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(54) **ABSORBENT ARTICLES COMPRISING
THERMOPLASTIC RESIN PRETREATED
FIBERS**

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ABSTRACT

One embodiment of the present invention is a fibrous structure that may comprise: cellulosic pulp fibers and pretreated cellulosic pulp fibers. The pretreated cellulosic pulp fiber is formed by pretreating cellulosic pulp fiber with a thermoplastic resin having a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof.

ABSORBENT ARTICLES COMPRISING THERMOPLASTIC RESIN PRETREATED FIBERS

BACKGROUND

[0001] This disclosure relates to tissue products comprising thermoplastic resin pretreated pulp fibers.

[0002] Cellulosic fibers made from wood pulp are used in a variety of tissue products, for example, facial tissue, bath tissue, paper towels, dinner napkins, wipes, and the like. It is known in the art to prepare such tissue products comprising natural wood pulp fibers, synthetic polymeric fibers, and combinations of natural wood pulp fibers and synthetic polymeric fibers to impart high dry and wet strength characteristics to the article.

[0003] Fibrous tissue webs having high strength and stretch are useful for many applications as they provide the user security that the tissue product will remain intact during use. Dry strength additives may be used such as starches or polyacrylamides. Unfortunately, use of these additives increase the strength of fibrous tissue webs but do not increase the stretch of the tissue product.

[0004] It is known that increased tensile strength generally decreases the tactile softness of fibrous tissue webs. Generally, the perceived stiffness of the fibrous tissue web is typically dependent of the tensile breaking strength and the elastic modulus of the fibrous tissue web, with high stiffness, low softness fibrous tissue webs resulting from properties of high elastic modulus and high tensile strength. The durability of the fibrous tissue web is typically dependent on both the tensile strength and stretch properties of the fibrous tissue web. In general, higher tensile strength and stretch provide the highest durability for fibrous tissue webs. Therefore, to maximize durability and softness of the fibrous tissue web, it is advantageous to have the highest stretch and lowest elastic modulus for a given tensile strength.

[0005] Fibrous tissue webs having a high strength when they become wet (known in the art as wet strength) are useful for many applications. One application for such fibrous tissue webs is as premoistened tissue products, such as wipes, often used by travelers for cleansing the body and for surface cleaning. Such fibrous tissue webs and their resulting tissue products must maintain sufficient strength when stored in wet conditions for an extended period of time to withstand wiping and rubbing actions. Other applications for high wet strength fibrous tissue webs is in tissue products that need to maintain integrity when wetted with body fluids, such as nasal secretions, urine, blood, mucus, menses and other body exudates.

[0006] In the art of papermaking, chemical additives exist for improving the wet strength of fibrous tissue webs and ultimately, the tissue products made from such fibrous tissue webs. These materials are known in the art as "wet strength agents" and are commercially available from a wide variety of sources. For example, a polyamide epichlorohydrin resin may be used to enhance the wet strength of the fibrous tissue web.

[0007] This cationic resin is typically added to the papermaking pulp fiber slurry whereupon it bonds to the anionically charged cellulose pulp fibers. During the papermaking process, the resin crosslinks and eventually becomes insoluble in water. The wet strength agent thus acts as a

"glue" to hold the pulp fibers together and enhances the wet strength of the fibrous tissue web. However, one may need to use chlorine in order to remove the resin and recycle or repulp tissue products containing pulp fibers treated with the resin, which presents environmental problems. "Repulping" refers to a recycling process used in the production of the fibrous tissue web and the tissue products from scrap fibrous tissue webs and tissue products accumulated during the production of the fibrous tissue web and the tissue products. Since scrap products is typically unused raw materials, a process to recycle it for future use eliminates the inefficient disposal of a valuable source of papermaking pulp fibers.

[0008] Cationic resins, as wet strength agents, may have other disadvantages, such as reacting with other anionic additives which may be added to the fibrous tissue web and, in many cases, increasing the dry strength of the fibrous tissue web as well, resulting in a less soft tissue product. Moreover, the effectiveness of cationic wet strength agents may be limited by low retention of the wet strength agent on the cellulose pulp fiber.

[0009] Fibrous tissue webs have been disclosed containing individualized, crosslinked pulp fibers, wherein the crosslinking agent is selected from the group consisting of C2 to C8 dialdehydes, with glutaraldehyde being most typical. The cost associated with producing pulp fibers crosslinked with dialdehyde crosslinking agents, such as glutaraldehyde, may be too high to result in commercially viable tissue products.

[0010] The use of C2 to C9 monomeric polycarboxylic acids to make individualized, crosslinked cellulosic pulp fibers having primarily intra-fiber crosslinking (crosslinks between cellulose units within a single pulp fiber) and purportedly having increased absorbency, has also been taught. Additionally, various resinous maleic anhydride compositions have been used in conjunction with fibrous tissue webs and tissue products. For example, fibrous tissue webs and/or tissue products may be coated with a composition including an amine salt of a low molecular weight C6 to C24 olefin/maleic anhydride copolymer in combination with a bisulfite. Such fibrous tissue webs and/or tissue products exhibit release properties. The application of a polymeric polyacid, a phosphorous containing accelerator, and an active hydrogen compound to a fibrous tissue web followed by curing at 120° C. to 400° C. for 3 seconds to 15 minutes has also been disclosed.

[0011] The terms "pretreat" and "pretreated" as used herein, mean treating pulp fibers and/or a fibrous sheet prior to the finishing operation at a pulp mill with a chemical additive, completing the finishing operation, redispersing the finished pretreated pulp fibers at the paper mill and using the finished pretreated pulp fibers in the production of a fibrous tissue web and/or a tissue product.

