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Dugan et al.(10) **Pub. No.: US 2006/0159918 A1**(43) **Pub. Date: Jul. 20, 2006**(54) **BIODEGRADABLE FIBERS EXHIBITING
STORAGE-STABLE TENACITY**(52) **U.S. Cl. 428/364**(75) Inventors: **Jeffrey S. Dugan**, Erwin, TN (US);
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(US)(57) **ABSTRACT**

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ALSTON & BIRD LLP**BANK OF AMERICA PLAZA****101 SOUTH TRYON STREET, SUITE 4000****CHARLOTTE, NC 28280-4000 (US)**(73) Assignee: **Fiber Innovation Technology, Inc.**(21) Appl. No.: **11/312,245**(22) Filed: **Dec. 20, 2005****Related U.S. Application Data**(60) Provisional application No. 60/638,860, filed on Dec.
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The invention provides a drawn and/or crimped fiber comprising a biodegradable polymer, such as polylactic acid, wherein the drawn and/or crimped fiber exhibits a storage-stable tenacity that does not decrease from an initial tenacity upon manufacture by more than about 10% after storage for 120 days in ambient conditions. The polymer composition used to form the fiber may comprise a softening agent. The fiber can be a drawn and crimped bicomponent fiber that is helically self-crimped and which comprises a first biodegradable polymer component and a second biodegradable polymer component, wherein the first polymer component and the second polymer component exhibit different polymer morphology such that each polymer component will undergo a different extent of longitudinal shrinkage upon application of heat. The outer surface of the fiber may carry a water-repellant coating. The invention also provides a method of forming a drawn and/or crimped fiber exhibiting storage-stable tenacity.

BIODEGRADABLE FIBERS EXHIBITING STORAGE-STABLE TENACITY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/638,860, filed Dec. 22, 2004, which is incorporated herein by reference in its entirety and for all purposes.

FIELD OF THE INVENTION

[0002] The invention is directed to fibers comprising a biodegradable polymer and methods of making such fibers.

BACKGROUND OF THE INVENTION

[0003] The use of nonwoven fabrics has become increasingly prevalent in a number of industries, and in particular, has found increasing usefulness as a component of a variety of consumer products. Exemplary uses for nonwoven fabrics include, without limitation, absorbent personal care products such as diapers, incontinence pads, feminine hygiene products and the like; medical products such as surgical drapes and sterile wipes; filtration devices; interlinings; disposable wipes; furniture and bedding construction; insulating products; apparel and the like. A variety of thermoplastic and thermobondable synthetic fibers have been found to be particularly useful for nonwoven fabric manufacture due to their advantageous strength and weight characteristics, as well as their ease of processing.

[0004] Conventional synthetic fibers, however, do not naturally degrade, thus creating problems associated with the disposal of products containing such fibers. The recycling of articles containing nonwoven fabrics is generally not cost-effective, leading to the creation of non-degradable waste material. The disposal of diapers provides a good example of the problems associated with non-degradable waste. Disposable diapers rely heavily on the use of nonwoven fabrics in their construction. Millions of diapers are discarded every year, thereby contributing to landfill capacity problems.

[0005] To address concerns about solid waste disposal, biodegradable polymers are increasingly used as a replacement for conventional synthetic polymers. Biodegradable aliphatic polyesters, such as polyglycolic acid and polylactic acid, are examples of biodegradable polymers that degrade by means of microorganisms under natural environmental conditions and/or by hydrolysis.

[0006] Although biodegradable fibers are known, problems have been encountered with their use. For example, problems associated with the storage stability of polylactic acid fibers have been noted. Drawn and crimped staple fibers comprising polylactic acid have a tendency to lose a significant degree of tenacity in a relatively short period of time, which limits their usefulness.

[0007] There remains a need in the art for a biodegradable fiber, particularly a fiber comprising polylactic acid, which maintains desirable fiber characteristics, such as stable strength levels, during periods of storage.

BRIEF SUMMARY OF THE INVENTION

[0008] The present invention provides a fiber comprising a biodegradable polymer, such as an aliphatic polyester.

Exemplary aliphatic polyesters include polyglycolic acid, polylactic acid, polyhydroxy butyrate, polyhydroxy valerate, polycaprolactone, and copolymers thereof. Preferred embodiments of the fiber of the invention exhibit a storage-stable tenacity, meaning tenacity does not decrease from an initial tenacity upon manufacture by more than about 10% after storage for 120 days in ambient conditions. As a result, the present invention provides a fiber comprising a biodegradable polymer that is capable of maintaining a desired level of strength for a longer period of time.

[0009] The fiber of the invention preferably has an initial tenacity upon manufacture of at least about 1.5 g/denier, more preferably an initial tenacity of at least about 3.0 g/denier. In certain embodiments, the fiber has an initial tenacity of about 1.5 to about 15 g/denier.

[0010] In some embodiments, the tenacity of the fiber does not decrease by more than about 10%, preferably by no more than about 5%, after storage for 120 days in ambient conditions. Thus, it is believed that the fibers of the invention are capable of maintaining a desired level of tenacity for periods of 120 days or more, preferably 180 days or more, and most preferably 240 days or more. In some embodiments, the tenacity of the fiber in the invention does not decrease from its initial level by more than about 10% after storage for more than 360 days.

[0011] It has been discovered that fibers formed of biodegradable polymers lose strength, in part, due to hydrolytic attack of the polymer by moisture present in an ambient storage environment. This gradual loss of strength (i.e., tenacity) over time reduces the value and usefulness of the fibers. The loss of strength under ambient conditions is surprising, since it was conventionally thought that such polymers would only degrade under relatively extreme, biotic conditions. Thus, in one embodiment of the invention, the fiber includes a water-repellant coating carried by the outer surface of the fiber, or the polymer composition includes one or more surface-active agents capable of migrating to the surface of the fiber and inhibiting water adsorption. The fiber coating or surface-active additive may comprise any water-repellant or waterproof material known in the art, such as various waxes, silicone-based materials, polymer resins, and fluorocarbon compounds.

