recent patents have reported several approaches to improve GPAM performance efficiency. US. Patents No. 8222303, No. 8703847, No. 9644320 claim new GPAM products prepared using a cationic polyacrylamide with an average molecule weight ranging from 30 kDa to 5 million Da. The final GPAM product had a GPAM content below 4%.

[0198] Polyamidoamine-epichlorohydrin (PAE) is the predominant chemical to provide wet strength for paper products. It is commonly used for paper towel, labels, and carrier board grade to provide strength while the paper products are wet. US Patents No. 2926154 and 2926116 describe the synthesis of PAE samples.

[0199] More recently an amphoteric polymer was designed to improve the runnability of the paper machine. US patent 10,590,604 B2 claim a new amphoteric polymer with a mass average molecular weight MW of 1 500 000-6 000 000 g/mol, and a total ionicity of 4-15 mol-%, whereby the polymer product has a polymer content of at least 60 wt%. Even more recently an emulsion amphoteric polymer is reported (patent application number: Docket No.: 1149704.048000) to improve drainage and retention of a papermaking system.

[0200] The present invention generally relates to methods and compositions for manufacture of tissue, paper, or board and for enhancing retention and drainage thereof. In particular, the disclosure provides methods for enhancing retention and drainage by addition of a retention and drainage aid comprising reactive cationic polymers (e.g., cationic strength resins), water-soluble amphoteric terpolymers, and optionally anionic organic or inorganic microparticles. Preparation of paper sheets under these conditions provides improved retention, drainage time, STFI and burst strength, and improved hydrophobic particle control.

[0201] In one aspect, the present invention provides a method for manufacture of tissue, paper, or board, the method comprising:

[0202] (a) forming or providing an aqueous suspension comprising cellulosic fibers;

[0203] (b) optionally diluting the aqueous suspension;

[0204] (c) flocculating the aqueous suspension to form a flocculated fiber suspension;

[0205] (d) delivering the flocculated fiber suspension to a headbox and draining on a wire screen to form a wet fibrous web; and

[0206] (e) pressing and drying the wet fibrous web to obtain a tissue, paper, or board;

[0207] wherein the method further comprises prior to step (c) treating the aqueous suspension comprising cellulosic fibers with a retention and drainage aid comprising:

[0208] (i) one or more reactive cationic polymers; and

[0209] (ii) one or more water-soluble amphoteric polymers.

[0210] In some exemplary embodiments of the method said retention and drainage aid optionally further comprises one or more anionic organic or inorganic microparticles.

[0211] In some exemplary embodiments of the method (i) said one or more reactive cationic polymers, (ii) said one or more water-soluble amphoteric polymers, and optionally (iii) said one or more anionic organic or inorganic microparticles:

[0212] (a) are added sequentially in any order, simultaneously, or premixed prior to addition; or

[0213] (b) are added sequentially in the order of (i), (ii), and then optionally (iii), wherein a mixing time is allowed after each addition and said mixing time ranges from 0.01-10 min, 0.1-5 min, or 1-2 min.

[0214] In some exemplary embodiments of the method said one or more reactive cationic polymers comprise:

[0215] (a) functional groups that are reactive to cellulosic or lignocellulosic fiber surfaces; and

[0216] (b) a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

[0217] and further comprise one of the following;

[0218] (c) one or more cationic glyoxalated polyacrylamides (GPAMs);

[0219] (d) one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or

[0220] (e) a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55, wherein said one or more cationic PAE resins and said one or more cationic GPAMs are added sequentially in any order, simultaneously, or premixed prior to addition to said aqueous suspension comprising cellulosic fibers.

[0221] In some exemplary embodiments of the method said one or more cationic GPAMs:

[0222] (a) are suitable for use as a dry and/or wet strengthening agent;

[0223] (b) are synthesized by reacting glyoxal with a base polymer, wherein said base polymer comprises a weight average molecular weight ranging from 5-5000 kDa, 50-2500 kDa, 80-2000 kDa, or 100-1000 kDa and comprises nonionic monomers, cationic monomers, and optional anionic monomers, wherein

[0224] (i) said nonionic monomers are selected from the group of primary amide-containing monomers comprising acrylamide, methacrylamide, ethyl acrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, N-ethyl methacrylamide, and any combination thereof;

[0225] (ii) said cationic monomers are selected from acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and

dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof; and

[0226] (iii) said optional anionic monomers contain functional groups selected from carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof;

[0227] (c) comprise a glyoxal:base polymer weight ratio ranging from 0.1:99.9 to 50:50, 5:95 to 20:80, or 5:95 to 10:90;

[0228] (d) comprise a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

[0229] (e) comprise a percent cationic monomer content ranging from 3-60% by weight, a percent anionic monomer content ranging from 0-50% by weight, wherein the remainder of the monomer content comprises nonionic monomers;

[0230] (f) are formulated optionally as a dry powder or as an aqueous composition comprising a GPAM solids percentage ranging from about 0.5% to about 20%, optionally from greater than about 2% to about 10%, further optionally from about greater than 4% to about 8%.

[0231] In some exemplary embodiments of the method said one or more cationic PAE resins:

[0232] (a) are suitable for use as a wet strengthening agent;

[0233] (b) are synthesized by reacting one or more polyamidoamine backbones with epichlorohydrin, wherein said one or more polyamidoamine backbones are synthesized by reacting a carboxylic acid and/or a carboxylic acid derivative with an amine, wherein said one or more polyamidoamine backbones comprise a molar ratio of the amine to the carboxylic acid and/or carboxylic acid derivative ranging from 1:1 to 2:1, 1.05:1 to 2:1, or 1.5:1 to 2:1;

[0234] (c) comprise a molar ratio of epichlorohydrin to secondary amine groups of the polyamidoamine backbone ranging from about 0.15 to about 1.7.

[0235] In some exemplary embodiments of the method said one or more water-soluble amphoteric polymers:

[0236] (a) are comprised of acrylamide (AM) monomers, one or more anionic monomers, and one or more cationic monomers, wherein,

[0237] (i) said one or more anionic monomers contain functional groups selected from the group consisting of carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof; and

[0238] (ii) said one or more cationic monomers are selected from the group consisting of acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof;

[0239] (b) comprise an inverse phase emulsion, a dry polymer, or an aqueous polymer solution, preferably an inverse phase emulsion;

[0240] (c) comprise a polymer standard viscosity (SV) ranging from <3.5 cPs, 1-3.5 cPs, 2-3.5 cPs, or 2.5-3.5 cPs;

[0241] (d) comprise a molecular weight ranging from 1.5-9 million Daltons, 1.5-8 million Daltons, 2-8 million Daltons, 4-8 million Daltons, or preferably 2-5 million Daltons;

[0242] (e) comprise an acrylamide (AM) monomer content ranging from 77-100 wt%, 78-100 wt%, 80-100 wt%, 90-100 wt%, or 95-100 wt%;

[0243] (f) comprise an anionic monomer content ranging from ⩽3 wt%, ⩽2 wt%, 0.01-3 wt%, 0.5-2 wt%, 1-2 wt%, 1.5-2 wt%, or 1.8-2 wt%;

[0244] (g) comprise a cationic monomer content ranging from ⩽20 wt%, 1-20 wt%, 2-16 wt%, 4-12 wt%, or 7-9 wt%; or

[0245] (h) any combination of the foregoing.

[0246] In some exemplary embodiments of the method said one or more anionic organic or inorganic microparticles are selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides.

[0247] In some exemplary embodiments of the method:

[0248] (a) said one or more reactive cationic polymers comprises said one or more cationic GPAMs and/or said one or more cationic PAE resins in aqueous form;

[0249] (b) said one or more cationic GPAMs comprise said base polymer comprising cationic monomers selected from DADMAC, AETAC, and combinations thereof; nonionic monomers selected from acrylamide, methacrylamide, and combinations thereof; and optionally anionic monomers selected from acrylic acid and/or corresponding water soluble salts, water dispersible alkali metal salts, alkaline earth metal salts, ammonium salts, and combinations thereof, or said base polymer comprises (i) acrylamide and DADMAC, (ii) acrylamide and AETAC, or (iii) acrylamide, DADMAC, and AETAC,

[0250] (c) said one or more water-soluble amphoteric polymers

[0251] (i) comprises an inverse emulsion of acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers;

[0252] (ii) preferably comprises an acrylic acid (AA) monomer content of no more than 2 wt %; and

[0253] (iii) preferably comprises a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7; and

[0254] (d) said one or more anionic organic or inorganic microparticles comprise colloidal silica.

[0255] In some exemplary embodiments of the method, when added to said aqueous suspension comprising cellulosic fibers:

[0256] (a) said one or more reactive cationic polymers are added at a dosage ranging from 0.1-15 g/kg, 0.5-5 g/kg, or 0.5-4 g/kg;

[0257] (b) said one or more water-soluble amphoteric polymers are added at a dosage ranging from 0.05-5 g/kg, 0.1-4 g/kg, or 0.3-1 g/kg;

[0258] (c) said one or more anionic organic or inorganic microparticles are added at a dosage ranging from 0.1-1 g/kg, 0.2-0.8 g/kg, or 0.4-0.6 g/kg.

[0259] In some exemplary embodiments of the method, said aqueous suspension comprising cellulosic fibers comprises a pH ranging from 4-8, 4-7.5, 4-7, 4.5-7, or 5-7 and further comprises:

[0260] (a) cellulosic fibers optionally obtained from sources selected from softwood fiber, hardwood fiber, recycled fiber, recycled old corrugated cardboard (OCC), recycled mixed office waste (MOW), recycled mixed office paper, refined fiber, mill broke fibers, coated broke, non-wood fibers, including but not limited to straw and wheat pulp, and a mixture of any of the foregoing;

[0261] (b) pulp selected from Kraft pulp, unbleached Kraft pulp, bleached pulp, unbleached pulp, process water from pulp, paper, and/or board production, neutral sulfite semi chemical (NSSC) pulp, mechanical pulp, non-wood pulp, and a mixture of any of the foregoing; or

[0262] (c) a stock selected from a thick stock, a thick stock diluted with chemical water, synthetic water, white water, and/or process water, and a thin stock, and a mixture of any of the foregoing.