[0012] The term "water dispersible" as used herein, means that the synthetic copolymers, such as the thermoplastic resin of the present invention, are either water soluble or capable of existing as stable colloidal, self-emulsifiable or other type dispersions in water with the presence of added emulsifiers. Added emulsifiers may also be employed within the scope of the present invention to aid in the polymerization of the thermoplastic resins or assist in compatibilizing the thermoplastic resins with other chemical additives used in the papermaking process, however, the emulsifiers are not

essential to the formation of stable dispersions or solutions of the thermoplastic resin in water.

[0013] Water solubility and/or water dispersability of the thermoplastic resin of the present invention enables the fibrous tissue web and/or tissue products containing the thermoplastic resin and/or other chemical additives to be repulpable. A surprising aspect of the present invention is that while the thermoplastic resins are water dispersible or water soluble, they are capable of being retained in the wet end of the papermaking process.

[0014] An additional disadvantage of using papermaking chemical additives, such as wet strength agents, is that at least a portion of the chemical additives are lost in pulping and/or repulping operations. Thus, while the virgin tissue product may be hydrophilic, use of an emulsion of a thermoplastic resin containing high levels of a chemical additive may result in a finished tissue product having unacceptable hydrophobicity due to loss of the chemical additive. As the chemical additive may be critical to dispersability of the thermoplastic resin, the fibrous tissue webs and/or tissue products made with the non-water soluble or dispersible thermoplastic resins are more likely to contain pulp fiber bundles called nits as hereinafter described.

[0015] Such nits are described as fiber/polymer bundles that create the appearance of white spots within the fibrous tissue web and/or tissue product. These white spots will generally be on the order of one square millimeter in size or greater. The nit count refers to the number of nits counted in a 7.5 inch by 7.5 inch sample of the fibrous tissue web and/or tissue product made from pretreated pulp fibers. The fibrous tissue web and/or tissue product should have a nit count of about 10 or less, more specifically about 5 or less, and still more specifically about 3 or less.

[0016] There, however, remains a need for tissue products having desired dry and wet strength, stretch, and modulus of elasticity characteristics. It is also desirable to have tissue products that may be easily dispersed to allow repulping.

BRIEF SUMMARY

[0017] Disclosed herein are fibrous tissue webs and/or tissue products comprising cellulosic pulp fibers pretreated with water dispersible, water soluble, or combination thereof thermoplastic resin and methods of making such fibrous tissue webs and/or tissue products. In one embodiment of the present invention, a fibrous structure may comprise: a fibrous tissue web having a pair of outer surfaces comprises greater than or equal to about 90 wt % cellulosic pulp fibers based upon a total weight of the fibrous tissue web, and a thermoplastic resin disposed between at least a portion of the cellulosic pulp fibers. The thermoplastic resin may have a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof.

[0018] In another embodiment of the present invention, the fibrous structure may comprise: a fibrous tissue web having a pair of outer surfaces comprises cellulosic pulp fibers, and a thermoplastic resin, wherein the thermoplastic resin may have a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof. The thermoplastic resin may at least partially coat the cellulosic pulp fibers.

[0019] In one embodiment of the present invention, the pretreated cellulosic pulp fibers may comprise: cellulosic

pulp fibers and a thermoplastic resin adhered to the cellulosic pulp fibers, wherein a weight ratio of thermoplastic resin to the cellulosic pulp fibers may be about 1:5 to about 1:1000. The thermoplastic resin may have a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof.

[0020] The above described and other features are exemplified by the following detailed description.

DETAILED DESCRIPTION

[0021] Disclosed herein are cellulosic pulp fibers, tissue products, and methods of making tissue products comprising pulp fibers pretreated with water dispersible, water soluble, or combinations thereof thermoplastic resin. The tissue products comprising the cellulosic pulp fibers and thermoplastic resin may have high wet strength characteristics, high wet/dry ratio, and be repulpable. All ranges disclosed herein are inclusive and combinable (e.g., ranges of "about 25 wt % or less, or, more specifically about 5 wt % to about 20 wt %" is inclusive of the endpoints and all intermediate values of the ranges of "about 5 wt % to about 25 wt %," etc.). The terms "first," "second," and the like, herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another, and the terms "a" and "an" herein do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context, (e.g., includes the degree of error associated with measurement of the particular quantity).

[0022] The pretreated pulp fibers may be cellulosic pulp fibers, or more specifically, natural pulp fibers, or, even more specifically, chemical pulp fibers. The pretreated pulp fibers may comprise about 80 wt % or greater of cellulosic pulp fibers, or, more specifically about 90 wt % or greater of cellulosic pulp fibers, and even more specifically about 95 wt % or greater of cellulosic pulp fibers, based upon the total weight of the tissue product. The remainder of the pulp fibers in the tissue product may include, for example bleached and unbleached pulp fibers, natural and synthetic pulp fibers (such as rayon, lyocel, polyethylene, polypropylene, and the like), and the like, as well as combinations comprising at least one of the foregoing pulp fibers.

[0023] The specific-size and geometry of the pulp fibers, e.g., aspect ratio and the like, may be based upon the tissue products into which the pulp fibers are incorporated.

[0024] Illustrative cellulosic pulp fibers include, but are not limited to, wood pulp fibers including hardwoods and softwoods; non-woody papermaking pulp fiber (e.g., from cotton, straw, grass (such as rice and esparto), cane, reed (such as bagasse), bamboo, bast fiber (such as jute, flax, kenaf, cannabis, linen, and ramie), leaf fibers, and the like), and the like, as well as combinations comprising at least one of the foregoing cellulosic pulp fibers.