[0012] Additionally, it has been discovered that the fiber forming process can be manipulated in a number of ways to decrease the susceptibility of the fiber to hydrolytic attack in ambient conditions. Specifically, it has been determined that stresses introduced into the fiber during fiber processing can lead to hydrolytic degradation of the polymer chain, even under ambient conditions, because stresses within the polymer chain can pull apart hydrolyzed bonds and prevent them from reattaching and "healing" the scission, as would normally occur in an unstressed polymer. Additionally, stresses in the polymer chain of the fiber can lead to the formation of voids in the fiber that further increase the susceptibility of the fiber to hydrolysis by providing increased space within the fiber for water to collect. It has also been discovered that the formation of internal stresses and voids in the fiber can be exacerbated by the presence of crystalline portions within the fiber.

[0013] Thus, in another embodiment, the invention provides a drawn and crimped bicomponent fiber, comprising a biodegradable polymer selected from the group consisting of

polyvinyl alcohol, aliphatic polyesters, aliphatic polyurethanes, cis-polyisoprene, cis-polybutadiene, polyhydroxy alkanates, and copolymers and blends thereof, the fiber exhibiting a storage-stable tenacity that does not decrease from an initial tenacity upon manufacture by more than about 10 percent after storage for 120 days in ambient conditions, wherein the initial tenacity is at least about 1.5 g/denier, and wherein the bicomponent fiber is helically self-crimped and comprises a first biodegradable polymer component and a second biodegradable polymer component, wherein the first polymer component and the second polymer component exhibit different polymer morphology such that each polymer component will undergo a different extent of longitudinal shrinkage upon application of heat. The self-crimping aspect of such a fiber design avoids the need to mechanically crimp the fiber, which can introduce undesirable stresses in the polymer that can lead to a loss of tenacity during storage.

[0014] In another aspect, the invention includes a method of forming a drawn and/or crimped fiber characterized by a storage-stable tenacity that does not decrease from an initial tenacity upon manufacture by more than about 10% after storage for 120 days in ambient conditions. In one embodiment utilizing a melt spinning technique, the method can include the steps of:

[0015] a) providing a viscous molten polymer composition comprising a biodegradable polymer;

[0016] b) extruding the viscous molten polymer composition through a spinneret to form a plurality of molten meltspun fibers;

[0017] c) passing the molten meltspun fibers through a quenching chamber;

[0018] d) contacting the molten meltspun fibers with a cooling fluid in the quenching chamber in order to solidify the meltspun fibers;

[0019] e) collecting the solidified meltspun fibers on a take-up surface;

[0020] f) drawing the solidified meltspun fibers in a manner sufficient to increase the tenacity of the fibers to at least about 1.5 g/denier; and

[0021] g) optionally, crimping the drawn meltspun fibers.

[0022] The present invention manipulates the above-described process in a manner that improves the storage stability of fiber tenacity. The method of manipulating the process can take a variety of forms. For example, the storage stability of fiber tenacity may be improved by one or more of the following steps:

[0023] 1) increasing the distance between the spinneret and the point at which the molten meltspun fibers solidify prior to reaching the take-up surface;

[0024] 2) using a spin-draw ratio of less than about 200:1;

[0025] 3) adding a softening agent to the polymer composition;

[0026] 4) applying a water-repellent coating to the meltspun fibers prior to, during, in-between, or shortly after said drawing (f) and crimping (g) steps;

[0027] 5) using a biodegradable polymer having a low weight average molecular weight of about 10,000 to about 30,000 Da, which is substantially lower than the molecular weight of poly(lactic acid) conventionally used in fiber processing;

[0028] 6) heat-treating the meltspun fibers in a relaxed state after one or both of said drawing (f) and crimping (g) steps, the heat treatment being conducted at a temperature and for a time sufficient to reduce internal fiber stresses;

[0029] 7) providing a self-crimping fiber by extruding the polymer composition comprising a biodegradable polymer with a second polymer composition, which can comprise a different polymer, or the same biodegradable polymer having dissimilar polymer morphology, thereby forming a multicomponent meltspun fiber, and wherein said crimping (g) step comprises subjecting the multicomponent meltspun fiber to a heat treatment conducted at a temperature and for a time sufficient to cause the multicomponent meltspun fiber to helically self-crimp; or

[0030] 8) any combination of two or more of steps 1-7.

[0031] Although the present invention is described in terms of fiber production useful in the nonwoven, woven and knit fabric industries, as will be apparent to one of ordinary skill in the art, the invention could also be applied to other common forms of polymer materials. For instance, the biodegradable polymers of the invention could be provided in the form of a coating or film, a molded product, a laminate, a foam, and the like.

DETAILED DESCRIPTION OF THE INVENTION

[0032] The present invention now will be described more fully hereinafter. However, this invention may be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will satisfy applicable legal requirements. As used in this specification and the claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

[0033] The term "fiber" as used herein means both fibers of finite length, such as conventional staple fiber, as well as substantially continuous structures, such as continuous filaments, unless otherwise indicated. The fibers of the invention can be hollow or non-hollow fibers, and further can have a substantially round or circular cross section or non-circular cross sections (for example, oval, rectangular, multi-lobed, and the like).

[0034] As used herein, the term "multicomponent fibers" includes staple and continuous filaments prepared from two or more polymers present in discrete structured domains in the fiber, as opposed to blends where the domains tend to be dispersed, random or unstructured. It should be understood that the scope of the present invention is meant to include fibers with two or more structured components.

[0035] The invention is directed to a polymer composition comprising a biodegradable polymer and, in preferred embodiments, the biodegradable polymer is in the form of a

drawn and/or crimped fiber. The present invention provides a fiber comprising a biodegradable polymer that exhibits a storage-stable tenacity when prepared using the method of the invention described below. In particular, it has been determined that the fibers of the invention exhibit a tenacity that does not decrease from an initial tenacity upon manufacture by more than about 10% after storage for 120 days in ambient conditions, more preferably no more than about 5%. In certain embodiments, the fibers of the invention exhibit storage-stable tenacity as defined above after storage for 180 days, 240 days, or even 360 days.