[0263] In some exemplary embodiments of the method, when used for manufacture of tissue, paper, or board, the method results in:

[0264] (a) improved retention of said cellulosic fibers; a

[0265] (b) improved drainage of said flocculated fiber suspension;

[0266] (c) improved STFI and/or burst strength;

[0267] (d) a reduced hydrophobic particle and/or hydrophobic agglomerate count;

[0268] (e) an improved dry tensile, immediate wet tensile, and/or soaked wet tensile strength; or

[0269] (f) any combination of (a)-(e)

[0270] compared to a tissue, paper, or board prepared by an identical method in the absence of (i) addition of said one or more reactive cationic polymers or (ii) addition of said one or more water-soluble amphoteric polymers.

[0271] In another aspect, the present invention provides a method for manufacture of tissue, paper, or board, the method comprising:

[0272] (a) forming or providing an aqueous suspension comprising cellulosic fibers;

[0273] (b) optionally diluting the aqueous suspension;

[0274] (c) flocculating the aqueous suspension to form a flocculated fiber suspension;

[0275] (d) delivering the flocculated fiber suspension to a headbox and draining on a wire screen to form a wet fibrous web; and

[0276] (e) pressing and drying the wet fibrous web to obtain a tissue, paper, or board;

[0277] wherein the method further comprises prior to step (c) treating the aqueous suspension comprising cellulosic fibers with a retention and drainage aid comprising:

[0278] (i) one or more reactive cationic polymers comprising functional groups that are reactive to cellulosic or lignocellulosic fiber surfaces and a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7, wherein said one or more reactive cationic polymers comprise one or more cationic glyoxalated polyacrylamides (GPAMs); one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55, wherein said one or more cationic PAE resins and said one or more cationic GPAMs are added sequentially in any order, simultaneously, or premixed prior to addition to said aqueous suspension comprising cellulosic fibers;

[0279] (ii) one or more water-soluble amphoteric polymers comprising an inverse emulsion of acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers; preferably comprising an acrylic acid (AA) monomer content of no more than 2 wt %; and preferably comprising a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7; and

[0280] (iii) optionally one or more anionic organic or inorganic microparticles comprising silica.

[0281] In another aspect, the present invention provides a fiber stock composition comprising:

[0282] (a) an aqueous suspension comprising cellulosic fibers; and

[0283] (b) a retention and drainage aid comprising

[0284] (i) one or more reactive cationic polymers;

[0285] (ii) one or more water-soluble amphoteric polymers; and

[0286] (iii) optionally one or more anionic organic or inorganic microparticles;

[0287] obtainable by a method according to any of the foregoing claims.

[0288] In another aspect, the present invention provides a composition for use as a retention and drainage aid in manufacture of tissue, paper, or board, the composition comprising:

[0289] (a) one or more reactive cationic polymers comprising a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7, wherein said one or more reactive cationic polymers comprise

[0290] (i) one or more cationic glyoxalated polyacrylamides (GPAMs) synthesized by reacting glyoxal with a base polymer, wherein said base polymer comprises a weight average molecular weight ranging from 5-5000 kDa, 50-2500 kDa, 80-2000 kDa, or 100-1000 kDa; (i) acrylamide and DADMAC, (ii) acrylamide and AETAC, or (iii) acrylamide, DADMAC, and AETAC and further wherein said one or more GPAMs comprises a glyoxal:base polymer weight ratio ranging from 0.1:99.0 to 50:50, 5:95 to 20:80, or 5:95 to 10:90; and a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

[0291] (ii) one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or

[0292] (iii) a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55;

[0293] (b) one or more water-soluble amphoteric polymers comprising acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers; wherein said one or more water-soluble amphoteric emulsion polymers preferably comprise an acrylic acid (AA) monomer content of no more than 2 wt % and a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7, wherein said one or more water-soluble amphoteric polymers is a an inverse emulsion, a dry polymer, an aqueous solution, preferably an inverse phase emulsion; and

[0294] (c) optionally one or more anionic organic or inorganic microparticles selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides.

[0295] The methods and compositions illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein and/or any element specifically

disclosed herein. Exemplary embodiments of the invention and its advantages are further disclosed in the following examples.

EXAMPLES

[0296] The examples provided herein are for illustrative purposes so that the invention may be more fully understood. These examples should not be construed as limiting the invention in any way.

[0297] EXPERIMENTAL PROCEDURES

[0298] Determination of drainage time by DDA Screening

[0299] Cellulosic fibrous webs were prepared and drainage times were analyzed by dynamic drainage analyzer (DDA) testing according to the following. An aliquot of cellulosic stock (500 mL) with a consistency of 0.4 to 0.7% by wt (Total Suspended solids, TSS) was mixed with chemical additives for 45 seconds while agitating. After mixing, the flocculated stock was drained through a 60 mesh screen under vacuum (250 mBar). Drainage time was determined by measuring the time needed to show a vacuum break (i.e., a rapid increase in vacuum pressure). The fiber mat left on the DDA screen and the filtrate were used for additional testing.

[0300] Determination of filtrate turbidity

[0301] Turbidity testing was performed on the filtrates from DDA screening as an indication of retention. Turbidity of treated filtrates was performed using a Hach 2100Q turbidimeter. The Model 2100Q Portable Turbidimeter operates on the nephelometric principle of turbidity measurement. The optical system includes a tungsten-filament lamp, a 90° detector to monitor scattered light and a transmitted light detector. The instrument's microprocessor calculates the ratio of the signals from the 90° and transmitted light detectors, which corrects for interferences from color and/or light-absorbing materials. The instrument range is 0 to 1000 NTU. A lower turbidity level generally trends with an increase in retention of filler, fines, and/or contaminants in the furnish in the fiber mat.

Example 1: Evaluation of amphoteric emulsion polymers with reactive strength resins and silica as retention and drainage aids in recycled OCC furnish

[0302] Amphoteric emulsion terpolymers with reactive strength resins were evaluated with and without silica as retention and drainage aids for 100% recycled old corrugated cardboard (OCC) stock. Retention and drainage aid additives are shown in **Table 1**.

[0303] A NA Tissue machine was used for formation of recycled towels using the recycled OCC cellulosic fiber stock. The pH of the stock was about 7.3 and the conductivity of the white water was 1.4 mS/cm. The total white water hardness was 140 ppm as $CaCO_3$ and alkalinity was 360 ppm as $CaCO_3$. The consistency was 0.60%, measured as total suspended solids (TSS).

[0304] **Table 1**: Chemical and polymeric additives tested as retention and drainage aids in **Examples 1-7**.

ID	Additive	SV, cPs	Monomer Composition, mol%
GPAM	Glyoxalated PAM strength resin	-	-
PAE	Polyamidoamine-epichlorohydrin strength resin	-	-

Amphoteric Polymer A	Amphoteric Emulsion PAM (AmEPAM A)	3.0-3.4	7% Q9, 2%AA, 91% AMD
Amphoteric Polymer B	Amphoteric Emulsion PAM (AmEPAM B)	3.0-3.4	9% Q9, 2% AA, 89% AMD
AmEPAM	Amphoteric Emulsion PAM	3.0-3.4	7-12% Q9, 2.1-2.26% AA
AmDPAM	Amphoteric Dry PAM	3.2	7% Q9, 2% AA
Polyamine	Medium MW structured polyamine	-	45% AA
CPAM1	High MW Cationic PAM	4.8-5.6	10% Q9
CPAM2	Low MW Cationic PAM	3.3	20% Q9
ANMicro	Anionic Micropolymer	-	45% AA
Silica	Colloidal Silica	-	-

[0305] *AA-Acrylic Acid; Q9-Acryloyloxyethyltrimethyl Ammonium Chloride; AMD-Acrylamide; PAM-Polyacrylamide

[0306] Preparation of sheets and determination of drainage time by DDA screening

[0307] Sheets (i.e., cellulosic fibrous mats) were prepared and drainage times were analyzed by dynamic drainage analyzer (DDA) testing according to the following. An aliquot of cellulosic stock (500 mL) was combined with reactive strength resin (GPAM or PAE, 3 kg/T, where T = metric ton) and mixed for up to 2 minutes, followed by addition of polymeric additive (AmEPAM A, AmEPAM B, or ANMicro). Where indicated, silica was added last.

[0308] After agitating for 45 seconds, the flocculated stock was drained through a 60 mesh screen under vacuum (250 mBar) to form a fiber mat. Drainage time was determined by measuring the time needed to show a vacuum break (i.e., a rapid increase in vacuum pressure). Filtrates were collected and used for determination of filtrate turbidity as a measure of fiber retention.

[0309] Determination of filtrate turbidity

[0310] Turbidity testing was performed on the filtrates from DDA screening as an indication of retention of cellulosic fiber material from the fiber stock in the fiber mat. Turbidity of treated filtrates was performed using a Hach 2100Q turbidimeter. The Model 2100Q Portable Turbidimeter operates on the nephelometric principle of turbidity measurement. The optical system includes a tungsten-filament lamp, a 90° detector to monitor scattered light and a transmitted light detector. The instrument's microprocessor calculates the ratio of the signals from the 90° and transmitted light detectors, which corrects for interferences from color and/or light-absorbing materials. The instrument range is 0 to 1000 NTU. A lower turbidity level generally trends with an increase in retention of filler, fines, and/or contaminants in the furnish in the fiber mat.

[0311] Additives, dosages, and retention and drainage results are shown in **FIGS 1-4**.