[0025] In one embodiment of the present invention, the cellulosic pulp fibers may be wood pulp fibers. Suitable wood sources for wood pulp fibers include, but are not limited to, softwood sources such as pines, spruces, hemlocks, and firs, and hardwood sources such as eucalyptuses, poplars, beeches, alder, oaks, and aspens. Possible wood species include, but are not limited to, southern hardwood

kraft, eucalyptus wood kraft, northern wood kraft, and the like, as well as combinations comprising at least one of the foregoing. Suitable wood pulp fibers may be prepared using various methods, which include, but are not limited to, chemical methods such as Kraft and sulfite processes, thermomechanical methods, chemithermomechanical methods, and combinations comprising at least one of the foregoing methods. Useful methods of preparing pulp fibers include dispersion to impart curl and improved drying properties, such as disclosed in U.S. Pat. No. 5,348,620 issued to Hermans et al.; U.S. Pat. No. 5,501,768 issued to Hermans et al.; and, U.S. Pat. No. 5,656,132 issued to Farrington, Jr. et al.

[0026] Some or all of the cellulosic pulp fibers may be pretreated with a thermoplastic resin (e.g., a water soluble, water dispersible, or combination thereof thermoplastic resin) prior to, during, or after the drying phase of the pulp fiber processing. The term "thermoplastic resin" as used herein, refers to a crystalline or amorphous polymer that softens when exposed to heat and returns to its original state when cooled to ambient temperature. As used herein, the term "water soluble" refers to solids or liquids that will form a homogenous solution in water at a temperature of about 100° C. or lower, more specifically between about 70° C. to about 100° C., when the thermoplastic resin is present in a concentration of 1% by weight or more of the total solution.

[0027] In order to be compatible with the processing and to facilitate formation of the pretreated cellulosic pulp fibers, the thermoplastic resin may have a glass transition temperature of about 50° C. or less, or, more specifically about 25° C. or less, and even more specifically about -5° C. or less. The thermoplastic resin may optionally have a sufficiently high molecular weight to enable the deposition of the thermoplastic resin on the external surface of the cellulosic pulp fibers, or more specifically, a sufficiently high molecular weight to enable the deposition of about 5 wt % or less of the thermoplastic resin within pores of the cellulosic pulp fibers, based upon the total weight of the thermoplastic resin. For example, the thermoplastic resin may have a weight average molecular weight (Mw) of about 1,000 atomic mass units (amu) or greater, or, more specifically about 10,000 amu or greater, or, even more specifically about 100,000 amu or greater.

[0028] Exemplary thermoplastic resins may include, but are not limited to water soluble, water dispersible, and combinations thereof polyesters, polyurethanes, polyethylene-co-vinyl acetate, polyvinyl acetate-co-vinyl alcohol, polyacrylates, polyvinyl ethers, polyamides, and the like, as well as combinations comprising at least one of the foregoing thermoplastic resins.

[0029] The amount of pulp fibers pretreated with the thermoplastic resin is dependent upon the type of the tissue product to be produced, desired structural integrity of the tissue product, and the location of the pretreated pulp fibers in the tissue product. In one embodiment of the present invention, the tissue product may comprise pulp fibers selectively pretreated with a thermoplastic resin. The term "pretreated" as used herein, means that the thermoplastic resin is applied to the pulp fiber during pulp manufacturing process. Examples suitable to the present invention are described in U.S. Pat. No. 6,582,560 issued to Runge et al. where additives are applied during the pulp sheet manufac-

turing process. The pulp fibers that have been pretreated is then transported to a different manufacturing process where it is diluted and reslurried and made into a fibrous structure. Use of water-soluble or water dispersible thermoplastics assists in the reslurrying process.

[0030] Pre-treating pulp fibers with these thermoplastic resins impart unique properties to the resulting fibrous structures as opposed to the traditional addition of chemical additives in the aqueous phase of the papermaking. While not being bound by theory it is believed that the pretreatment provides improved retention of the thermoplastic resin, by allowing the fiber to become partially coated by the thermoplastic, which allows greater retention of the material. The coating interferes with the natural bonding of the cellulose fibers during drying and replaces this bonding with a lower stiffness thermoplastic bond.

[0031] A tissue product comprising the pretreated pulp fibers (e.g., the fibrous tissue web or the like), may comprise a weight ratio of thermoplastic resin to cellulosic pulp fibers of about 1:5 to about 1:1,000, or, more specifically, about 1:10 to about 1:500, or, even more specifically, about 1:25 to about 1:200.

[0032] The pulp fibers may be pretreated with the thermoplastic resin in various fashions, such as in a wet laid process. In one embodiment of the present invention, the process comprises mixing pulp fibers with water to form a pulp fiber slurry. The pulp fiber slurry may be transported to a web-forming apparatus of a papermaking machine to form a wet fibrous tissue web. The wet fibrous tissue web may be dewatered to a predetermined consistency, thereby forming a dewatered fibrous tissue web. The thermoplastic resin may be converted to a liquid form (e.g., heated, dispersed and/or dissolved in water, and/or the like) and added to the dewatered fibrous tissue web, thereby forming a chemically pretreated, dewatered, fibrous tissue web containing chemically pretreated pulp fibers. These chemically pretreated pulp fibers may have an increased or improved level of chemical retention of the water insoluble chemical additive through the paper making process. In another embodiment of the present invention, the process may, additionally or alternatively, comprise adding the thermoplastic resin to the pulp fiber during a pulp processing stage.

[0033] Possible tissue products comprising the pretreated pulp fibers may include, but are not limited to, bath tissue, facial tissue, towels, wipes, dinner napkins, and the like.