[0036] As used herein, the term “ambient conditions” refers to an environment wherein the temperature is 20-30° C., the relative humidity is about 70-100%, and the fiber is under no external tensile or compressive stresses.

[0037] The term “drawn” refers to a fiber that has undergone a strengthening process wherein the fiber is subjected to longitudinal stretching that reduces the diameter of the fiber and increases strength in terms of tenacity.

[0038] The term “crimped” refers to the presence of undulations in the fiber, typically in an amount of at least about 4 crimps per inch (counted peak-to-peak), more preferably at least about 8 crimps per inch.

[0039] The initial tenacity upon manufacture of the fibers of the invention is preferably at least about 1.5 g/denier, more preferably at least about 3.0 g/denier, and typically falls within the range of about 1.5 to about 15 g/denier. In one embodiment, initial tenacity upon manufacture falls within the range of about 3 to about 10 g/denier. Tenacity of the drawn and/or crimped fiber of the invention can be measured by the procedure described in ASTM test method D 3822 95A, “Standard Test Method for Tensile Properties of Single Textile Fibers,” ASTM International, which is incorporated by reference in its entirety. For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at [service\[@000a\]stm.org](mailto:service[@000a]stm.org).

[0040] As used herein, the term “biodegradable polymer” refers to a polymeric material that degrades under aerobic and/or anaerobic conditions in the presence of bacteria, fungi, algae, and other microorganisms to carbon dioxide/methane, water and biomass, although materials containing heteroatoms can also yield other products such as ammonia or sulfur dioxide. “Biomass” generally refers to the portion of the metabolized materials incorporated into the cellular structure of the organisms present or converted to humus fractions indistinguishable from material of biological origin. As a result, the biodegradable fiber, either in its initial form or after incorporation into a fabric, will begin to degrade (in some cases following hydrolysis) when exposed to such microorganisms even if such exposure occurs prior to the expiration of the useful life of the fiber.

[0041] Exemplary biodegradable polymers include, without limitation, polyvinyl alcohol, aliphatic polyesters, aliphatic polyurethanes, cis-polyisoprene, cis-polybutadiene, polyhydroxy alkanates, and the like and copolymers and blends thereof. Aliphatic polyesters such as polylactic acid are preferred. The skilled artisan will appreciate that when polylactic acid is used, the polylactic acid polymer is first hydrolyzed before microorganisms can consume the hydrolysis products. However, hydrolysis may be acceler-

ated by heat and/or chemicals (e.g., acids or enzymes) generated by the microorganisms.

[0042] The term “aliphatic polyester” refers to polymers having the structure $—[C(O)—R—O]_n—$, wherein n is an integer representing the number of monomer units in the polymer chain and R is an aliphatic hydrocarbon, preferably a C1-C10 alkylene, more preferably a C1-C6 alkylene (e.g., methylene, ethylene, propylene, isopropylene, butylene, isobutylene, and the like), wherein the alkylene group can be a straight chain or branched. Exemplary aliphatic polyesters include polyglycolic acid (PGA), polylactic acid (PLA), polyhydroxy butyrate (PHB), polyhydroxy valerate (PHV), polycaprolactone (PCL), and copolymers thereof. The term “copolymer” as used herein is intended to encompass polymers formed from any combination of monomers of two or more of the above-described polymers. The aliphatic polyester polymers of the invention can be homopolymers of any of the foregoing polymers, random copolymers, block copolymers, alternating copolymers, and the like. The copolymers of the invention also include copolymers formed from monomer units of one or more of the above polymers and one or more comonomers that form diacid esters or glycol esters.

[0043] Polylactic acid, which is a preferred aliphatic polyester, is generally prepared by the polymerization of lactic acid or lactide. Therefore, as used herein, the term “polylactic acid polymer” is intended to encompass polymers that are prepared by the polymerization of either lactic acid or lactide. Reference is made to U.S. Pat. Nos. 5,698,322; 5,142,023; 5,760,144; 5,593,778; 5,807,973; and 5,010,145, the entire disclosure of each of which is hereby incorporated by reference.

[0044] Lactic acid and lactide are known to be asymmetrical molecules, having two optical isomers referred to, respectively as the levorotatory (hereinafter referred to as “L”) enantiomer and the dextrorotatory (hereinafter referred to as “D”) enantiomer. As a result, by polymerizing a particular enantiomer or by using a mixture of the two enantiomers, it is possible to prepare polymers that are chemically similar yet which have widely differing properties.

[0045] In a preferred embodiment, the only fiber-forming polymer components of the fibers of the invention are biodegradable polymers, and fibers formed exclusively of polylactic acid, and comprising no other fiber-forming polymer component, are particularly preferred. The polymer composition comprising the biodegradable polymer may optionally include other additives or components that do not adversely affect the desired properties of the composition. Exemplary conventional additives include, without limitation, pigments, antioxidants, stabilizers, waxes, flow promoters, solid solvents, particulates, and other materials added to enhance processability. These additives can be used in conventional amounts, which typically do not exceed about 10% by weight based on the total weight of the polymer composition.

[0046] The invention includes a method of forming the fibers of the invention characterized by a storage-stable tenacity as described above. The fibers are preferably formed using a “melt spinning” technique, which is understood to refer to a fiber-forming technique wherein a fiber is prepared by forcing a viscous polymer composition through

a device comprising a plurality of orifices of predetermined size and shape, such as a spinneret. In one embodiment utilizing a melt spinning technique, the method includes the steps of:

[0047] a) providing a viscous molten polymer composition comprising a biodegradable polymer;

[0048] b) extruding the viscous molten polymer composition through a spinneret to form a plurality of molten meltspun fibers;

[0049] c) passing the molten meltspun fibers through a quenching chamber;

[0050] d) contacting the molten meltspun fibers with a cooling fluid (e.g., chilled or ambient air or an aqueous bath) in the quenching chamber in order to solidify the meltspun fibers;

[0051] e) collecting the solidified meltspun fibers on a godet or other take-up surface;

[0052] f) drawing the solidified meltspun fibers in a manner sufficient to increase the tenacity of the fibers to at least about 1.5 g/denier; and

[0053] g) optionally, crimping the drawn meltspun fibers.