[0312] The results indicate that the inventive retention and drainage aids (e.g., reactive strength resin with amphoteric emulsion terpolymer) significantly improve the drainage and retention (i.e., shorter drainage time and lower turbidity) of sheets prepared from a 100% recycled furnish over GPAM or PAE alone. The inventive retention and drainage aids improve both drainage and turbidity in a dose dependent manner as the AmEPAM polymer dosage increased.

[0313] Addition of silica alone to a cellulosic fiber suspension is known to have no effect or detrimental effects on both retention and drainage in the absence of PAE, GPAM and/or AmEPAM. Addition of silica to the inventive retention and drainage aids provided a synergistic improvement in both retention and drainage, with the shortest drainage times and lowest turbidities observed in the presence of 0.5 kg/T silica.

[0314] These results provide proof of concept that the inventive retention and drainage aids (e.g., reactive strength resin + amphoteric polymer) provide synergistic enhancements in retention and drainage over reactive strength resin alone. The optional addition of silica adds additional synergistic benefit.

Example 2: Evaluation of AmEPAM and AmDPAM with reactive strength resins and silica as retention and drainage aids in recycled MOW furnish

[0315] Amphoteric emulsion terpolymers and amphoteric dry polymers were evaluated with reactive strength resin (PAE), with and without silica or ANMicro, as retention and drainage aids for recycled mixed office waste (MOW) furnish. The inventive retention and drainage aids were evaluated against chemical additives (polyamines and CPAMs) that are known for their performance on wet pulp pressability. Retention and drainage aid additives are shown in **Table 1**.

[0316] A NA Tissue machine was used for formation of recycled white towels using the recycled MOW cellulosic fiber stock. The pH of headbox furnish was 6.28 and the conductivity measurement of the white water was 1.5 mS/cm. The total hardness of white water was 600 ppm as $CaCO_3$ and alkalinity was 360 ppm as $CaCO_3$. The consistency was 0.63%, measured as total suspended solids (TSS).

[0317] Towel fiber mats were prepared and evaluated for drainage time by DDA screening and the resulting filtrates were evaluated for turbidity according to **Example 1**. An aliquot of cellulosic stock (500 mL) was combined with reactive strength resin (PAE) or control resin (CPAM2) and mixed for up to 2 minutes, followed by addition of amphoteric polymeric additive (AmEPAM or AmDPAM) or control polymer (CPAM1 or Polyamine). Where indicated, anionic additive (silica or ANMicro) was added last. Additionally, the hydrophobic particle (HP) count and HP agglomerate count were determined.

[0318] Conditions, dosages, and results are summarized in **Table 2**.

[0319] **Table 2**: Additives and results for recycled towels

Polymer Additive	Polymer Dosage, kg/T	Resin Additive	Resin Dosage, kg/T	Anionic Additive	Anionic Dosage, kg/T	Drain Time (Sec)	Filtrate Turbidity (NTU)	HP Count Reduction	HP Agglomerate Count Reduction
Blank	-	-	-	-	-	31.82	180	-	-
Polyamine	1	none	0	ANMicro	0.5	24.3	67.8	42.7%	43.0%
AmDPAM	0.33	none	0	ANMicro	0.5	30.92	78.5	45.0%	4.0%
AmEPAM	1	none	0	ANMicro	0.5	31.11	62.8	41.8%	25.0%
Polyamine	1	none	0	Silica	0.5	28.39	77	42.2%	53.0%
AmDPAM	0.33	none	0	Silica	0.5	23.63	71.1	41.0%	44.0%

CPAM1	1	none	0	Silica	0.5	24.58	71.3	44.1%	58.0%
AmEPAM	1	none	0	Silica	0.5	19.78	71.4	35.1%	50.0%
AmDPAM	0.33	PAE	1	ANMicro	0.5	19.03	62.4	50.5%	50.0%
AmDPAM	0.33	PAE	1	Silica	0.5	19.22	65.4	46.8%	74.0%
AmEPAM	1	PAE	1	ANMicro	0.5	23.24	65.3	63.3%	43.0%
AmEPAM	1	PAE	1	Silica	0.5	17.53	49	48.0%	77.0%
AmDPAM	0.33	CPAM2	0.5	Silica	0.5	9.8	58.4	35.5%	63.0%
AmEPAM	1	CPAM2	10.5	Silica	0.5	7.66	56.1	36.4%	72.8%

[0320] These results indicate that the inventive retention and drainage aids (e.g., amphoteric polymer + PAE) significantly improve the drainage and retention (i.e., shorter drainage time and lower turbidity) of a recycled MOW furnish over commonly used additives (CPAM1 or polyamine) and an anionic additive. Optional addition of an anionic additive (e.g., silica or ANMicro) provides additional benefits to drainage and retention.

[0321] Results also indicate that both amphoteric emulsion polymers (AmEPAM) and amphoteric dry polymers (AmDPAM) significantly improve the drainage and retention when used with PAE or a cationic polyacrylamide (CPAM2) and an anionic additive.

[0322] These results provide further proof of concept that the inventive retention and drainage aids (e.g., amphoteric polymer + PAE + anionic additive) provide synergistic enhancements in retention and drainage over polymeric additive + anionic additive.

Example 3: Evaluation of AmEPAM vs. CPAM with GPAM as retention and drainage aids in packaging grade furnish

[0323] Amphoteric emulsion terpolymers (AmEPAM) + GPAM were evaluated against a cationic polyacrylamide (CPAM) + GPAM as retention and drainage aid along with common additives (e.g., rosin and alum) in a commercial packaging grade furnish at different conductivity levels.

[0324] NA Packaging Liner sheets were prepared and evaluated for drainage time by DDA screening and the resulting filtrates were evaluated for turbidity according to **Example 1**.

[0325] Liner sheets were prepared using furnish comprised of 69% unbleached kraft and 31% recycled OCC. Thick stock was collected from the machine chest prior to the introduction of any papermaking additives. Tray water was collected and was used to dilute the thick stock to headbox consistency (0.6%), measured as total suspended solids (TSS). The resulting thin stock furnish had the following characteristics: pH 6.02, conductivity 3.84 µS/cm, alkalinity 320 mg/L as $CaCO_3$ and total hardness 800 mg/L as $CaCO_3$. A portion of the stock was also treated with a 10% $CaCl_2$ solution and a 10% Na_2SO_4 solution to increase the conductivity of the system. Total conductivity was measured at three distinct levels: 3.84 mS/cm, 5.09 mS/cm and 8.01 mS/cm.

[0326] A commercial chemical additive sequence and dosage was followed, with the polymer being the independent variable. The sequence was comprised of 1.5 kg/ton GPAM, 0.1 kg/ton rosin, 5 kg/ton alum, and polymer, where the polymer was either a cationic polyacrylamide (CPAM) or the inventive amphoteric polyacrylamide (AmEPAM) at dosages ranging from 0.1-0.3 kg/T.

[0327] Conditions, dosages, and drainage time results for two conductivity levels are shown in **FIGS 5-6**. Conditions, dosages, and filtrate turbidity results for three conductivity levels are shown in **FIG 7**.

[0328] Results from **FIG 5** indicate that packaging grade furnish at conductivity 3.84 mS/cm, when treated with AmEPAM provides significantly better drainage time than the CPAM. Results from **FIG 6** indicate that AmEPAM continues to outperform the CPAM as a drainage aid for packaging grade furnish at conductivity 5.09 mS/cm. Results from **FIG 7** indicate that AmEPAM outperforms CPAM in filtrate turbidity test results across all three conductivity levels at all dosages.

[0329] These results provide proof of concept that the inventive retention and drainage aid system (AmEPAM + GPAM) outperforms a conventional combination (CPAM + GPAM) in packaging grade furnish with rosin and alum across several conductivity levels and polymer dosages.

Example 4: Evaluation of strength of packaging liner sheets made with AmEPAM vs. AmDPAM with GPAM

[0330] NA packaging liner sheets were prepared using amphoteric emulsion terpolymers (AmEPAM) or amphoteric dry polymers (AmDPAM) across several GPAM dosages (1.5-4.5 kg/T) according to **Example 3**. The resulting sheets were evaluated using a standard strength test, e.g., Short Span Compressive Test (STFI). Geometric mean STFI results are shown in **FIG 8**.

[0331] These results indicate that, when used with GPAM, both AmEPAM and AmDPAM provide a strength benefit over GPAM alone. These results also indicate that, when used with GPAM, the amphoteric emulsion polymers (AmEPAM) provide a strength benefit over amphoteric dry polymer (AmDPAM).

Example 5: Evaluation of strength of handsheets made with AmEPAM vs. CPAM with GPAM and silica as retention and drainage aids in recycled OCC furnish

[0332] NA Handsheets were prepared using retention and drainage aids consisting of amphoteric emulsion terpolymers (AmEPAM) + GPAM + silica or cationic polyacrylamide (CPAM) + GPAM + silica according to **Example 1**.

[0333] This example used 100% recycled OCC. Thick stock was collected from the machine chest prior to the introduction of any papermaking additives. Tray water was collected and was used to dilute the thick stock to headbox consistency (0.6%), measured as total suspended solids (TSS). The resulting thin stock furnish had the following characteristics: pH 6.3, conductivity 2.9 mS/cm, alkalinity 300 mg/L as $CaCO_3$ and total hardness 900 mg/L as $CaCO_3$.

[0334] GPAM was added at 4 kg/ton. AmEPAM or CPAM was added at 0.125 kg/ton as active polymer. Silica was added at 0.125 kg/ton. NA Handsheets were prepared and tested for strength using standard STFI and burst strength tests. STFI and burst strength results are shown in **FIG 9**.

[0335] These results indicate that, when used with GPAM and silica, the amphoteric emulsion polymers (AmEPAM) provide a strength benefit over CPAM. Without being bound to theory, it can be rationalized that the amphoteric polymer allows for better retention of GPAM treated fines than CPAM when used with silica. This results in better strength properties of paper.

