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(54) Title: PRODUCTION OF NON-WOVEN MATERIALS FROM POLYHYDROXYALKANOATE

(57) Abstract: Methods and compositions for making non-woven materials from polyhydroxyalkanoate polymers are provided. In certain aspects, the invention pertains to an extruded fiber comprising a polyhydroxyalkanoate polymer, a wet milled nucleating agent and a plasticizer, wherein the average particle size of the wet-milled nucleating agent is about 20 microns and is dispersed in the polymer.



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PRODUCTION OF NON-WOVEN MATERIALS FROM POLYHYDROXYALKANOATE

RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Application No. 61/203,542, filed on December 23, 2008.

[0002] This application also claims priority to International Application No. PCT/US2009/041023, which designated the United States and was filed on April 17, 2009 and published in English. The entire teachings of the above applications are incorporated herein by reference.

BACKGROUND

[0003] Biodegradable plastics are of increasing industrial interest as replacements or supplements for non-biodegradable plastics in a wide range of applications. One class of biodegradable polymers is the polyhydroxyalkanoates (PHAs). These polymers are synthesized by soil microbes for use as intracellular storage material. Articles made from the polymers are generally recognized by soil microbes as a food source. There has therefore been a great deal of interest in the commercial development of these polymers, particularly for disposable consumer items. To date, however, PHAs have seen limited commercial availability, with only the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) being available in development quantities.

[0004] Although various PHAs are capable of being processed on conventional processing equipment, many problems have been found with the polymers. These include lack of processability in some situations, which can limit the commercial applications available for use of the polymer. Molecular weight can be difficult to maintain, and a loss of molecular weight can lead to brittleness of the final product. In addition, the crystallization kinetics of the polymer are poorly understood, and long cycle times are often required during processing of these polymers, further limiting their commercial acceptance. This especially limits the use of the polymers in applications involving non-woven materials. A need exists for addressing these problems.

SUMMARY

[0005] The invention pertains to fiber compositions for use in making polymeric non-woven materials. In certain embodiments, the extruded melt-blown fibers comprise a polyhydroxyalkanoate polymer, a wet milled nucleating agent and a plasticizer. In certain embodiments, the nucleating agent is boron nitride. In other embodiments, the nucleating agent is in a nucleating composition. In other embodiments, the average particle size of the wet-milled nucleating agent is about 20 microns. In yet other embodiments, the plasticizer is acetyl tri-n-butyl citrate. In certain embodiments, the fiber is melt-blown. In certain embodiments, the basis weight is from about 20 to about 160 GSM (grams per square meter). In certain embodiments, the fibers comprise about 75% to about 95% by weight polyhydroxyalkanoate polymer. In other embodiments, the fiber diameter is about 0.1 to about 50 microns.

[0006] The invention also pertains to a fiber comprising a polymer, a plasticizer and a nucleating agent, wherein the nucleating agent is dispersed in the polymer and wherein at least 5% of the cumulative solid volume of the nucleating agent exists as particles with a particle size of 5 microns or less.

[0007] Disclosed herein is an extruded melt-blown fiber that includes a biologically-produced polyhydroxyalkanoate, a wet-milled nucleating agent and a plasticizer, where the fiber has a weight-average molecular weight of at least about 150 kg/mol. In other embodiments, the weight-average molecular weight is at least about 200 kg/mol, at least about 250 kg/mol.

[0008] In a particular embodiment, the fiber contains between about 75% and about 95% by weight biologically-produced polyhydroxybutyrate and between about 5% and about 15% acetyl tri-n-butyl citrate. In certain embodiment, the fiber contains between about 0.1% to about 10 % nucleating agent or nucleating composition by weight of the total composition, for example, between about 1% to about 10% nucleating agent.

[0010] In certain embodiment, the molecular weight of the fibers is about 150 kg/mol to about 250 kg/mol. In any of the embodiments disclosed herein, the fiber has a molecular weight of at least about 150 kg/mol, for example, about 160 kg/mol, about 170 kg/mol, about 180 kg/mol. The fiber can have a molecular weight of at least about 200 kg/mol. In particular embodiments, the fiber can have a molecular

weight of about 160 kg/mol to about 170 kg/mol, such as 166 kg/mol, 167 kg/mol, 168 kg/mol, 169 kg/mol. In other embodiments, the fiber can have a molecular weight of at least about 250 kg/mol.