[0054] The melt spinning process also typically includes the application of a spin finish to the meltspun fibers prior to collecting the solidified meltspun fibers on a take-up device or at later stages of the fiber-forming process, such as during drawing, between drawing and crimping, or between crimping and cutting. The melt spinning method of the invention may include other conventional processing steps known in the art, such as washing, cutting, twisting, and coning.

[0055] The above melt spinning process is typically used to form staple fibers and filament yarns. However, other melt spinning processes could also be used in the present invention, such as processes used to form meltblown and spunbond fibers. The term "meltblown" is used herein in the conventional sense to refer to fibers formed by extruding a molten thermoplastic polymer composition through a plurality of fine, usually circular, die capillaries of a spinneret as molten threads or filaments into converging high velocity gas streams (e.g., air) which function to attenuate the threads or filaments to reduced diameters. Thereafter, the filaments or threads are carried by the high velocity gas streams and deposited onto a collecting surface to form a web of dispersed meltblown fibers with average diameters generally smaller than 10 microns. The term "spunbond" is used herein in the conventional sense to refer to fibers formed by extruding a molten thermoplastic polymer composition as filaments through a plurality of fine, usually circular, die capillaries of a spinneret with the diameter of the extruded filaments then being rapidly reduced and thereafter depositing the filaments onto a collecting surface to form a web of dispersed spunbond fibers with average diameters generally between about 7 and about 30 microns.

[0056] Methods and apparatuses for making fibers are well known in the art and need not be described here in detail. Generally, the fibers of the invention are prepared using conventional textile fiber spinning processes and apparatus and utilizing mechanical drawing and crimping techniques known in the art. Processing conditions for melt extrusion and fiber formation are well known in the art and may be

employed in the invention, except as modified by the remainder of this specification. An exemplary fiber spinning apparatus useful for producing the fibers of the invention is described in U.S. Pat. No. 6,361,736, issued Mar. 26, 2002, the entire disclosure of which is hereby incorporated by reference.

[0057] As noted above, the continuous filaments collected by the take-up device may be crimped or texturized to form a continuous tow, and cut to a desired fiber length, thereby producing staple fiber. The lengths of staple fibers generally range from about 25 to about 75 millimeters, although the fibers can be longer or shorter as desired. In general, staple fibers, tow, continuous filaments, and spunbond fibers formed in accordance with the present invention can have a fineness of about 0.5 to about 100 denier. Meltblown filaments can have a fineness of about 0.001 to about 10.0 denier. Monofilament fibers can have a fineness of about 50 to about 10,000 denier. Advantageously, the fibers or filaments of the invention are directed to a suitable apparatus as known in the art to form a yarn of the fibers or filaments. The resultant yarn can include a plurality of fibers in accordance with the present invention.

[0058] It has been surprisingly discovered that the loss of tenacity during storage that can occur under ambient conditions in fibers comprising a biodegradable polymer, particularly fibers that have been drawn and/or crimped, is caused by hydrolytic attack and breakdown of the polymer structure. It has been conventionally thought that biodegradable polymers, such as polylactic acid, do not hydrolyze in the absence of relatively extreme, biotic conditions characterized by high temperatures and high humidity, because hydrolyzed bonds along the polymer chain will "heal" themselves by reattachment of the ester linkages. However, it has been discovered that biodegradable polymer under longitudinal stress, such as the stress experienced by a fiber during processing, recoil too quickly and forcefully to allow the hydrolyzed bonds to reattach. As a result, the healing process is forestalled and the fiber loses strength due to a breakdown in the polymer structure.

[0059] It is believed that mechanical stresses experienced by the fibers during various processing steps, such as, for example, the drawing and crimping processes, can also lead to "crazing" or cavitation, wherein openings or voids are formed in the fiber that provide a convenient place for water to collect. Thus, formation of voids in a fiber can further exacerbate the problem of hydrolysis under ambient conditions due to the ability of voids to act as water reservoirs. Therefore, in another aspect of the invention, the fiber-forming process is manipulated in order to reduce the formation of polymer stresses and voids in the fiber.

[0060] In one aspect, the invention provides a method for improving the storage stability of the tenacity of a fiber by providing a barrier that prevents water from interacting with the biodegradable polymer chain. In one embodiment of the invention, a drawn and crimped fiber comprising a biodegradable polymer is provided, wherein the outer surface of the fiber carries a water-repellant coating. Alternatively, the biodegradable polymer composition can include one or more surface-active agents capable of migrating to the surface of the fiber and inhibiting water adsorption. As used herein, the term "water-repellant" encompasses coatings that are either water-repellant or waterproof, as those terms are normally

used in the field of textiles. Such materials include any known material suitable for use as a coating that is either hydrophobic and/or provides a barrier that inhibits the passage of water. Exemplary materials include various waxes, silicone-based coatings, certain polymeric resins, and fluorocarbon compounds (e.g., polytetrafluoroethylene).

[0061] The water-repellant coating may be applied before, during, in-between, or after the drawing and crimping processes. Preferably, the coating is applied no later than shortly after the drawing and crimping processing steps in order to minimize the time period during which the fiber is exposed to water. In one embodiment, the coating is applied within about six hours, more preferably within about two hours, and most preferably the coating is applied in-line after the crimping process, meaning less than about 1 minute after crimping. In another preferred embodiment, the coating is applied to the fiber prior to the drawing and crimping processes.