[0336] These results provide further proof of concept that the inventive retention and drainage aid system (AmEPAM + GPAM) outperforms a conventional combination (CPAM + GPAM).

Example 6: Evaluation of amphoteric emulsion polymers with reactive strength resins and silica as retention and drainage aids in recycled towel grade OCC furnish

[0337] Amphoteric emulsion terpolymers (Amphoteric EPAM) were evaluated against other commonly used polymers (ANMicro or CPAM), along with reactive strength resin (PAE or GPAM), with and without silica, as retention and drainage aids for 100% recycled towel grade OCC stock. Retention and drainage aid additives are shown in **Table 1**. The backbone MW for GPAM A is 10-50 kDa, and backbone MW for GPAM B is 100-200 kDa.

[0338] This example used 100% OCC for brown towel grade. Thick stock was collected from the machine chest prior to the introduction of any papermaking additives. Tray water was collected and was used to dilute the thick stock to headbox consistency (0.5% TSS). The resulting thin stock furnish had the following characteristics: pH 6.45, conductivity 1.9 mS/cm, total hardness 600 mg/L as $CaCO_3$.

[0339] Towel fiber mats were prepared and evaluated for drainage time by DDA screening and the resulting filtrates were evaluated for turbidity according to **Example 1**. Conditions, dosages, and results shown in **FIGS 10-11**.

[0340] These results indicate that, the combination of GPAM A or B with amphoteric PAM, with or without silica, showed better drainage and retention than the combination of GPAM with anionic polymer (ANMicro) or cationic polymer (CPAM) with or without silica. The combination of GPAM B with amphoteric PAM with silica showed the best retention and drainage.

[0341] These results provide further proof of concept that the inventive retention and drainage aids consisting of reactive strength resin (GPAM or PAE) + amphoteric PAM provide synergistic enhancements in retention and drainage over polymer (e.g., amphoteric PAM or ANMicro) alone and over reactive strength resin (GPAM or PAE) alone. The optional addition of silica provides additional synergistic enhancement to the retention and drainage aids.

[0342] Without being bound to theory, it can be rationalized that the observed synergism may result from a mechanism wherein (i) reactive strength resins (GPAM, PAE), which are cationic and highly reactive, efficiently bind to anionic cellulosic fiber and fines that would otherwise be lost, thereby providing better retention because; (ii) the simultaneous presence of the amphoteric PAM, which is a terpolymer containing anionic and cationic monomers (*see* **Table 1**), causes flocculation to occur and allows for the reactive strength resin to react with the anionic monomers of the amphoteric terpolymer, thereby forming large and stable flocs comprising fiber, fines, amphoteric PAM, and strength resin, and causing a synergistic increase in retention and drainage; and (iii) the optional addition of silica causes the flocs to shrink by collapsing bonds between strength resin and polymer and extruding water, thereby forming a higher density floc structure which allows for additional synergistic increase in retention, faster drainage, and likely better wet pressability.

[0343] Taken together, the results of **Examples 1-6** indicate that synergistic increase in retention and drainage has potential to greatly improve retention, drainage, and hydrophobic particle/agglomerate incorporation into sheet formation from recycled fibers. These result also prove that optional addition of silica provides additional drainage and retention benefits.

Example 7: Evaluation of amphoteric emulsion polymers with reactive strength resins (PAE and DPAM) and silica as retention and drainage aids in recycled mixed office paper furnish

[0344] Amphoteric emulsion terpolymers (Amphoteric PAM) were evaluated with a combination of reactive strength resins (PAE and GPAM), with and without silica, as retention and drainage aids for 100% recycled mixed office paper stock.

[0345] In this example, 100% recycled mixed office paper was used to make recycled white towel. The thick stock was diluted with white water to consistency of 0.83%. Towel fiber mats were prepared and evaluated for drainage time by DDA screening and the resulting filtrates were evaluated for turbidity according to **Example 1**. Conditions, dosages, and results are shown in **Table 3**.

[0346] **Table 3**: Additives, dosage, and results for recycled towels

Additive Program	**Drain Time, sec**	**Turbidity, NTU**
Blank	25.66	-
1.5 kg/ton PAE	27.19	88.8
2.5 kg/ton PAE	23.96	90.1
2.5 kgt/ton PAE + 0.25 kg/ton Silica	22.86	60.8
2.5 kg/ton PAE + 0.5kg/ton Silica	22.23	55.0
1.5 kg/ton PAE + 1.0 kg/ton GPAM A + 0.25 kg/ton Silica	24.54	63.3
1.5 kg/ton PAE + 1.0 kg/ton GPAM A + 0.5 kg/ton Silica	22.69	57.1
0.5 kg/ton AmEPAM	20.02	74.8
1 kg/ton AmEPAM	19.51	65.5
1 kg/ton AmEPAM + 1.5 kg/ton PAE + 1.0.0 kg/ton GPAM A + 0.25 kg/ton Silica	13.94	52.2
1 kg/ton AmEPAM + 1.5 kg/ton PAE + 1.0 kg/ton GPAM A + 0.25 kg/ton Silica	9.57	49.1

[0347] These results indicate synergy between amphoteric polyacrylamide with a combination of both PAE and GPAM with silica. The best results were achieved by addition of both GPAM and PAE. These results provide proof of concept that GPAM and PAE may be added together to the inventive retention and drainage aids to enhance drain time and turbidity.

CLAIMS

What is claimed is:

1. A method for manufacture of tissue, paper, or board, the method comprising:

   (a) forming or providing an aqueous suspension comprising cellulosic fibers;

   (b) optionally diluting the aqueous suspension;

   (c) flocculating the aqueous suspension to form a flocculated fiber suspension;

   (d) removing sufficient water from the flocculated fiber suspension to form a wet fibrous web, preferably by introducing the flocculated fiber suspension into a headbox and draining the flocculated fiber suspension on a wire screen; and

   (e) pressing and drying the wet fibrous web to obtain a tissue, paper, or board;

   wherein the method further comprises prior to step (c) treating the aqueous suspension comprising cellulosic fibers with a retention and drainage aid comprising:

   (i) one or more reactive cationic polymers; and

   (ii) one or more water-soluble amphoteric polymers.

2. The method of **claim 1**, said retention and drainage aid optionally further comprises one or more anionic organic or inorganic microparticles.

3. The method of **claim 1 or 2**, wherein (i) said one or more reactive cationic polymers, (ii) said one or more water-soluble amphoteric polymers, and optionally (iii) said one or more anionic organic or inorganic microparticles:

   (a) are added sequentially in any order, simultaneously, or premixed prior to addition; or

   (b) are added sequentially in the order of (i), (ii), and then optionally (iii), wherein a mixing time is allowed after each addition and said mixing time ranges from 0.01-10 min, 0.1-5 min, or 1-2 min.

4. The method of **any of the foregoing claims**, wherein said one or more reactive cationic polymers comprise:

   (a) functional groups that are reactive to cellulosic or lignocellulosic fiber surfaces; and

   (b) a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

   and further comprise one of the following;

   (c) one or more cationic glyoxalated polyacrylamides (GPAMs);

   (d) one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or

   (e) a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55, wherein said one or more cationic PAE resins and said one or more cationic GPAMs are added sequentially in any order, simultaneously, or premixed prior to addition to said aqueous suspension comprising cellulosic fibers.

5. The method of **claim 4**, wherein said one or more cationic GPAMs:

(a) are suitable for use as a dry and/or wet strengthening agent;

(b) are synthesized by reacting glyoxal with a base polymer, wherein said base polymer comprises a weight average molecular weight ranging from 5-5000 kDa, 50-2500 kDa, 80-2000 kDa, or 100-1000 kDa and comprises nonionic monomers, cationic monomers, and optional anionic monomers, wherein

(i) said nonionic monomers are selected from the group of primary amide-containing monomers comprising acrylamide, methacrylamide, ethyl acrylamide, crotonamide, N-methyl acrylamide, N-butyl acrylamide, N-ethyl methacrylamide, and any combination thereof;

(ii) said cationic monomers are selected from acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof; and

(iii) said optional anionic monomers contain functional groups selected from carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl

phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof;

(c) comprise a glyoxal:base polymer weight ratio ranging from 0.1:99.9 to 50:50, 5:95 to 20:80, or 5:95 to 10:90;

(d) comprise a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

(e) comprise a percent cationic monomer content ranging from 3-60% by weight, a percent anionic monomer content ranging from 0-50% by weight, wherein the remainder of the monomer content comprises nonionic monomers;

(f) are formulated optionally as a dry powder or as an aqueous composition comprising a GPAM solids percentage ranging from about 0.5% to about 20%, optionally from greater than about 2% to about 10%, further optionally from about greater than 4% to about 8%.

6. The method of **claim 4**, wherein said one or more cationic PAE resins:

(a) are suitable for use as a wet strengthening agent;

(b) are synthesized by reacting one or more polyamidoamine backbones with epichlorohydrin, wherein said one or more polyamidoamine backbones are synthesized by reacting a carboxylic acid and/or a carboxylic acid derivative with an amine, wherein said one or more polyamidoamine backbones comprise a molar ratio of the amine to the carboxylic acid and/or carboxylic acid derivative ranging from 1:1 to 2:1, 1.05:1 to 2:1, or 1.5:1 to 2:1;

(c) comprise a molar ratio of epichlorohydrin to secondary amine groups of the polyamidoamine backbone ranging from about 0.15 to about 1.7.