[0034] In one embodiment of the present invention, the fibrous tissue web is made into a tissue product. The tissue product may be a single or multi-ply tissue product; e.g., the tissue product can be a three-ply facial tissue product. Facial tissue, bath tissue, and towel products, as used herein, are differentiated from other paper products in terms of their bulk. The bulk of the tissue products may be calculated as the quotient of the caliper (hereinafter defined) in micrometers, divided by the basis weight in grams per square meter (g/m^2). The resulting bulk may be expressed in cubic centimeters per gram (cm^3/g). Writing papers, newsprint, and other such paper products typically have higher strength, stiffness, and density (low bulk) in comparison to tissue products which tend to have much higher calipers for a given basis weight. The tissue products may have a bulk of about 2 cm^3/g or greater, more specifically about 2.5 cm^3/g or greater, and even more specifically about 3 cm^3/g

or greater. The basis weight of the tissue product may be about 5 g/m² to about 200 g/m², or, more specifically about 7 g/m² to about 150 g/m², and, even more specifically, about 10 g/m² to about 100 g/m².

[0035] The tissue products may comprise layered and/or blended fibrous tissue webs.

[0036] The term “blended fibrous tissue web”, as used herein, refers to the process of blending various pulp fiber types prior to formation of the fibrous tissue web. In accordance with some embodiments of the present invention, pretreated pulp fibers may be blended with non-pretreated pulp fibers prior to formation of fibrous tissue web(s). In one embodiment of the present invention, a fibrous tissue web may comprise a cellulosic pulp fiber layer with pulp fibers selectively pretreated with the thermoplastic resin, e.g., the center portion of the fibrous tissue web may be coated on one side with the thermoplastic resin. Such an arrangement may increase the structural integrity of the fibrous tissue web in an area generally subjected to higher stresses. In another embodiment of the present invention, an entire area of the fibrous tissue web may comprise pretreated pulp fibers; e.g., the center of the fibrous tissue web. In other words, all or a portion of a fibrous tissue web may comprise the thermoplastic resin. In yet another embodiment of the present invention, fibrous tissue web(s) comprising pretreated pulp fibers may be disposed adjacent and/or between fibrous tissue web(s) of non-pretreated pulp fibers. For example, a fibrous tissue web comprising pretreated pulp fibers comprising about 25 wt % to about 100 wt % pretreated pulp fibers (based upon the total weight of the fibrous tissue web) may be disposed between fibrous tissue webs comprising about 25 wt % or less of pretreated pulp fiber, or more specifically about 10 wt % or less of pretreated pulp fibers, and even more specifically about 5 wt % or less of pretreated pulp fibers, based upon the total weight of the specific fibrous tissue web. In yet another embodiment of the present invention, a concentration gradient of pretreated pulp fibers within a fibrous tissue web may be established across a layer of the fibrous tissue web, where areas of higher stress have a greater concentration. For example, a concentration gradient may increase from an edge of a fibrous tissue web toward a center of the fibrous tissue web.

[0037] Various tissue production methods may be employed, including those for imprinted fibrous tissue webs and/or tissue products (e.g., that may have a network of densified regions that have been imprinted against a drum dryer by an imprinting fabric, and regions that are relatively less densified), both creped and uncreped methods of manufacture, and the like. For example, the preparation of the fibrous tissue web and/or tissue product may be carried out in a papermaking machine by mixing dried pretreated pulp fibers with water to form a pretreated pulp fiber slurry. Non-pretreated pulp fibers may optionally be added to the pretreated pulp fiber slurry to form a blended pulp fiber slurry. The pretreated pulp fiber slurry or blended pulp fiber slurry may then be forwarded to a headbox, deposited onto a moving wire or belt (hereinafter belt), dewatered, dried, and processed to form a fibrous tissue web.

[0038] Optionally, additional pulp fiber slurry(ies) comprising non-pretreated pulp fibers may be prepared in the same manner as the pretreated pulp fiber slurry. The pulp slurry(ies), separately or individually, may then be directed

to a stratified headbox where they are deposited onto a moving belt to form a fibrous tissue web. The fibrous tissue web may be dewatered, dried, and processed to form a dried layered fibrous tissue web. For example, as in the wetlaid process for papermaking, the wet fibrous tissue web (formed by depositing the aqueous pulp fiber slurry from the headbox onto the moving belt to filter out the pulp fibers and form an embryonic fibrous tissue web) may be dewatered using suction box(es), wet press(es), dryer unit(s), and the like, as well as combinations comprising at least one of the foregoing processes. Examples of known dewatering and other operations of the papermaking process are set forth in U.S. Pat. No. 5,656,132 issued to Farrington, Jr. et al.; U.S. Pat. No. 5,598,643 issued to Chuang et al.; and, U.S. Pat. No. 4,556,450 issued to Chuang et al. Other examples of possible drying methods include, but are not limited to, drum drying, through air drying, steam drying (e.g., superheated steam drying), displacement dewatering, Yankee drying, infrared drying, microwave drying, radio frequency drying, differential gas pressure drying, impulse drying, and the like, as well as combinations comprising at least one of the above drying techniques. Some exemplary paper making machines are disclosed in U.S. Pat. No. 5,230,776 issued to Andersson et al.

[0039] Optionally, the fibrous tissue webs and/or tissue products may comprise a design, e.g., the fibrous tissue webs and/or tissue products may be embossed with a design, and/or a design may be applied thereto. In one embodiment of the present invention, the pretreated pulp fibers may bond with themselves upon the application of an externally applied stress (e.g., heat, pressure, and/or the like) thereto (e.g., to the fibrous tissue web comprising such pulp fibers).

[0040] The disclosure is further illustrated by the following non-limiting examples. The following test methods were used in the examples.