[0062] As noted above, it is preferable to minimize the stresses experienced by the biodegradable polymer during fiber processing so that internal stresses within the resulting fiber are not of sufficient magnitude to promote hydrolytic degradation of the polymer chains at ambient conditions. In one embodiment, substantially all of the internal stresses exhibited by the fiber are less than the craze stress for the particular polymer being processed (i.e., the craze stress for the particular polymer type, grade, and molecular weight). As would be understood, the term "craze stress" refers to the stress at which "crazing" occurs in the polymer chain, which is the initiation of a narrow crack or void that is bridged at intervals across its surface by fibrils of polymer chains. The formation of crazes is sometimes referred to as "stress whitening" due to the white color that results from light scattering by the void. In preferred embodiments, the stress levels of the polymer chains within the fibers of the invention are less than about 80% of the craze stress, more preferably less than about 70% of the craze stress, most preferably less than about 60% of the craze stress, in order to reduce or eliminate the occurrence of hydrolyzable bonds in the polymer chain that are under internal stress sufficient to prevent healing of the bonds upon hydrolysis at ambient conditions.

[0063] The craze stress can be measured using conventional tensile strength testing equipment designed to record a stress-strain curve, which typically include:

[0064] a means of gripping a standard specimen;

[0065] a means of stretching the specimen at constant rate;

[0066] a range of strain rates;

[0067] a means of measuring strain, strain rate and load; and

[0068] a means of imposing appropriate loads to the material under investigation, e.g., an INSTRON tensile tester.

[0069] To determine craze stress, master stress/strain curves can be determined by performing a series of tensile tests at various strain rates and temperatures. The resulting data can be presented as plots of nominal yield stress/T vs. ln (strain rate) for the temperatures tested. A craze stress test can then be performed by notching polymer specimens and

stretching the specimens in the longitudinal direction. The resulting fracture surfaces can be examined using a Scanning Electron Microscope (e.g., Hitachi S800) to determine the craze nucleation site. Craze stress is the stress it takes to initiate craze-type fractures.

[0070] One method for reducing the formation of overstressed polymer chains is to include a softening agent in the polymer composition prior to processing. It is believed that a softening agent will improve the ability of the polymer to stretch during processing steps without forming undesirably high internal stresses within the polymer chains. As used herein, the term "softening agent" refers to an additive that increases polymer ductility. Exemplary softening agents include two commercially available aromatic-aliphatic copolyesters comprising butanediol, adipic acid and terephthalic acid monomers; namely, EASTAR BIO manufactured by Eastman Chemical and ECOFLEX manufactured by BASF.

[0071] The softening agent can be a plasticizer, wherein the term "plasticizer" refers to a polymer additive that softens the polymer by increasing the free volume within a polymer chain, thereby lowering the glass transition temperature (T_g) of the polymer. Any plasticizer known in the art can be utilized. Exemplary plasticizers include alkyl or aliphatic esters and ethers, such as alkyl phosphate esters, dialkylether diesters, tricarboxylic esters, epoxidized oils and esters, polyesters, polyglycol diesters, alkyl alkylether diesters, aliphatic diesters, alkylether monoesters, citrate esters, dicarboxylic esters, vegetable oils, glycerin esters and derivatives thereof. A single softening agent or a mixture of softening agents can be used. Typically, a softening agent is added at a concentration level of about 1 to 25%, more preferably about 1 to 10% by weight, most preferably about 2 to about 5% by weight, based on the total weight of the polymer composition. The softening agents should be miscible or semi-miscible with the biodegradable polymer.

[0072] It has also been surprisingly discovered that reducing the crystallinity of the polymer structure prior to drawing can decrease the formation of stressed polymer chains that can lead to hydrolytic degradation under ambient conditions. Although it is conventionally understood that polymer orientation and crystal formation in melt spinning results in increased fiber strength once the fiber is drawn, it has been discovered that crystal regions in the polymer do not fully or readily yield during drawing or crimping processes, and this failure to yield can lead to undesirably high internal polymer stresses or the formation of voids in the polymer chains between the crystals. Such fibers exhibit commercially unacceptable reduction in tenacity after more than 90 days in ambient storage. One solution is to include an additive in the polymer composition that serves to retard crystal nucleation and growth. Certain softening agents, such as the preferred softening agents described above, can also serve as crystallization retardants that introduce irregularities in the crystalline order and/or increase free volume.

[0073] Another solution is to adjust the conditions experienced by the fiber during melt spinning in a manner that reduces or minimizes crystal formation. There are a number of process manipulations that result in reduced crystal formation. For instance, any manipulation of the process that results in maintaining the meltspun fibers in a molten state for a greater distance from the spinneret will reduce crystal

formation. In other words, the meltspun fibers travel in a molten state for a greater percentage of the distance between the spinneret and the take-up surface, such as the take-up godet. Moving the "stick point," i.e., the point at which the fibers solidify, closer to the take-up surface allows greater drawing or attenuation of the fibers without inducing orientation and, thus, crystallization of the polymer. The meltspun fibers can be maintained in the molten state for a greater distance from the spinneret by increasing the spinning temperature or increasing the quenching temperature (e.g., by reducing the fluid flow through the quenching chamber, increasing the temperature of the fluid flowing through the quenching chamber or insulating the quenching chamber). The meltspun fibers should solidify before reaching the godet or other take-up device to prevent adherence of the fiber to the take-up surface. The actual increase in spinning or quenching temperature that is required will depend on the polymer involved, but can be readily ascertained without undue experimentation. Drawing speed can also affect the stick point, as slower drawing allows time for polymer relaxation to occur before solidification. For purposes of the invention, it is preferred to perform spin-drawing while the material can still relax, meaning before solidification. The stick point in conventional PLA spinning commonly occurs in about the first 40 inches below the spinneret. In a preferred embodiment of the present invention, the stick point occurs greater than about 40 inches below the spinneret, more preferably greater than about 50 inches, most preferably greater than about 60 inches.