[0011] Another embodiment discloses a non-woven web that includes any of the fibers disclosed herein.

[0012] Also disclosed is a disposable article that includes any of the fibers disclosed herein.

[0013] Other features and advantages of the invention will be apparent from the following detailed description, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a diagram showing the general melt blowing process.

[0015] FIG. 2 is a graph showing the Universal non-woven tensile strength / elongation curve for six samples of 90% PHB and 10% CITROFLEX[®] A4 plasticizer.

[0016] FIG. 3 is a photomicrograph showing fibers made from 90% PHB and 10% CITROFLEX[®] A4 plasticizer.

[0017] FIG. 4 is a graph showing the Universal non-woven tensile strength for six samples of 90% PHB and 10% CITROFLEX[®] A4 plasticizer.

[0018] FIG. 5 is a graph showing apparent melt viscosity (pa-s) versus dwell time of the fibers made in Example 5.

[0019] FIG. 6 is a photomicrograph showing fibers made in Example 5.

DETAILED DESCRIPTION

[0020] The invention provides non-woven materials made from biologically produced polyhydroxyalkanoate (PHA) polyesters. The non-woven material can optionally include other polymers, including biodegradable or non-biodegradable polymers.

[0021] The fibers produced by the methods described herein, in particular, melt blown fibers, have reduced brittleness and improved physical properties, such as resiliency, strength and elasticity.

[0022] Many physical properties and rheological properties of polymeric materials depend on the molecular weight and distribution of the polymer.

Molecular weight is calculated in a number of different ways. Unless otherwise indicated, “molecular weight” refers to weight average molecular weight.

[0023] “Weight average molecular weight” (M_w) is the sum of the products of the molecular weight of each fraction, multiplied by its weight fraction ($\sum N_i M_i^2 / \sum N_i M_i$). M_w is generally greater than or equal to M_n . M_z is the Z-average of the molecular weight distribution ($\sum N_i M_i^3 / \sum N_i M_i^2$).

[0024] “Number average molecular weight” (M_n) represents the arithmetic mean of the distribution, and is the sum of the products of the molecular weights of each fraction, multiplied by its mole fraction ($\sum N_i M_i / \sum N_i$).

[0025] “Molecular weight retention” is the weight-average molecular weight of the extruded fibers as a percentage of the weight average molecular weight of the starting material.

[0026] As used herein, “basis weight” is the weight of a unit area of fabric formed by the fibers described herein. It is measured in grams per square meter (GSM).

[0027] “Crystallinity” as used herein refers to the presence of three-dimensional order on the level of atomic dimensions. In polymers, the range of order may be as small as about 2 nm in one (or more) crystallographic direction(s) and is usually below 50 nm in at least one direction. Polymer crystals frequently do not display the perfection that is usual for low-molecular mass substances. Polymer crystals that can be manipulated individually are often called polymer single crystals.

[0028] “Embrittlement,” as used herein, is the loss or reduction of toughness, generally caused by the loss of plasticizers by aging or overheating. Fibers become brittle and easily break over time.

[0029] “Elasticity,” as used herein is a physical property that corresponds to the flexibility of a fiber or non-woven that has reversible deformation under stress. In other words, after removal of a stress the material has the ability to return to its original state.

[0030] The “thermal stability” of a polymer sample is measured in two different ways. The thermal stability is represented herein by a sample’s “k,” which shows the change in M_w over time. It can also be measured by melt capillary stability (MCS), which shows the change in the capillary shear viscosity over time.

[0031] Tensile properties are measured according to ASTM D412, Test method A-Standard Test Method for Vulcanized Rubber and Thermoplastic Elastomers as provided by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA.

[0032] “Tensile strength” refers to the measure of the ability of a polymer to withstand pulling stresses.

[0033] “Tensile modulus” refer to the ratio of stress to strain for a given material within its proportional limit.