EXAMPLES

[0041] The dry tensile index or the tensile index of the handsheet strip samples set forth in the examples was determined by performing a dry tensile test on a handsheet strip of 1 inch wide. The handsheet strip sample was placed into a tensile frame at a gauge length of 5 inches. The handsheet strip sample was then subjected to a strain of 0.5 inches per minute and the resulting stress was recorded with an appropriate load cell. The peak load force divided by the width of the handsheet strip sample was recorded as the tensile index after normalization for the basis weight of the handsheet strip sample. The tensile index is expressed in Newton meter per gram (Nm/g). The amount of strain that the handsheet strip sample underwent to obtain a peak load was recorded as a stretch of the handsheet strip sample. The stretch is expressed as a percent (%) of the test length. The slope, in kilogram force (kgf), describes the maximum stress/strain slope recorded by the test during the application of the first 5% of strain. The tensile energy absorbed (TEA), in Joules per square meter (J/m²), describes the integrated area of the stress strain curve divided by the area of the handsheet strip sample being tested.

[0042] The wet tensile index was determined by performing a wet tensile test similar to the dry tensile test on a handsheet strip sample of 1 inch where the handsheet strip sample was wetted thoroughly, by looping the handsheet

strip sample and contacting the bottom of the loop of the handsheet strip sample in deionized water at an ambient temperature. The loop of the handsheet strip sample is held there until the wetted area extends 1 to 1.5 inches lengthwise and is uniform across the entire width of the handsheet strip sample. Excess water is removed from the handsheet strip sample by gently touching the wetted area of the handsheet strip sample once to a blotter paper. A wet tensile index, in Nm/g, was recorded, describing a peak load force divided by the width of the wet handsheet strip sample. The wet tensile index divided by the dry tensile index provided a wet/dry ratio.

Example 1

[0043] This example describes a method to manufacture handsheet strip samples.

[0044] Handsheet strip samples having a basis weight of 60 grams per square meter (g/m^2) were prepared by diluting a pulp fiber sample in water to a consistency of 1.2 wt % in a British Pulp Disintegrator (commercially available from Lorentzen and Wettre located in Atlanta, Ga.). The pulp fiber sample was allowed to soak for 5 minutes before being pulped for 5 minutes at ambient temperature (i.e., about 25° C.), diluted to 0.3 wt % consistency, and formed into a handsheet on a 9 inch by 9 inch Valley Handsheet Mold (commercially available from Voith Inc. Appleton, Wis.). The handsheet was couched off the mold by hand using a blotter paper and pressed wire-side up at 100 psi for 1 minute. The handsheet was dried, wire-side up, for 2 minutes to absolute dryness using a Valley Steam Hotplate (commercially available from Voith Inc. located in Appleton, Wis.) and a standard weighted canvas cover having a weighted tube (4.75 pounds) at one end to maintain constant tension. The resulting handsheet was then conditioned in a humidity controlled room (at 23 degree centigrade (° C.) and 50 percent relative humidity) prior to preparation as a handsheet strip sample and testing.

Example 2

[0045] A first set of bleached Northern softwood kraft pulp fibers comprising 1,000 grams per square meter (g/m^2) dry pulp fiber sheet were soaked with water and allowed to dry to create a control, hereinafter referred to as Control 1, for the handsheet strip sample experiments. These pulp fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples, Control 1, were tested for tensile properties in accordance to the procedure as set forth above.

Example 3

[0046] A second set of bleached Northern softwood kraft pulp fibers were pretreated with a dispersed sulfonated polyester polymer under the trade name Eastman AQ 38D Copolyester (commercially available from Eastman Chemicals located in Kingsport, Tenn.). The treatment involved soaking a 1,000 g/m^2 dry pulp fiber sheet with a solution and allowing the pulp fiber to dry. The dispersion solids were controlled to provide a 1% treatment on a pulp fiber dry weight basis. These pulp fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples,

hereinafter referred to as Sample 1, were tested for tensile properties in accordance to the procedure set forth above.

Example 4

[0047] Additionally a subset of the handsheet strip samples of Sample 1 described in Example 3 were hot-calendared using a steel to steel calendar at 100° C., 120 pounds per linear inch pressure, at a line speed of approximately 25 feet per minute (ft/min). The hot calendared handsheet strip samples, hereinafter referred to as Sample 2, were tested for tensile properties in accordance to the procedure set forth above.

Example 5

[0048] A third set of bleached Northern softwood kraft pulp fibers were pretreated with a dispersed sulfonated polyester polymer under the trade name Eastman AQ 38D Copolyester. The treatment involved soaking a 1,000 g/m^2 dry pulp fiber sheet with a dilute dispersion and allowing the pulp fiber to dry. The dispersion solids were controlled to provide a 2% treatment on a pulp fiber dry weight basis. These fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples, hereinafter referred to as Sample 3, were tested for tensile properties in accordance to the procedure set forth above.

Example 6

[0049] Additionally a subset of the handsheet strip samples from Example 5 were hot-calendared using a steel to steel calendar at 100° C., 120 pounds per linear inch pressure, at a line speed of approximately 25 ft/min. The hot calendared handsheet strip samples, hereinafter referred to as Sample 4, were tested for tensile properties in accordance to the procedure set forth above.

[0050] The resulting properties for the Control 1 as well as Samples 1-4 are shown in Table 1.