[0074] Reducing the spin-draw ratio will also reduce crystal formation. The term "spin-draw ratio" is used in its conventional sense to refer to the ratio of the spinneret capillary cross-sectional area to the cross sectional area of the solid, undrawn filament. In preferred embodiments of the present invention, the spin-draw ratio is less than about 200:1, more preferably less than about 100:1. Exemplary ranges of spin-draw ratios include about 200:1 to about 10:1, more preferably about 100:1 to about 30:1.

[0075] It has also been discovered that, contrary to conventional wisdom, use of high molecular weight biodegradable polymers does not increase fiber strength, but rather contributes to losses in fiber strength during storage. It is believed that high molecular weight causes so many bridging chains between crystals that the biodegradable polymer chain cannot plastically deform without creating undesirable stresses between two lamellae that have shifted their relative positions during yielding of the fiber. Thus, in one embodiment of the invention, the biodegradable polymer, such as PLA, has a weight average molecular weight in the range of about 10,000 to about 100,000 Da, more preferably about 20,000 to about 50,000 Da.

[0076] Furthermore, it has been discovered that certain regions within the polymer can be oriented during melt spinning, but remain in amorphous form. These oriented amorphous regions can remain under stress, which also invites a loss of strength due to hydrolysis. Thus, in one aspect of the invention, the biodegradable polymer is subjected to a heat treatment after the drawing and crimping processes in order to remove the internal stresses within the oriented amorphous regions of the polymer. The heat treatment step is conducted at a temperature and for a time sufficient to reduce internal fiber stresses. Typically, the heat treatment temperature is near, but below, the T_g of the

polymer. For PLA, the preferred heat treatment is conducted at a temperature of about 40 to about 60° C., and for about 30 to about 90 minutes. It is important that the heat treatment step occur while the fiber is in a relaxed state, meaning the fiber is under no external tensile or compressive forces.

[0077] In yet another embodiment of the present invention, the drawn and/or crimped fiber containing a biodegradable polymer is a multicomponent fiber capable of self-crimping, meaning the fiber will helically contract upon application of heat without subjecting the fiber to mechanical stresses associated with conventional crimping equipment. Conventional mechanical crimping techniques stress the polymer chain of the fiber at the points in the fiber where the crimps or bends are formed. Use of a self-crimping fiber avoids the forceful mechanical introduction of bends in the fiber and thereby removes a potential source of polymer stresses. A self-crimping fiber can be formed by preparing a multicomponent fiber comprising two or more polymers having dissimilar polymer morphology. As used herein, the term "dissimilar polymer morphology" refers to differences in polymer structure that lead to differences in the extent of longitudinal shrinkage that a polymer chain will undergo upon the application of heat while the fiber is in a relaxed state. Examples of dissimilar polymer morphology would include polymer compositions of different molecular weight or different isomeric content, or polymer compositions having differences in orientation, which can be achieved by differing the heat history of each polymer material prior to extrusion. As would be understood, the term "heat history" refers to the accumulated total thermal energy input into the polymer system. In a preferred embodiment, the multicomponent fiber is a bicomponent fiber in an eccentric sheath/core arrangement or a side-by-side arrangement. Although less preferred, other multicomponent fiber configurations arranged such that the average geometrical centers of the cross sectional domain areas of each respective polymer component are significantly distant from each other may be used without departing from the invention.

[0078] In one preferred embodiment, each polymer component of the multicomponent fiber is an aliphatic polyester as described above, such as polylactic acid, having different polymer morphology, such as molecular weight, D-isomer content, or orientation. For example, one embodiment of a multicomponent fiber of the invention comprises a first polylactic acid component and a second polylactic acid component, wherein each component has a different amount of L and D-isomer. An exemplary multicomponent fiber of this embodiment comprises a first polylactic acid component having an L-isomer content of about 98% by weight and a D-isomer content of about 2% by weight, based on the total weight of the polymer, and a second polylactic acid component having an L-isomer content of 95% by weight and a D-isomer content of about 5% by weight. In another exemplary multicomponent fiber of the invention, the above weight percentages for the L- and D-isomer are reversed in each polymer component. Typically, one of the L- or D-isomer will be present in each polymer component of the fiber in a range of 1 to about 10% by weight and the other will be present in a range of about 90 to 99% by weight.

[0079] In an example of a multicomponent fiber comprising two components with different molecular weights, a first polylactic acid component has a weight average molecular weight of about 200,000 Da and a second polylactic acid

component has a weight average molecular weight of about 300,000 Da. Preferably, the difference in molecular weight of each component is at least about 15% of the higher molecular weight, more preferably at least about 25%, and most preferably at least about 33%.

[0080] In an embodiment of a multicomponent fiber having two components with different heat history, separate streams of polymer with identical molecular weight and chemical composition are extruded together, with one stream extruded at about 210° C. and the other stream extruded at about 240° C. Both streams must pass through the spinneret together, and the spinneret can be at only one temperature, but the dwell time in the spin pack can be limited to minimize the ability of the two streams to converge toward a common temperature. In such a case, the spin pack temperature can be set between the two stream temperatures to minimize the driving force for both streams to heat up/cool down. After extruding the bicomponent fiber from the spinneret, the quench conditions can be arranged to maintain the temperature differences as much as possible. For instance, a side-by-side fiber can be extruded with the “hot” polymer component facing away from a quench air stream impinging the fibers from one side only, while the “cool” polymer would be oriented to face into the quench stream.

[0081] In preferred embodiments of the method of the invention, two or more of the above process manipulations are combined to reduce internal polymer stresses and the overall susceptibility of the fiber to hydrolytic degradation. For instance, a softening agent can be added to the polymer composition prior to extrusion and, in addition, the spin-draw ratio and quenching chamber conditions can be controlled as described above to further reduce crystallization and the introduction of internal stresses or voids in the polymeric fiber.