7. The method of **any of the foregoing claims**, wherein said one or more water-soluble amphoteric polymers:

(a) are comprised of acrylamide (AM) monomers, one or more anionic monomers, and one or more cationic monomers, wherein,

(i) said one or more anionic monomers contain functional groups selected from the group consisting of carboxylic acids, sulfonic acids, phosphonic acids, their corresponding water soluble salts, their corresponding water dispersible salts, and any combination thereof, including but not limited to, acrylic acid, methacrylic acid, maleic acid, itaconic acid, vinyl sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS), acrylamido methanesulfonic acid, acrylamido ethanesulfonic acid, 2-hydroxy-3-acrylamide propane sulfonic acid, styrene sulfonic acid, vinyl benzene sulfonic acid, and vinyl phosphonic acid, their corresponding alkali metal, alkaline earth metal, and ammonium salts, and any combination thereof; and

(ii) said one or more cationic monomers are selected from the group consisting of acryloyloxyethyltrimethyl ammonium chloride ("AETAC"), methacryloyloxyethyltrimethylammonium chloride ("MAETAC"), methacrylamidopropyltrimethylammonium chloride ("MAPTAC"), acrylamidopropyltrimethylammonium chloride ("APTAC"), methacryloyloxyethyldimethylammonium sulfate, diallyldimethylammonium

chloride ("DADMAC"); dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates and their quaternary or acid salts, including but not limited to, dimethylaminoethyl acrylate ("DMAEA"), dimethylaminoethyl methacrylate ("DMAEA"), dimethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl acrylate methyl sulfate quaternary salt, dimethylaminoethyl acrylate benzyl chloride quaternary salt, dimethylaminoethyl acrylate sulfuric acid salt, dimethylaminoethyl acrylate hydrochloric acid salt, diethylaminoethyl acrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl chloride quaternary salt, dimethylaminoethyl methacrylate methyl sulfate quaternary salt, dimethylaminoethyl methacrylate benzyl chloride quaternary salt, dimethylaminoethyl methacrylate sulfuric acid salt, dimethylaminoethyl methacrylate hydrochloric acid salt, dimethylaminoethyl methacryloyl hydrochloric acid salt; dialkylaminoalkylacrylamides and methacrylamides and their quaternary or acid salts, including but not limited to, acryloylamidopropyltrimethylammonium chloride, dimethylaminopropyl acrylamide, dimethylaminopropyl acrylamide methyl sulfate quaternary salt, dimethylaminopropyl acrylamide sulfuric acid salt, dimethylaminopropyl acrylamide hydrochloric acid salt, methacrylamidopropyltrimethylammonium chloride, dimethylaminopropyl methacrylamide, dimethylaminopropyl methacrylamide methyl sulfate quaternary salt, dimethylaminopropyl methacrylamide sulfuric acid salt, dimethylaminopropyl methacrylamide hydrochloric acid salt, diethylaminoethylacrylate, diethylaminoethylmethacrylate; and diallyldialkylammonium halides, including but not limited to, diallyldiethylammonium chloride and diallyldimethylammonium chloride ("DADMAC"), and any combination thereof;

(b) comprise an inverse phase emulsion, a dry polymer, or an aqueous polymer solution, preferably an inverse phase emulsion;

(c) comprise a polymer standard viscosity (SV) ranging from ≤3.5 cPs, 1-3.5 cPs, 2-3.5 cPs, or 2.5-3.5 cPs;

(d) comprise a molecular weight ranging from 1.5-9 million Daltons, 1.5-8 million Daltons, 2-8 million Daltons, 4-8 million Daltons, or preferably 2-5 million Daltons;

(e) comprises an acrylamide (AM) monomer content ranging from 77-100 wt%, 78-100 wt%, 80-100 wt%, 90-100 wt%, or 95-100 wt%;

(f) comprise an anionic monomer content ranging from ≤3 wt%, ≤2 wt%, 0.01-3 wt%, 0.5-2 wt%, 1-2 wt%, 1.5-2 wt%, or 1.8-2 wt%;

(g) comprise a cationic monomer content ranging from ≤20 wt%, 1-20 wt%, 2-16 wt%, 4-12 wt%, or 7-9 wt%; or

(h) any combination of the foregoing.

8. The method of **any of claims 2-7**, wherein said one or more anionic organic or inorganic microparticles are selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides.

9. The method of **any of the foregoing claims**, wherein

(a) said one or more reactive cationic polymers comprises said one or more cationic GPAMs and/or said one or more cationic PAE resins in aqueous form;

(b) said one or more cationic GPAMs comprise said base polymer comprising cationic monomers selected from DADMAC, AETAC, and combinations thereof; nonionic monomers selected from acrylamide, methacrylamide, and combinations thereof; and optionally anionic monomers selected from acrylic acid and/or corresponding water soluble salts, water dispersible alkali metal salts, alkaline earth metal salts, ammonium salts, and combinations thereof, or said base polymer comprises (i) acrylamide and DADMAC, (ii) acrylamide and AETAC, or (iii) acrylamide, DADMAC, and AETAC,

(c) said one or more water-soluble amphoteric polymers

(i) comprises an inverse emulsion of acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers;

(ii) preferably comprises an acrylic acid (AA) monomer content of no more than 2 wt %; and

(iii) preferably comprises a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7; and

(d) said one or more anionic organic or inorganic microparticles comprise colloidal silica.

10. The method of **any of the foregoing claims**, wherein when added to said aqueous suspension comprising cellulosic fibers:

(a) said one or more reactive cationic polymers are added at a dosage ranging from 0.1-15 g/kg, 0.5-5 g/kg, or 0.5-4 g/kg;

(b) said one or more water-soluble amphoteric polymers are added at a dosage ranging from 0.05-5 g/kg, 0.1-4 g/kg, or 0.3-1 g/kg;

(c) said one or more anionic organic or inorganic microparticles are added at a dosage ranging from 0.1-1 g/kg, 0.2-0.8 g/kg, or 0.4-0.6 g/kg.

11. The method of **any of the foregoing claims**, wherein said aqueous suspension comprising cellulosic fibers comprises a pH ranging from 4-8, 4-7.5, 4-7, 4.5-7, or 5-7 and further comprises:

(a) cellulosic fibers optionally obtained from sources selected from softwood fiber, hardwood fiber, recycled fiber, recycled old corrugated cardboard (OCC), recycled mixed office waste (MOW), recycled mixed office paper, refined fiber, mill broke fibers, coated broke, non-wood fibers, including but not limited to straw and wheat pulp, and a mixture of any of the foregoing;

(b) pulp selected from Kraft pulp, unbleached Kraft pulp, bleached pulp, unbleached pulp, process water from pulp, paper, and/or board production, neutral sulfite semi chemical (NSSC) pulp, mechanical pulp, non-wood pulp, and a mixture of any of the foregoing; or

(c) a stock selected from a thick stock, a thick stock diluted with chemical water, synthetic water, white water, and/or process water, and a thin stock, and a mixture of any of the foregoing.

12. The method of **any of the foregoing claims**, wherein when used for manufacture of tissue, paper, or board, the method results in:

(a) improved retention of said cellulosic fibers; a

(b) improved drainage of said flocculated fiber suspension;

(c) improved STFI and/or burst strength;

(d) a reduced hydrophobic particle and/or hydrophobic agglomerate count;

(e) an improved dry tensile, immediate wet tensile, and/or soaked wet tensile strength; or

(f) any combination of (a)-(e)

compared to a tissue, paper, or board prepared by an identical method in the absence of (i) addition of said one or more reactive cationic polymers or (ii) addition of said one or more water-soluble amphoteric polymers.

13. A method for manufacture of tissue, paper, or board, the method comprising:

(a) forming or providing an aqueous suspension comprising cellulosic fibers;

(b) optionally diluting the aqueous suspension;

(c) flocculating the aqueous suspension to form a flocculated fiber suspension;

(d) delivering the flocculated fiber suspension to a headbox and draining on a wire screen to form a wet fibrous web; and

(e) pressing and drying the wet fibrous web to obtain a tissue, paper, or board;

wherein the method further comprises prior to step (c) treating the aqueous suspension comprising cellulosic fibers with a retention and drainage aid comprising:

(i) one or more reactive cationic polymers comprising functional groups that are reactive to cellulosic or lignocellulosic fiber surfaces and a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7, wherein said one or more reactive cationic polymers comprise one or more cationic glyoxalated polyacrylamides (GPAMs); one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55, wherein said one or more cationic PAE resins and said one or more cationic GPAMs are added sequentially in any order, simultaneously, or premixed prior to addition to said aqueous suspension comprising cellulosic fibers;

(ii) one or more water-soluble amphoteric polymers comprising an inverse emulsion of acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers; preferably comprising an acrylic acid (AA) monomer content of no more than 2 wt %; and preferably comprising a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7; and

(iii) optionally one or more anionic organic or inorganic microparticles comprising silica.