TABLE 1

Properties	Pretreated Pulp Properties				
	Control 1	Sample 1	Sample 2	Sample 3	Sample 4
Dry Tensile Index (Nm/g)	21.38	20.93	26.56	23.45	38.45
Stretch (%)	1.56	2.35	2.17	2.88	3.13
TEA (J/m^2)	15.02	21.42	23.17	24.68	35.67
slope (kgf)	456	386	274	322	254
Wet Tensile Index (Nm/g)	1.23	1.84	2.54	1.95	8.32
Wet/dry ratio (%)	5.8	8.8	9.6	8.3	21.6

[0051] The results as shown in Table 1 indicate an increase in strength and stretch, and a decrease in slope on addition of the copolyester, especially after hot calendaring, in the handsheet strip samples, Samples 1-4. As can be seen from the Samples 1-4, tissue products and/or fibrous tissue webs having the following properties may be prepared using the cellulosic pulp fibers and water soluble and/or water dispersible thermoplastic resin of the present invention:

[0052] (i) a stretch of about 2% or greater, or, more specifically about 2.25% or greater, and even more specifically about 2.5% or greater;

[0053] (ii) a wet tensile index of about 1.5 Nm/g or greater, more specifically about 1.8 Nm/g or greater, prior to hot calendaring, while capable of attaining a wet tensile index of about 2.5 Nm/g or greater after hot calendaring, more specifically about 5 Nm/g or greater after hot calendaring;

[0054] (iii) a wet/dry strength ratio of about 8% or greater, more specifically to about 9% or greater, and more specifically about 15% or greater;

[0055] (iv) a TEA of greater than or equal to about 21 J/m² or greater, more specifically about 23 J/m² or greater, more specifically about 30 J/m² or greater; and/or,

[0056] (v) a slope of about 400 kgf or less, more specifically about 350 kgf or less, and more specifically about 300 kgf or less.

Example 7

[0057] A first set of bleached eucalyptus kraft pulp fibers comprising 1,000 g/m² dry pulpsheet were soaked with water and allowed to dry to create a control, hereinafter referred to as Control 2, for the handsheet strip sample experiments. These pulp fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples, Control 2, were tested for tensile properties in accordance with the procedure set forth above.

Example 8

[0058] A second set of bleached eucalyptus kraft pulp fibers were pretreated with a dispersed sulfonated polyester polymer (Eastman AQ 38D Copolyester). The treatment involved soaking a 1,000 g/m² dry pulp fiber sheet with a dilute dispersion and allowing the pulp fibers to dry. The dispersion solids and volume added were controlled to provide a 5% treatment on a pulp fiber dry weight basis. The pretreated pulp fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples, hereinafter referred to as Sample 5, were tested for tensile properties in accordance with the procedure set forth above.

Example 9

[0059] A third set of bleached eucalyptus kraft pulp fibers were pretreated with a polyurethane polymer under the trade name Permax 120 (commercially available from Noveon located in Cleveland, Ohio). The treatment involved soaking a 1,000 g/m² dry pulp fiber sheet with a dilute dispersion and allowing the pulp fibers to dry. The dispersion solids and volume added were controlled to provide a 5% treatment on a pulp fiber dry weight basis. The pretreated pulp fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples, hereinafter referred to as Sample 6, were tested for tensile properties in accordance with the procedure set forth above.

Example 10

[0060] A fourth set of bleached eucalyptus kraft pulp fibers were pretreated with a vinyl acetate polymer under the trade name Vinac 911 (commercially available from Air Products located in Allentown, Pa.). The treatment involved soaking a 1,000 g/m² dry pulp fiber sheet with a dilute dispersion and allowing the pulp fibers to dry. The dispersion solids and volume added were controlled to provide a 5% treatment on a pulp fiber dry weight basis. The pretreated

pulp fibers were slurried and made into standard handsheets, and ultimately handsheet strip samples, as described in Example 1. The handsheet strip samples, hereinafter referred to as Sample 7, were tested for tensile properties in accordance to the procedure as set forth above.

[0061] The resulting properties of Control 2 and Samples 5-7 are shown in Table 2.

TABLE 2

Handsheet Properties				
Properties	Control 2	Sample 5	Sample 6	Sample 7
Dry Tensile Index (Nm/g)	13.5	19.5	13.0	16.9
Stretch (%)	1.3	2.5	3.0	2.9
TEA (J/m ²)	3.5	9.5	5.9	7.9
slope (kgf)	375	254	284	301
Wet Tensile Index (Nm/g)	1.1	3.5	2.9	3.6
Wet/dry ratio (%)	8.1	18.0	22.3	21.3

[0062] The results shown in Table 2 indicate that the handsheet strip samples, Samples 5-7, comprising pulp fibers pretreated with the thermoplastic resin of the present invention have a higher stretch (e.g., about 2.00% or greater, more specifically about 2.50% or greater, versus less than about 1.35% for Control 2) and higher wet tensile index (e.g., about 2.00 Nm/g or greater, more specifically about 2.50 Nm/g or greater, and more specifically about 3.25 Nm/g or greater, versus less than about 1.15 Nm/g for Control 2), and higher wet/dry ratio (e.g., about 12% or greater, more specifically about 15% or greater, and more specifically about 20% or greater, versus less than about 9% for Control 2) while maintaining a lower slope (e.g., about 325 kgf or less, more specifically about 300 kgf or less, and more specifically about 290 kgf or less, versus greater than about 370 kgf for Control 2). Without being bound by theory, it has been discovered that decreasing the slope results in a tissue product and/or fibrous tissue web having higher strength at lower stiffness compared to methods such as refining. This provides a more durable fibrous tissue web and/or tissue product while allowing the fibrous tissue web and/or tissue product to be less brittle which is particularly advantageous for soft tissue products.

[0063] A third set of handsheet experiments were done to provide an example of the effect of the thermoplastic addition through typical wet-end addition of the polymer. The data for the second handsheet experiments, Control 2, was used for this set of experiments.