[0082] The fibers of the invention are useful in the production of a wide variety of products, including without limitation, nonwoven structures, such as, but not limited to, carded webs, wet laid webs, dry laid webs, spunbonded webs, meltblown webs, and the like. The term “nonwoven” as used herein and in the conventional sense means a web or fabric having a structure of individual fibers or threads that are interlaid in an irregular manner rather than in an identifiable pattern as is the case for a knitted fabric. The fibers of the invention can also be used to make other textile structures such as woven and knit fibers. Fibers other than the fibers of the invention may be present in articles produced therefrom, including any of the various synthetic and/or natural fibers known in the art. Exemplary synthetic

fibers include polyolefin, polyester, polyamide, acrylic, rayon, cellulose acetate, thermoplastic multicomponent fibers, and the like. Exemplary natural fibers include wool, cotton, wood pulp fibers, and the like.

[0083] In addition, although the focus of the specification is on biodegradable polymers in the form of drawn and/or crimped fibers, it will be appreciated that the biodegradable polymer compositions of the invention will find usefulness in other forms. Although the process of fiber spinning intrinsically leads to the creation of more polymer stresses than many other types of polymer processing, the concepts underlying the present invention are equally applicable to other polymer processing techniques that cause residual stresses in the polymer. For example, film materials comprising the biodegradable polymer composition can be formed, which may find usefulness as a packaging material or in the production of garbage bags. Additionally, the biodegradable polymer composition can be used to form various molded products, which can be made using a variety of processes, including blow molding, injection molding, and thermoforming. Exemplary molded products include disposable cutlery, bottles, and the like. Other material types include laminates and coextrudates. Film laminates and coextruded films are composite materials in which each layer provides a functional utility that compliments the rest of the structure. The biodegradable polymer composition of the invention would be useful where a degradable layer is needed in a laminate or coextrudate. Further, the biodegradable polymer composition may be used in the form of a foam. Foam thermoplastics have large markets in food packaging. The biodegradable polymer composition of the invention can also be used in the form of a coating, such as a coating designed to temporarily protect an underlying substrate against abrasion or other harm.

[0084] The present invention will be further illustrated by the following non-limiting examples.

EXPERIMENTAL

[0085] A number of PLA fibers were meltspun to illustrate the present invention. All examples used the standard PLA grade from Cargill-Dow, 6200D, except Example 4, which is a sheath/core fiber comprising two different PLA grades, one having elevated D isomer content (Cargill-Dow, 5039D). The fibers of Comparative Examples 1-3 were made using conventional PLA processing parameters. All spinning conditions were standard except as noted. All aging was done under ambient storage conditions. Tables 1 and 2 set forth key processing parameters and results of tenacity testing.

TABLE 1

	Ex. No.					
	1	2	3	4	5	6
Type	Control	Control	Control	1.6D/5.2D eccentric sheath/core	2% BIO*	Unoriented, Cold-Draw
Crimp?	No	Yes	Yes	Yes (Spiral)	Yes	No
Spin Speed, (m/min)	1450	1450	1440	1440	1240	193
Hole Size (mm)	0.35	0.35	0.6	0.6	0.6	0.4
Spin-Draw Ratio	339:1	339:1	998:1	816:1	744:1	79:1
Spun Denier (g/9000 m)	3.5	3.5	3.5	4.4	4.8	20
Drawn Denier (g/9000 m)	1.5	1.5	1.5	2.5	1.2	12.5

TABLE 1-continued

	Ex. No.					
	1	2	3	4	5	6
1st Stage Draw @70° C.						1.5
2nd Stage Draw @70° C.						na
2nd Stage Draw @100° C.						na
Total Draw Ratio	2.7	2.7	3.3	1.9	3.9	1.5
Original Tenacity (g/d)	4.7	3.7	4.4	3.0	4.5	1.4
Aged Tenacity (g/d)	3.7	2.7	2.2	2.8	5.4	1.4
Aging Time (mos.)	5	5	6	6	15	7
% Change	-20	-26	-50	-6	+20	0

*EASTAR BIO GP available from Eastman Chemical Company

[0086]

TABLE 2

	Ex. No.				
	7	8	9	10	11
Type	Unoriented, Cold-Draw	Unoriented, Staged Draw	Unoriented, Cold-Draw	Unoriented, Staged Draw	Unoriented, Staged Draw
Crimp?	No	No	No	No	No
Spin Speed, (m/min)	193	193	193	193	193
Hole Size (mm)	0.4	0.4	0.4	0.4	0.4
Spin-Draw Ratio	79:1	79:1	79:1	79:1	79:1
Spun Denier (g/9000 m)	20	20	20	20	20
Drawn Denier (g/9000 m)	10.5	2.3	7.7	2.8	2.1
1st Stage Draw @70° C.	2.0	2.0	2.9	2.9	2.9
2nd Stage Draw @70° C.	na	1.1	na	1.14	1.71
2nd Stage Draw @100° C.	na	4.0	na	2.23	2.22
Total Draw Ratio	2.0	8.8	2.9	7.4	11.1
Original Tenacity (g/d)	1.6	5.8	2.2	5.7	6.4
Aged Tenacity (g/d)	1.8	6.2	2.5	4.6	5.8
Aging Time (mos.)	7	7	7	7	7
% Change	+9	+7	+14	-19	-9

[0087] Comparative Examples 1-3 show the typical behavior of PLA. Example 1 was uncrimped, but presumably crazed upon drawing after high-speed spinning (crystallization in spinning). Examples 2 and 3 show increasingly inferior properties when mechanical crimping is added. In all three comparative examples, tenacity was reduced by 20% or more after 5 or 6 months of storage.

[0088] Example 4 shows the effect of generating spiral crimp with eccentric sheath/core spinning of two different PLA grades (one with elevated D isomer, PLA 5039D). The lesser draw results in reduced tenacity but the fiber only loses 6% on aging and is useful given the spiral crimp.