14. A fiber stock composition comprising:

(a) an aqueous suspension comprising cellulosic fibers; and

(b) a retention and drainage aid comprising

(i) one or more reactive cationic polymers;

(ii) one or more water-soluble amphoteric polymers; and

(iii) optionally one or more anionic organic or inorganic microparticles;

obtainable by a method **according to any of the foregoing claims.**

15. A composition for use as a retention and drainage aid in manufacture of tissue, paper, or board, the composition comprising:

(a) one or more reactive cationic polymers comprising a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7, wherein said one or more reactive cationic polymers comprise

(i) one or more cationic glyoxalated polyacrylamides (GPAMs) synthesized by reacting glyoxal with a base polymer, wherein said base polymer comprises a weight average molecular weight ranging from 5-5000 kDa, 50-2500 kDa, 80-2000 kDa, or 100-1000 kDa; (i) acrylamide and DADMAC, (ii) acrylamide and AETAC, or (iii) acrylamide, DADMAC, and AETAC and further wherein said one or more GPAMs comprises a glyoxal:base polymer weight ratio ranging from 0.1:99.9 to 50:50, 5:95 to 20:80, or 5:95 to 10:90; and a cationic charge density ranging from below 5.0 mEq/g, 0.5-5.0 mEq/g, 1.0-4.0 mEq/g, or 1.5-2.5 mEq/g as dry solids at pH 7;

(ii) one or more cationic polyamidoamine-epichlorohydrin (PAE) resins; or

(iii) a combination of one or more cationic GPAMs and one or more cationic PAE resins having a ratio of PAE to GPAM ranging from 1:99 to 99:1, 20:80 to 80:20, 40:60 to 60:40, or 45:55;

(b) one or more water-soluble amphoteric polymers comprising acrylamide (AM), acrylic acid (AA), and [2-(acryloyloxy)ethyl] trimethylammonium chloride (Q9) monomers; wherein said one or more water-soluble amphoteric emulsion polymers preferably comprise an acrylic acid (AA) monomer content of no more than 2 wt % and a ratio of AM:AA:Q9 ranging from 89:2:9 to 91:2:7, wherein said one or more water-soluble amphoteric polymers is a an inverse emulsion, a dry polymer, an aqueous solution, preferably an inverse phase emulsion; and

(c) optionally one or more anionic organic or inorganic microparticles selected from the group of microparticles and nanoparticles consisting of silica microparticles; colloidal silica; aluminum phyllosilicate mineral particles, including but not limited to bentonite, sodium bentonite, calcium bentonite, and montmorillonite; and anionic polymer microparticles, including but not limited to highly structured anionic polyacrylamides; optionally obtainable by a method **according to any of the foregoing claims.**

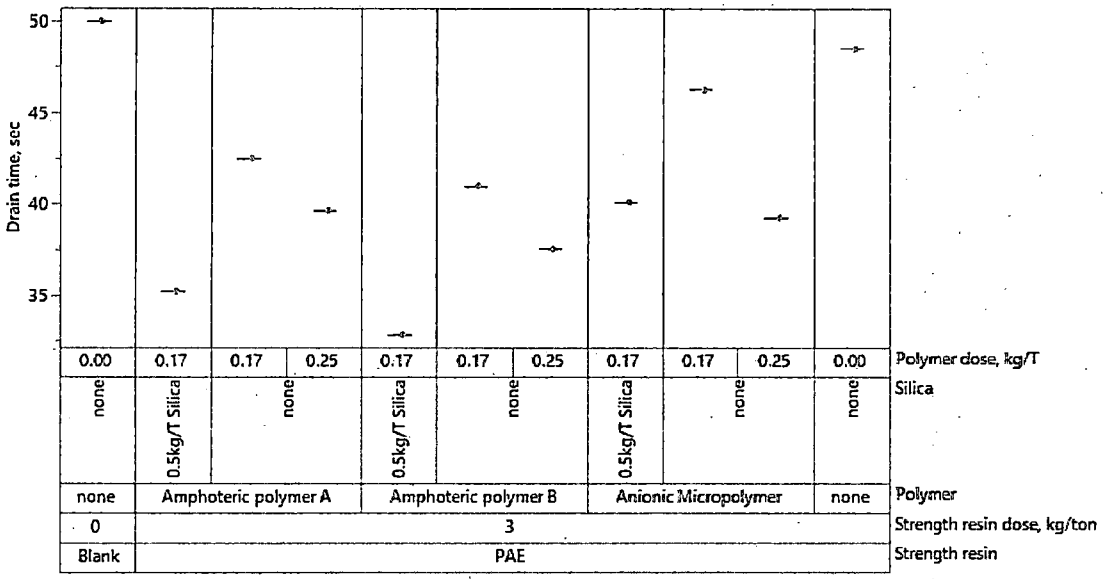

Drain time, sec
50
45
40
35
0.00 0.17 0.17 0.25 0.17 0.17 0.25 0.17 0.17 0.25 0.00
Polymer dose, kg/T
none 0.5kg/T Silica none 0.5kg/T Silica none 0.5kg/T Silica none none
Silica
none Amphoteric polymer A Amphoteric polymer B Anionic Micropolymer none
Polymer
0 3
Strength resin dose, kg/ton
Blank PAE
Strength resin

FIG 1

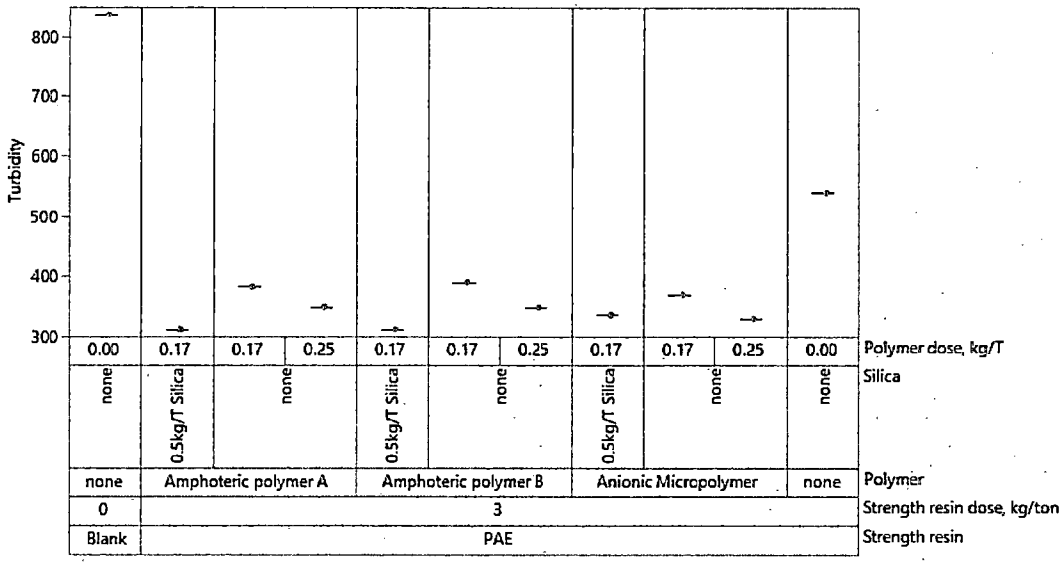

Turbidity
800
700
600
500
400
300
0.00 0.17 0.17 0.25 0.17 0.17 0.25 0.17 0.17 0.25 0.00
Polymer dose, kg/T
none 0.5kg/T Silica none 0.5kg/T Silica none 0.5kg/T Silica none none
Silica
none Amphoteric polymer A Amphoteric polymer B Anionic Micropolymer none
Polymer
0 3
Strength resin dose, kg/ton
Blank PAE
Strength resin

FIG 2

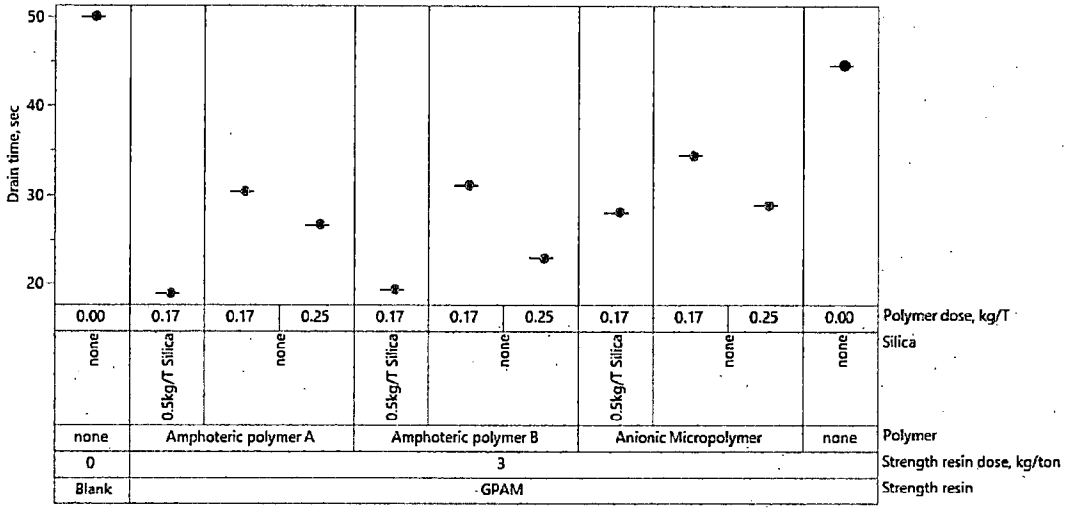
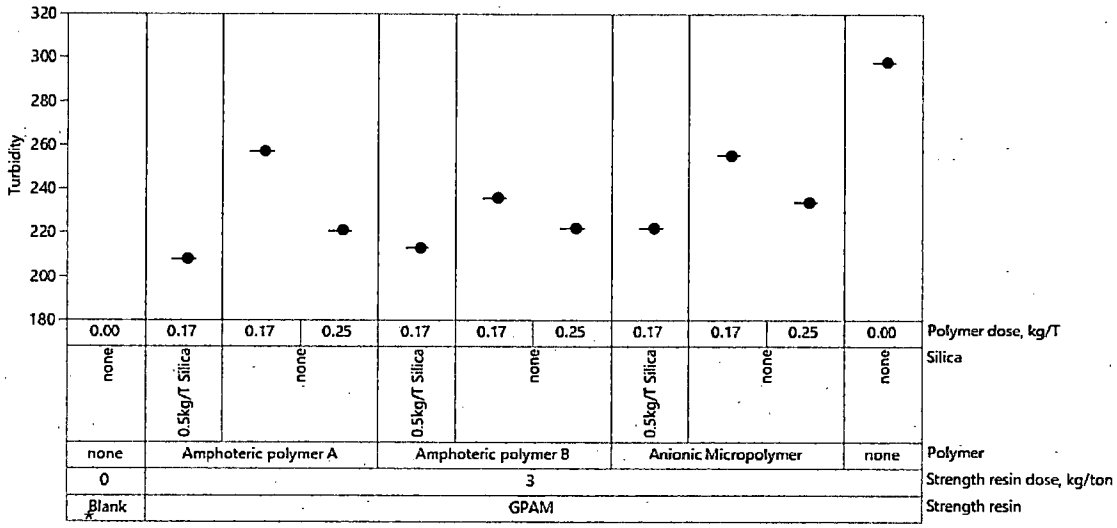