Example 11

[0064] A fifth set of bleached eucalyptus kraft pulp fibers were made with the wet-end addition of Eastman AQ polymer, hereinafter referred to as Sample 8, for the handsheet strip sample experiments. Handsheet strip samples having a basis weight of 60 grams per square meter (g/m²) were prepared by diluting a pulp fiber sample in water to a consistency of 1.2 wt % in a British Pulp Disintegrator (commercially available from Lorentzen and Wettre located in Atlanta, Ga.). The pulp fiber sample was allowed to soak for 5 minutes before being pulped for 5 minutes at ambient temperature (i.e., about 25° C.), and diluted to 0.3 wt % consistency. A diluted dispersion of Eastman AQ 38D Copolyester was added to the pulp suspension to provide a treatment of approximately 5% on a pulp fiber dry weight

basis and mixed for 5 minutes. This suspension was formed into a handsheet on a 9 inch by 9 inch Valley Handsheet Mold (commercially available from Voith Inc. Appleton, Wis.). The handsheet was couched off the mold by hand using a blotter paper and pressed wire-side up at 100 psi for 1 minute. The handsheet was dried, wire-side up, for 2 minutes to absolute dryness using a Valley Steam Hotplate (commercially available from Voith Inc. located in Appleton, Wis.) and a standard weighted canvas cover having a weighted tube (4.75 pounds) at one end to maintain constant tension. The handsheet strip samples, Sample 8, were tested for tensile properties in accordance with the procedure set forth above.

Example 12

[0065] A sixth set of bleached eucalyptus kraft pulp fibers were made with the wet-end addition of a polyurethane polymer under the trade name Permax 120 (commercially available from Noveon located in Cleveland, Ohio). The treatment was identical to Example 11 with the exception that a dispersion of Permax 120 polymer was used instead of the Eastman AQ 38D to provide a treatment of approximately 5% on a pulp fiber dry weight. The pulp fibers and polymer were mixed, made into standard handsheets, and ultimately made into handsheet strip samples, as described in Example 11. The handsheet strip samples, hereinafter referred to as Sample 9, were tested for tensile properties in accordance with the procedure set forth above.

Example 13

[0066] A seventh set of bleached eucalyptus kraft pulp fibers were made with the wet-end addition of a polyurethane polymer under the trade name Vinac 911 (commercially available from Air Products located in Allentown, Pa.). The treatment was identical to Example 11 with the exception that a dispersion of Permax 120 polymer was used instead of the Eastman AQ 38D to provide a treatment of approximately 5% on a pulp fiber dry weight. The pulp fibers and polymer were mixed, made into standard handsheets, and ultimately made into handsheet strip samples, as described in Example 11. The handsheet strip samples, hereinafter referred to as Sample 10, were tested for tensile properties in accordance with the procedure set forth above.

[0067] The resulting properties of Control 2 and Samples 8-10 are shown in Table 3.

TABLE 3

Properties	Handsheet Properties			
	Control 2	Sample 8	Sample 9	Sample 10
Dry Tensile Index (Nm/g)	13.5	14.1	13.8	12.5
Stretch (%)	1.3	1.4	1.1	1.3
TEA (J/m ²)	3.5	4.1	3.6	3.1
slope (kgf)	375	386	412	391
Wet Tensile Index (Nm/g)	1.1	1.0	1.1	1.0
Wet/dry ratio (%)	8.1	7.1	8.0	8.0

[0068] The results shown in Table 3 indicate that the handsheet strip samples, Samples 8-10, comprising pulp fibers treated with the thermoplastic resin in the wet-end have properties very similar to the control. These examples show the utility of the present invention's pretreatment step which provides unique tensile, stretch, and elastic modulus properties.

[0069] The cellulosic pulp fibers, tissue product, and method of using the cellulosic fibers and water soluble and/or water dispersible thermoplastic resin enables enhanced properties within a fibrous tissue web and/or tissue product when compared to cellulosic pulp fibers with either no pretreatment or treated using a typical wet-end addition. The fibrous tissue webs and/or tissue products comprising pretreated cellulosic pulp fibers and/or layers of the pretreated cellulosic pulp fibers, have a dry and wet strength that imparts durability to the fibrous tissue web and/or tissue product comprising such pretreated cellulosic pulp fibers. Additionally, due to the present process, the pretreated cellulosic pulp fibers may be selectively located within the fibrous tissue web and/or tissue product to attain the desired structural integrity while retaining a desired texture (e.g., softness) of the fibrous tissue web and/or tissue product. Furthermore, since the thermoplastic resin of the present invention is water soluble and/or water dispersible, the fibrous tissue web and/or tissue product may be easily recycled, and, in particular repulped.

[0070] While the disclosure has been described with reference to exemplary embodiments of the present invention, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the disclosure. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the disclosure without departing from the essential scope thereof. Therefore, it is intended that the disclosure not be limited to the particular embodiment of the present invention disclosed as the best mode contemplated for carrying out this disclosure, but that the disclosure will include all embodiments of the present invention falling within the scope of the appended claims.

We claim:

1. A fibrous tissue web, comprising:

cellulosic pulp fibers; and,

pretreated cellulosic pulp fibers, wherein the pretreated cellulosic pulp fiber is formed by pretreating cellulosic pulp fiber with a thermoplastic resin having a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof.

2. The fibrous tissue web of claim 1, wherein the thermoplastic resin is present in an amount of about 0.1 wt % to about 20 wt %, based upon the total weight of the fibrous tissue web.

3. The fibrous tissue web of claim 1, wherein the thermoplastic resin is present in an amount of about 0.5 wt % to about 10 wt %, based upon the total weight of the fibrous tissue web.

4. The fibrous tissue web of claim 1, wherein the cellulosic pulp fibers comprise wood pulp fibers.

5. The fibrous tissue web of claim 1, wherein the pretreated cellulosic pulp fibers comprise wood pulp fibers.

6. The fibrous tissue web of claim 1, wherein the thermoplastic resin is selected from the group consisting essentially of polyurethane, polyethylene-co-vinyl acetate, polyvinyl acetate-co-vinyl alcohol, polyester, polyacrylate, polyvinyl ether, polyamide, and a combination comprising at least one of the foregoing thermoplastic resins.