[0034] “Toughness”, as used herein, refers to a property of a material by virtue of which it can absorb energy; the actual work per unit volume or unit mass of material that is required to rupture it. Toughness is typically proportional to the area under the load-elongation curve such as the tensile stress-strain curve.

[0035] “Elongation” or “extensibility” of a material means the amount of increase in length resulting from, as an example, the tension to break a specimen. It is expressed usually as a percentage of the original length. When a material is tested for tensile strength it elongates a certain amount before fracture takes place. The two pieces are placed together and the amount of extension is measured against marks made before starting the test and is expressed as a percentage of the original gauge length. “Peak elongation” refers to the greatest amount of length expanded prior to breakage. “Peak force” refers to the greatest amount of force applied prior to breakage. “Max Load” refers to the total superimposed weight that the specimen (*e.g.*, a fiber) can carry without breaking.

[0036] A nucleating agent is an agent that provides sites for crystal formation in polymer melts. A nucleating composition is a composition that comprises a nucleating agent. A wet-milled nucleating agent is one that has been milled in a liquid carrier to an average particle size of less than 20 microns in diameter. In other embodiments, the nucleating agent has been wet milled to an average particle size of between about 6 microns to about 20 microns in diameter. The wet milled nucleating agent is dispersed (mixed throughout the composition) in the composition or prepared in a nucleating pellet with a carrier polymer and is dispersed in a liquid carrier that is then added to the composition for producing a fiber.

[0037] The nucleating agent of the methods and compositions herein include boron nitride, cyanuric acid or related compounds, carbon black, mica talc, silica,

clay, calcium carbonate, synthesized silicic acid and salts, metal salts of organophosphates, kaolin, and other materials. In particular methods and compositions, the nucleating agent is boron nitride. Other nucleating agents known to the skilled person can be used in the compositions and methods of the invention.

[0038] Wet-milling means milling or grinding a composition in a liquid (*e.g.*, liquid carrier) until a desired average particle size is achieved, as distinguished from micronized or air jet milled versions of the composition. For purposes of the present invention, grinding is commonly continued until the average particle size is reduced. In air jet milling, compressed air is forced through a nozzle to be accelerated to supersonic speeds. At these speeds, it enters the crushing chamber, and fluidizes the powder that has been placed within it. An air jet milling machine usually has several nozzles pointed into the chamber from different angles. The fluidized powder converges at the meeting point of the nozzles, and is subjected to violent collision, shearing and grinding. Fine particles are transported by updraft to a sorting area where they are classified by centrifugal force, while coarser materials remain in the grinding chamber. For example, this process can be used for reducing a nucleating agent from 50-250 microns in size down to less than 20 microns.

[0039] In certain aspects of the invention, after wet-milling the average particle size is less than 20 microns. In other aspects of the invention, after wet-milling at least 5 % of the cumulative solid volume of the nucleating agents exists as particles with an average particle size of 5 microns or less, in other embodiments, at least 10% of the cumulative solid volume of the nucleating agent exists as particles with an average particle size of 5 microns or less. In other aspects, at least 20% of the cumulative solid volume of the nucleating agent exists as particles with an average particle size of 5 microns. In still other aspects, at least 30% of the cumulative solid volume of the nucleating agent exists as particles with an average particle size of 5 microns. In yet other aspects, at least 40% or at least 50% of the cumulative solid volume of the nucleating agent exists as particles with an average particle size of 5 microns. In the foregoing aspects, the nucleating agent has an average particle size of 20 microns or less or 1 micron or less.

[0040] Nucleating agents dispersed as fine particles, with reduced agglomeration of the particles into larger particle sizes, or degradation of the polymer during the

compounding step are obtained for use in the methods and compositions of the invention.

[0041] “Non-woven” as generally used herein refers to a manufactured construct that is made of a randomly aligned collection of fibers that are bonded by cohesion and/or adhesion, as opposed to knitted or woven constructs in which the fibers or threads are wrapped around one another in a regular fashion.

[0042] “Melt processing,” as generally used herein, refers to a thermal process in which a material is melted, formed into a shape and then cooled to retain a desired shape. For example, typical melt processing techniques include melt extrusion and injection molding.