Drain time, sec
50
40
30
20
0.00
0.17
0.17
0.25
0.17
0.17
0.25
0.17
0.17
0.25
0.00
Polymer dose, kg/T
none
0.5kg/T Silica
none
0.5kg/T Silica
none
0.5kg/T Silica
none
none
Silica
none
Amphoteric polymer A
Amphoteric polymer B
Anionic Micropolymer
none
Polymer
0
3
Strength resin dose, kg/ton
Blank
GPAM
Strength resin

FIG 3



*Turbidity off scale

FIG 4

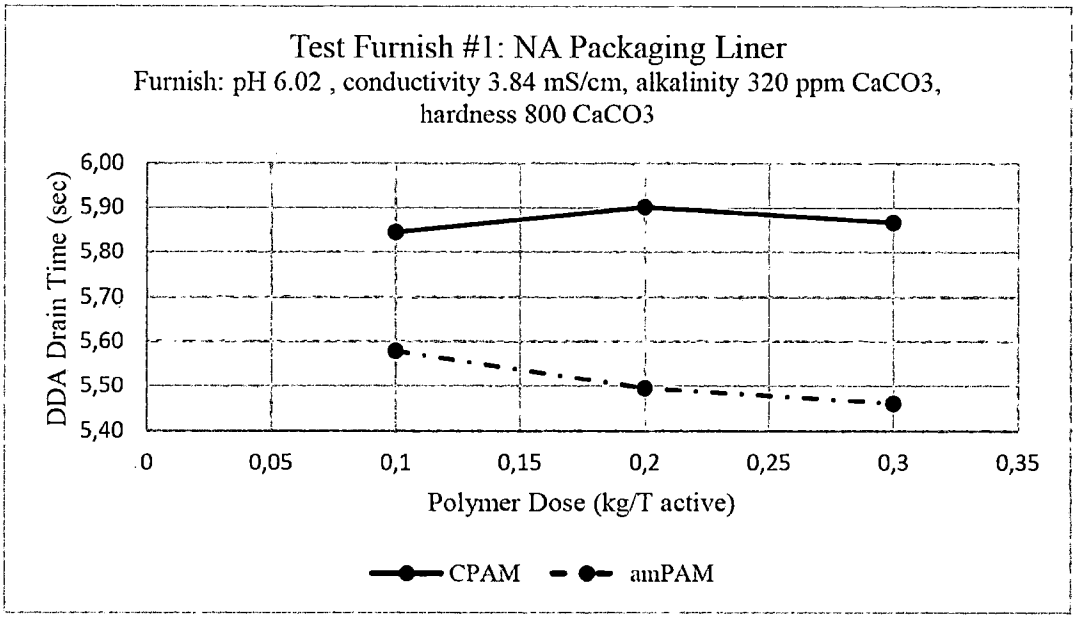

Test Furnish #1: NA Packaging Liner
Furnish: pH 6.02 , conductivity 3.84 mS/cm, alkalinity 320 ppm CaCO3, hardness 800 CaCO3
DDA Drain Time (sec)
6,00
5,90
5,80
5,70
5,60
5,50
5,40
0
0,05
0,1
0,15
0,2
0,25
0,3
0,35
Polymer Dose (kg/T active)
CPAM
amPAM

FIG 5

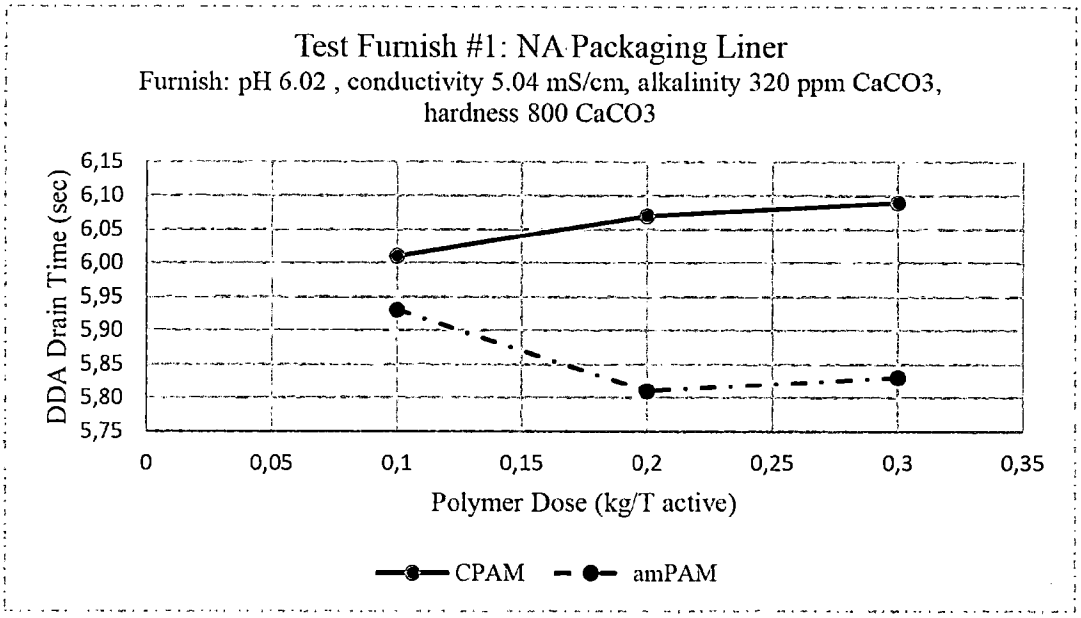

Test Furnish #1: NA Packaging Liner
Furnish: pH 6.02 , conductivity 5.04 mS/cm, alkalinity 320 ppm CaCO3, hardness 800 CaCO3
DDA Drain Time (sec)
6,15
6,10
6,05
6,00
5,95
5,90
5,85
5,80
5,75
0
0,05
0,1
0,15
0,2
0,25
0,3
0,35
Polymer Dose (kg/T active)
CPAM
amPAM

FIG 6

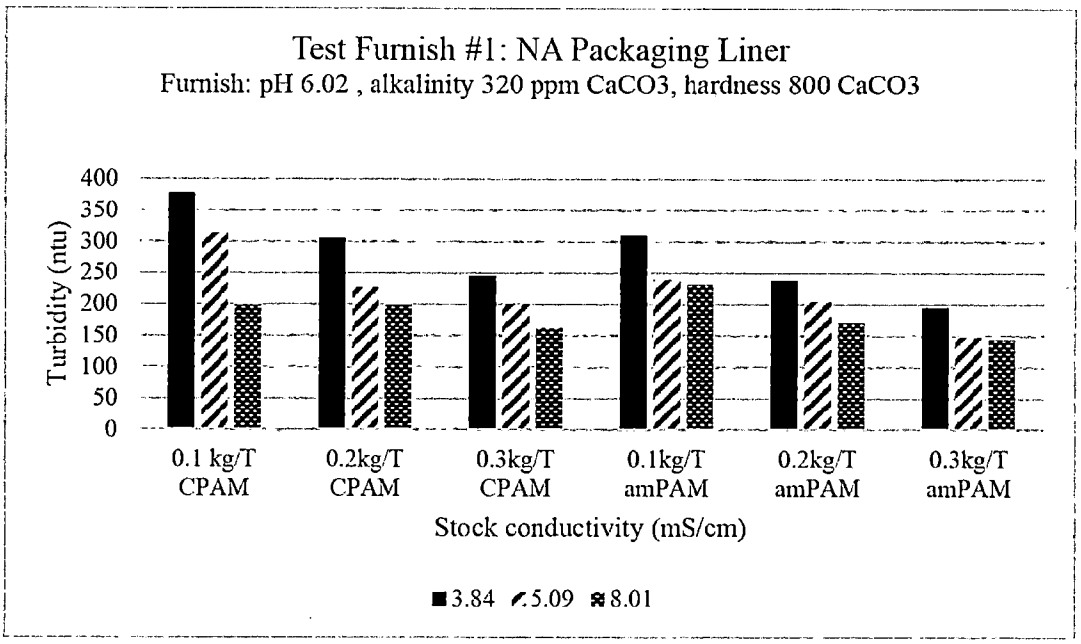

Test Furnish #1: NA Packaging Liner
Furnish: pH 6.02 , alkalinity 320 ppm CaCO3, hardness 800 CaCO3
Turbidity (ntu)
400
350
300
250
200
150
100
50
0
0.1 kg/T CPAM
0.2kg/T CPAM
0.3kg/T CPAM
0.1kg/T amPAM
0.2kg/T amPAM
0.3kg/T amPAM
Stock conductivity (mS/cm)
3.84
5.09
8.01