[0089] Example 5 shows the effect of incorporating just 2% EASTAR BIO GP from Eastman Chemical Company. EASTAR BIO is a copolyester of butylene glycol with a mixture of 57 mole % adipic acid and 43 mole % terephthalic acid. The softening effect of the EASTAR BIO allows the fiber to be drawn to a high degree and crimped without loss of properties and actually increases tenacity upon aging.

[0090] Examples 6, 7, and 9 show the effect of low speed spinning followed by moderate amounts of draw in a single subsequent stage at 70° C. Note that with increasing draw, the tenacity increases but also an observed increase in tenacity upon aging is seen to increase with drawing. In all

these cases, the relatively amorphous, unoriented material is drawn without creating internal stresses or crazes.

[0091] Example 8 shows that it is possible to take the minimally drawn PLA from Example 7 and draw it again to a high degree, resulting in high tenacity and a fiber that improves tenacity upon aging.

[0092] Examples 10 and 11 shows that, in contrast to Example 8, once a fiber has been drawn beyond a certain point, as in Example 9, the fiber can no longer be drawn in a second stage without sacrificing properties. A second stage draw increases tenacity but at the expense of shelf stability, resulting in a product that degrades significantly upon ambient aging. It is presumed that the initial 2.9× draw created crystallinity which resisted further draw, which then resulted in stresses and crazes that were susceptible to permanent hydrolytic degradation upon aging.

[0093] Note in particular that Example 9 shows the 2.9× draw alone did not damage the shelf life, and that Example 8 shows that the final total draw alone does not characterize the process, since it falls between the draw ratios of Examples 10 and 11. The damage to shelf life clearly comes from a high initial draw that hardens the material, followed by additional processing.

[0094] Many modifications and other embodiments of the inventions set forth herein will come to mind to one skilled

in the art to which these inventions pertain having the benefit of the teachings presented in the foregoing description. Therefore, it is to be understood that the inventions are not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation.

That which is claimed:

1. A fiber that has been drawn or crimped or both, comprising a biodegradable polymer selected from the group consisting of polyvinyl alcohol, aliphatic polyesters, aliphatic polyurethanes, cis-polyisoprene, cis-polybutadiene, polyhydroxy alkanoates, and copolymers and blends thereof, the fiber exhibiting a storage-stable tenacity that does not decrease from an initial tenacity upon manufacture by more than about 10 percent after storage for 120 days in ambient conditions, wherein the initial tenacity is at least about 1.5 g/denier.

2. The fiber of claim 1, wherein the internal stresses of the polymer are less than about 80% of the craze stress of the polymer.

3. The fiber of claim 2, wherein the internal stresses of the polymer are less than about 70% of the craze stress of the polymer.

4. The fiber of claim 1, wherein the biodegradable polymer is an aliphatic polyester.

5. The fiber of claim 4, wherein the aliphatic polyester is selected from the group consisting of polyglycolic acid (PGA), polylactic acid (PLA), polyhydroxy butyrate (PHB), polyhydroxy valerate (PHV), polycaprolactone (PCL), and copolymers thereof.

6. The fiber of claim 4, wherein the polyester is polylactic acid (PLA).

7. The fiber of claim 1, wherein the fiber has an initial tenacity upon manufacture of at least about 3.0 g/denier.

8. The fiber of claim 1, wherein the fiber has an initial tenacity upon manufacture of about 1.5 to about 15 g/denier.

9. The fiber of claim 1, wherein the fiber is a staple fiber or continuous filament.

10. The fiber of claim 1, wherein the tenacity does not decrease by more than about 5 percent.

11. The fiber of claim 1, wherein the tenacity does not decrease by more than about 10 percent after 360 days of storage.

12. The fiber of claim 1, wherein the fiber is a bicomponent self-crimping fiber.

13. The fiber of claim 12, wherein the fiber comprises a first biodegradable polymer component and a second biodegradable polymer component, wherein the first polymer

component and the second polymer component exhibit different polymer morphology such that each polymer component will undergo a different extent of longitudinal shrinkage upon application of heat.

14. The fiber of claim 13, wherein said first polymer component and said second polymer component comprise the same biodegradable polymer, and wherein the difference in molecular weight between the first and second polymer components is at least about 15 percent of the higher molecular weight.

15. The fiber of claim 13, wherein the heat history of said first polymer component is different from the heat history of said second polymer component.

16. The fiber of claim 13, wherein said first polymer component and said second polymer component comprise polylactic acid (PLA).

17. The fiber of claim 16, wherein said first polymer component and said second polymer component each comprise a mixture of L and D-isomers of poly(lactic acid), and wherein said first and second polymer components differ in the relative amounts of L and D-isomer.

18. The fiber of claim 1, wherein the outer surface of the fiber carries a water-repellent coating.

19. The fiber of claim 1, wherein the polymer is poly(lactic acid) having a weight average molecular weight of about 10,000 to about 100,000 Da.

20. The fiber of claim 19, wherein the weight average molecular weight of the poly(lactic acid) is about 20,000 to about 50,000 Da.

21. The fiber of claim 1, wherein the fiber comprises a softening agent.

22. The fiber of claim 21, wherein the softening agent comprises an aromatic-aliphatic copolyester comprising butanediol, adipic acid and terephthalic acid monomers.

23. A drawn and crimped bicomponent fiber, comprising a biodegradable polymer selected from the group consisting of polyvinyl alcohol, aliphatic polyesters, aliphatic polyurethanes, cis-polyisoprene, cis-polybutadiene, polyhydroxy alkanoates, and copolymers and blends thereof, the fiber exhibiting a storage-stable tenacity that does not decrease from an initial tenacity upon manufacture by more than about 10 percent after storage for 120 days in ambient conditions, wherein the initial tenacity is at least about 1.5 g/denier, and wherein the bicomponent fiber is helically self-crimped and comprises a first biodegradable polymer component and a second biodegradable polymer component, wherein the first polymer component and the second polymer component exhibit different polymer morphology such that each polymer component will undergo a different extent of longitudinal shrinkage upon application of heat.

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