[0043] Melt blowing is a process for producing fibrous webs directly from polymeric resins using high velocity air to attenuate the filaments. The general scheme of the process is presented in FIG. 1. The melt blown process is a one step process in which high velocity air blows a molten thermoplastic resin from the extruder die tip onto a conveyor or take up screen to form a fine fibrous and self bonded web. A typical process consists of the following elements: an extruder, metering pumps, die assembly, web formation and winding.

[0044] The melt blowing process is one of the newer non-woven processes and is growing in popularity. This process is unique because it is used almost exclusively to produce microfibers rather than fibers the size of normal textile fibers. Melt blown fibers have a diameter of about 0.1 to about 50 microns. Melt blown microfibers generally have diameters in the range of about 2 to about 4 microns and may be as small as about 0.1 micron and as large as about 15 microns. Differences between melt blown nonwoven fabrics and other non-woven fabrics, such as degree of softness, opacity and porosity can be generally traced to the differences in filament size.

[0045] General properties of non wovens include but are not limited to: random fiber orientation; lower to moderate web strength, generally high opacity (having a high cover factor); basis weight ranges from about 8 to about 350 g/m²; typically about 20 to about 200 g/m²; high surface area for good insulation and filtration characteristics; produce webs that are layered or shingled in construction with the number of layers increasing with basis weight; able to be layered with other

nonwoven structures and or films, able to produce multicomponent melt blown nonwovens by co-extruding different polymers through different dies.

[0046] The market for meltblown fibers is vast, and the fibers are used in products such as wipes, barrier products and filtration products.

Polyhydroxyalkanoates (PHAs) are suitable for the melt blown technology and for the formation of different web types, and are attracting the interest of many manufacturers because of their biodegradability and biobased source.

[0047] POLYHYDROXYALKANOATES (PHAS)

[0048] The polymers (*e.g.*, base and/or carrier polymers) for use in the methods and compositions described herein are polyhydroxyalkanoate (hereinafter referred to as PHAs). Polyhydroxyalkanoates are biological polyesters synthesized by a broad range of natural and genetically engineered bacteria as well as genetically engineered plant crops (Braunegg *et al.*, (1998), *J. Biotechnology* 65: 127-161; Madison and Huisman, 1999, *Microbiology and Molecular Biology Reviews*, 63: 21-53; Poirier, 2002, *Progress in Lipid Research* 41: 131-155). These polymers are biodegradable thermoplastic materials, produced from renewable resources, with the potential for use in a broad range of industrial applications (Williams & Peoples, *CHEMTECH* 26:38-44 (1996)). Useful microbial strains for producing PHAs, include *Alcaligenes eutrophus* (renamed as *Ralstonia eutropha*), *Alcaligenes latus*, *Azotobacter*, *Aeromonas*, *Comamonas*, *Pseudomonads*, and genetically engineered organisms including genetically engineered microbes such as *Pseudomonas*, *Ralstonia* and *Escherichia coli*.

[0049] In general, a PHA is formed by enzymatic polymerization of one or more monomer units inside a living cell. Over 100 different types of monomers have been incorporated into the PHA polymers (Steinbüchel and Valentin, *FEMS Microbiol. Lett.* 128; 219-228 (1995)). Examples of monomer units incorporated in PHAs include 2-hydroxybutyrate, lactic acid, glycolic acid, 3-hydroxybutyrate (hereinafter referred to as 3HB), 3-hydroxypropionate (hereinafter referred to as 3HP), 3-hydroxyvalerate (hereinafter referred to as 3HV), 3-hydroxyhexanoate (hereinafter referred to as 3HH), 3-hydroxyheptanoate (hereinafter referred to as 3HHep), 3-hydroxyoctanoate (hereinafter referred to as 3HO), 3-hydroxynonanoate (hereinafter referred to as 3HN), 3-hydroxydecanoate (hereinafter referred to as 3HD), 3-

hydroxydodecanoate (hereinafter referred to as 3HDd), 4-hydroxybutyrate (hereinafter referred to as 4HB), 4-hydroxyvalerate (hereinafter referred to as 4HV), 5-hydroxyvalerate (hereinafter referred to as 5HV), and 6-hydroxyhexanoate (hereinafter referred to as 6HH). 3-hydroxyacid monomers incorporated into PHAs are the (D) or (R) 3-hydroxyacid isomer with the exception of 3HP which does not have a chiral center.