FIG 7

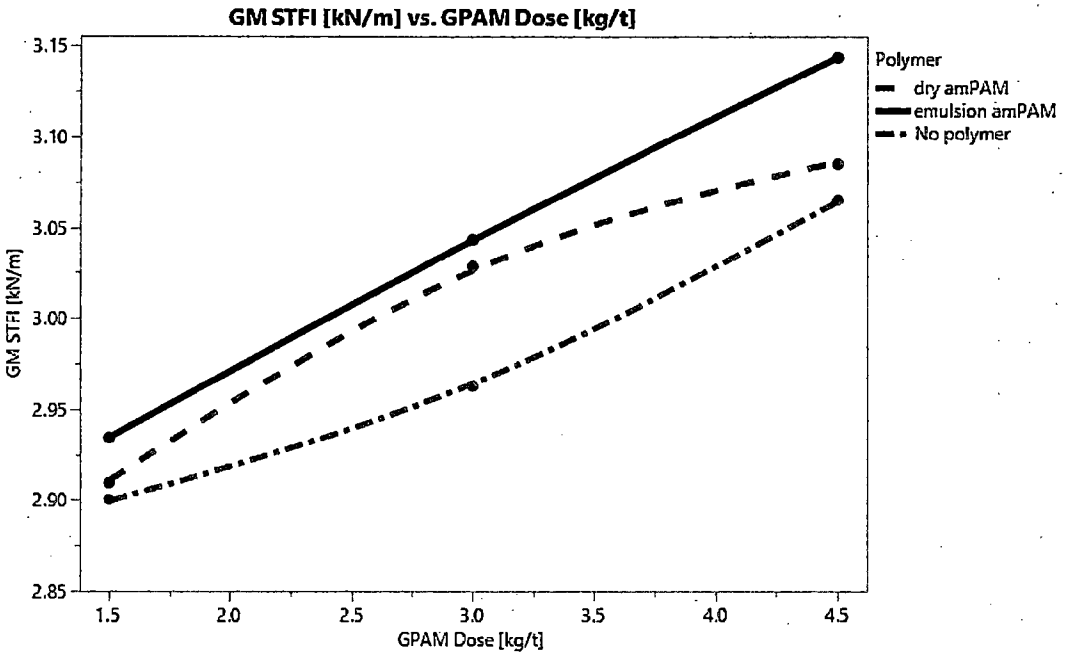

GM STFI [kN/m] vs. GPAM Dose [kg/t]
GM STFI [kN/m]
3.15
3.10
3.05
3.00
2.95
2.90
2.85
1.5
2.0
2.5
3.0
3.5
4.0
4.5
GPAM Dose [kg/t]
Polymer
dry amPAM
emulsion amPAM
No polymer

FIG 8

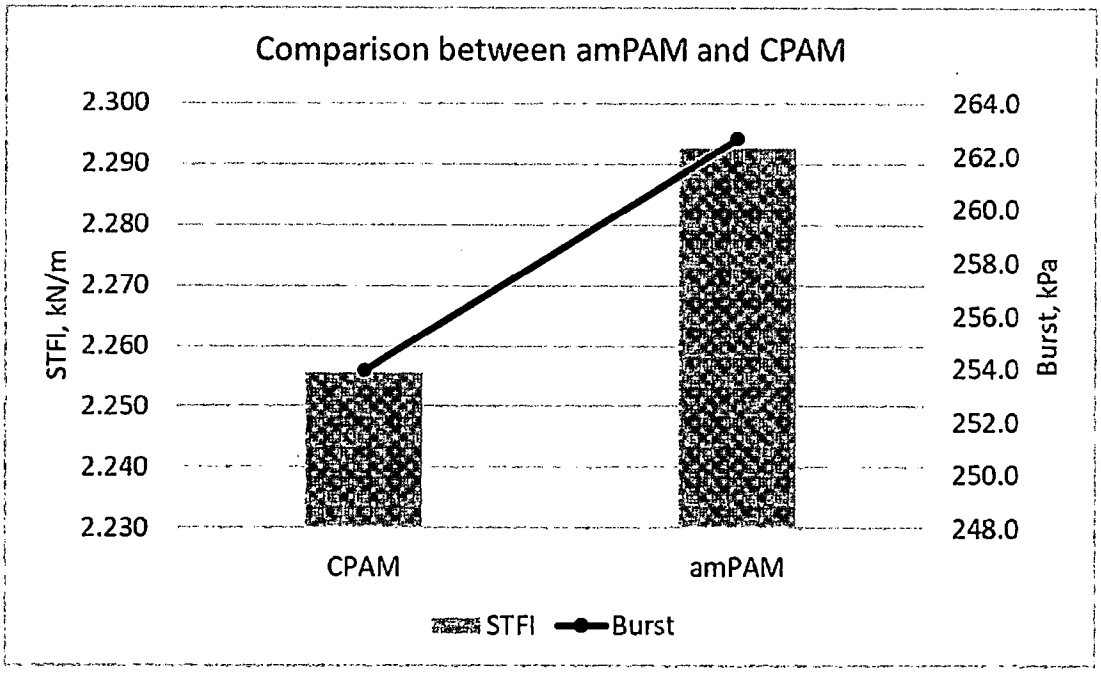

Comparison between amPAM and CPAM
2.300
2.290
2.280
2.270
2.260
2.250
2.240
2.230
STFI, kN/m
264.0
262.0
260.0
258.0
256.0
254.0
252.0
250.0
248.0
Burst, kPa
CPAM
amPAM
STFI
Burst

FIG 9

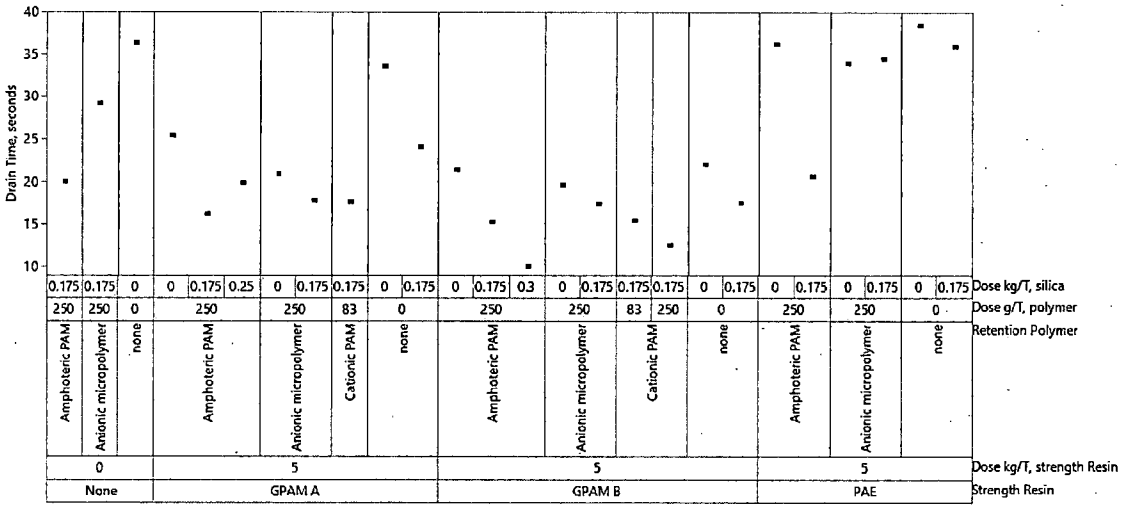

Drain Time, seconds
40
35
30
25
20
15
10
0.175 0.175 0 0 0.175 0.25 0 0.175 0.175 0 0.175 0 0.175 0.3 0 0.175 0.175 0.175 0 0.175 0 0.175 0 0.175 0 0.175
Dose kg/T, silica
250 250 0 250 250 83 0 250 250 83 250 0 250 250 0
Dose g/T, polymer
Amphoteric PAM
Anionic micropolymer
none
Amphoteric PAM
Anionic micropolymer
Cationic PAM
none
Amphoteric PAM
Anionic micropolymer
Cationic PAM
none
Amphoteric PAM
Anionic micropolymer
none
Retention Polymer
0 5 5 5
Dose kg/T, strength Resin
None GPAM A GPAM B PAE
Strength Resin

FIG 10

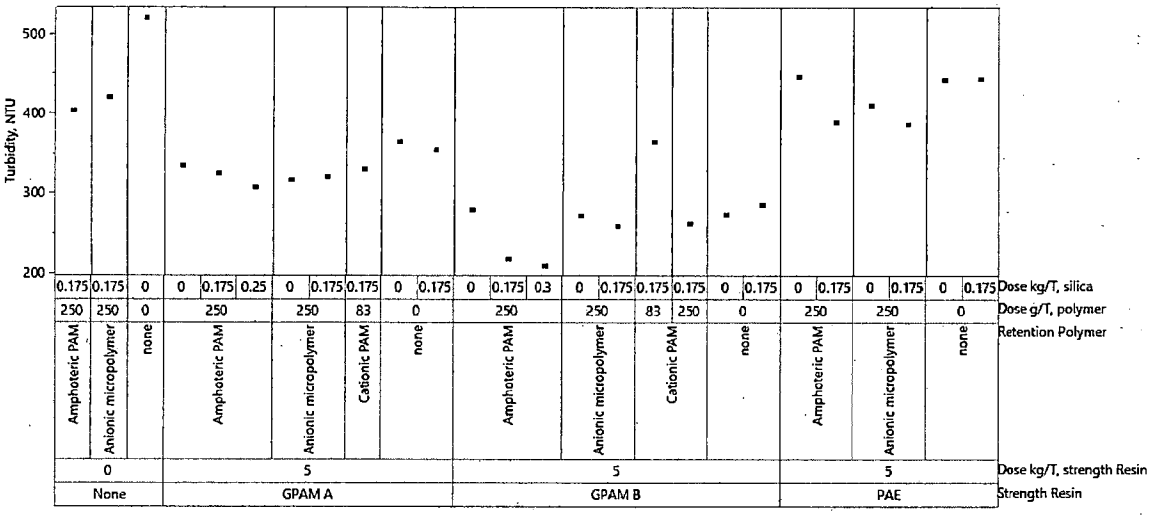

Turbidity, NTU
500
400
300
200
0.175 0.175 0 0 0.175 0.25 0 0.175 0.175 0 0.175 0 0.175 0.175 0.3 0 0.175 0.175 0.175 0 0.175 0 0.175 0 0.175 0 0.175
Dose kg/T, silica
250 250 0 250 250 83 0 250 250 83 250 0 250 250 0
Dose g/T, polymer
Amphoteric PAM
Anionic micropolymer
none
Amphoteric PAM
Anionic micropolymer
Cationic PAM
none
Amphoteric PAM
Anionic micropolymer
Cationic PAM
none
Amphoteric PAM
Anionic micropolymer
none
Retention Polymer
0 5 5 5
Dose kg/T, strength Resin
None GPAM A GPAM B PAE
Strength Resin

FIG 11