7. The fibrous tissue web of claim 1, wherein the fibrous tissue web is a wet laid fibrous structure.

8. The fibrous tissue web of claim 1, wherein the fibrous tissue web has been hot calendared.

9. The fibrous tissue web of claim 1, wherein the thermoplastic resin substantially fully coats the pretreated cellulosic pulp fibers.

10. The fibrous tissue web of claim 1, wherein the thermoplastic resin at least partially coats the pretreated cellulosic pulp fibers.

11. The fibrous tissue web of claim 1, wherein a weight ratio of the thermoplastic resin to the pretreated cellulosic pulp fibers is about 1:5 to about 1:1,000.

12. A fibrous tissue web, comprising pretreated cellulosic pulp fibers, wherein the pretreated cellulosic pulp fiber is formed by pretreating cellulosic pulp fiber with a thermoplastic resin having a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof.

13. The fibrous tissue web of claim 12, wherein the thermoplastic resin is present in an amount of about 0.1 wt % to about 20 wt %, based upon the total weight of the fibrous tissue web.

14. The fibrous tissue web of claim 12, wherein the thermoplastic resin is present in an amount of about 0.5 wt % to about 10 wt %, based upon the total weight of the fibrous tissue web.

15. The fibrous tissue web of claim 12, wherein the pretreated cellulosic pulp fibers comprise wood pulp fibers.

16. The fibrous tissue web of claim 12, wherein the thermoplastic resin is selected from the group consisting essentially of polyurethane, polyethylene-co-vinyl acetate, polyvinyl acetate-co-vinyl alcohol, polyester, polyacrylate, polyvinyl ether, polyamide, and a combination comprising at least one of the foregoing thermoplastic resins.

17. The fibrous tissue web of claim 12, wherein the fibrous tissue web is a wet laid fibrous structure.

18. The fibrous tissue web of claim 12, wherein the fibrous tissue web has been hot calendared.

19. The fibrous tissue web of claim 12, wherein the thermoplastic resin substantially fully coats the pretreated cellulosic pulp fibers.

20. The fibrous tissue web of claim 12, wherein the thermoplastic resin at least partially coats the pretreated cellulosic pulp fibers.

21. The fibrous tissue web of claim 12, wherein a weight ratio of the thermoplastic resin to the pretreated cellulosic pulp fibers is about 1:5 to about 1:1,000.

22. Pretreated cellulosic pulp fibers, comprising cellulosic pulp fibers, wherein the cellulosic pulp fibers are pretreated with a thermoplastic resin having a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof, thereby forming the pretreated cellulosic pulp fibers.

23. The pretreated cellulosic pulp fibers of claim 22, wherein the thermoplastic resin is present in an amount of about 0.1 wt % to about 20 wt %, based upon the total weight of the pretreated cellulosic pulp fibers.

24. The pretreated cellulosic pulp fibers of claim 22, wherein the thermoplastic resin is present in an amount of about 0.5 wt % to about 10 wt %, based upon the total weight of the pretreated cellulosic pulp fibers.

25. The pretreated cellulosic pulp fibers of claim 22, wherein the pretreated cellulosic pulp fibers comprise wood pulp fibers.

26. The pretreated cellulosic pulp fibers of claim 22, wherein the thermoplastic resin is selected from the group consisting essentially of polyurethane, polyethylene-co-vinyl acetate, polyvinyl acetate-co-vinyl alcohol, polyester, polyacrylate, polyvinyl ether, polyamide, and a combination comprising at least one of the foregoing thermoplastic resins.

27. The pretreated cellulosic pulp fibers of claim 22, wherein the thermoplastic resin substantially fully coats the pretreated cellulosic pulp fibers.

28. The pretreated cellulosic pulp fibers of claim 22, wherein the thermoplastic resin at least partially coats the pretreated cellulosic pulp fibers.

29. The pretreated cellulosic pulp fibers of claim 22, wherein a weight ratio of the thermoplastic resin to the pretreated cellulosic pulp fibers is about 1:5 to about 1:1,000.

30. A method for making a tissue product, comprising:

treating cellulosic pulp fibers with a thermoplastic resin having a property selected from the group consisting essentially of water soluble, water dispersible, and combinations thereof thereby forming pretreated cellulosic pulp fibers;

forming a fibrous tissue web comprised of the pretreated cellulosic pulp fibers;

and, drying the fibrous tissue web to form the tissue product.

31. The method of claim 31, wherein the thermoplastic resin is present in an amount of about 0.1 wt % to about 20 wt %, based upon the total weight of the fibrous tissue web.

32. The method of claim 31, wherein the thermoplastic resin is present in an amount of about 0.5 wt % to about 10 wt %, based upon the total weight of the fibrous tissue web.

33. The method of claim 31, wherein the pretreated cellulosic pulp fibers comprise wood pulp fibers.

34. The method of claim 31, wherein the thermoplastic resin is selected from the group consisting essentially of polyurethane, polyethylene-co-vinyl acetate, polyvinyl acetate-co-vinyl alcohol, polyester, polyacrylate, polyvinyl ether, polyamide, and a combination comprising at least one of the foregoing thermoplastic resins.

35. The method of claim 31, wherein the fibrous tissue web is a wet laid fibrous structure.

36. The method of claim 31, wherein the fibrous tissue web has been hot calendared.

37. The method of claim 31, wherein the thermoplastic resin substantially fully coats the pretreated cellulosic pulp fibers.

38. The method of claim 31, wherein the thermoplastic resin at least partially coats the pretreated cellulosic pulp fibers.

39. The method of claim 31, wherein a weight ratio of the thermoplastic resin to the pretreated cellulosic pulp fibers is about 1:5 to about 1:1,000.

40. The method of claim 31, wherein the tissue product further comprises cellulosic pulp fibers.

41. The method of claim 40, wherein the cellulosic pulp fibers comprise wood pulp fibers.

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