[0050] In some embodiments, the PHA can be a homopolymer (where all monomer units are the same). Examples of PHA homopolymers include poly 3-hydroxyalkanoates (*e.g.*, poly 3-hydroxypropionate (hereinafter referred to as P3HP), poly 3-hydroxybutyrate (hereinafter referred to as PHB) and poly 3-hydroxyvalerate), poly 4-hydroxyalkanoates (*e.g.*, poly 4-hydroxybutyrate (hereinafter referred to as P4HB), or poly 4-hydroxyvalerate (hereinafter referred to as P4HV)) and poly 5-hydroxyalkanoates (*e.g.*, poly 5-hydroxyvalerate (hereinafter referred to as P5HV)).

[0051] In certain embodiments, the PHA can be a copolymer (containing two or more different monomer units) in which the different monomers are randomly distributed in the polymer chain. Examples of PHA copolymers include poly 3-hydroxybutyrate-co-3-hydroxypropionate (hereinafter referred to as PHB3HP), poly 3-hydroxybutyrate-co-4-hydroxybutyrate (hereinafter referred to as PHB4HB), poly 3-hydroxybutyrate-co-4-hydroxyvalerate (hereinafter referred to as PHB4HV), poly 3-hydroxybutyrate-co-3-hydroxyvalerate (hereinafter referred to as PHB3HV), poly 3-hydroxybutyrate-co-3-hydroxyhexanoate (hereinafter referred to as PHB3HH) and poly 3-hydroxybutyrate-co-5-hydroxyvalerate (hereinafter referred to as PHB5HV).

[0052] By selecting the monomer types and controlling the ratios of the monomer units in a given PHA copolymer a wide range of material properties can be achieved. Although examples of PHA copolymers having two different monomer units have been provided, the PHA can have more than two different monomer units (*e.g.*, three different monomer units, four different monomer units, five different monomer units, six different monomer units). An example of a PHA having 4 different monomer units would be PHB-co-3HH-co-3HO-co-3HD or PHB-co-3-HO-co-3HD-co-3HDd (these types of PHA copolymers are hereinafter referred to as PHB3HX). Typically where the PHB3HX has 3 or more monomer units the 3HB monomer is at least 70% by weight of the total monomers, preferably 85% by

weight of the total monomers, most preferably greater than 90% by weight of the total monomers for example 92%, 93%, 94%, 95%, 96% by weight of the copolymer and the HX comprises one or more monomers selected from 3HH, 3HO, 3HD, 3HDd.

[0053] The homopolymer (where all monomer units are identical) PHB and 3-hydroxybutyrate copolymers (PHB3HP, PHB4HB, PHB3HV, PHB4HV, PHB5HV, PHB3HHP, hereinafter referred to as PHB copolymers) containing 3-hydroxybutyrate and at least one other monomer are of particular interest for commercial production and applications. It is useful to describe these copolymers by reference to their material properties as follows. Type 1 PHB copolymers typically have a glass transition temperature (T_g) in the range of 6°C to -10°C , and a melting temperature T_M of between 80°C to 180°C . Type 2 PHB copolymers typically have a T_g of -20°C to -50°C and T_M of 55°C to 90°C .

[0054] Preferred Type 1 PHB copolymers have two monomer units have a majority of their monomer units being 3-hydroxybutyrate monomer by weight in the copolymer, for example, greater than 78% 3-hydroxybutyrate monomer. Preferred PHB copolymers for this invention are biologically produced from renewable resources and are selected from the following group of PHB copolymers:

[0055] PHB3HV is a Type 1 PHB copolymer where the 3HV content is in the range of 3% to 22% by weight of the polymer and preferably in the range of 4% to 15% by weight of the copolymer for example: 4% 3HV; 5% 3HV; 6% 3HV; 7% 3HV; 8% 3HV; 9% 3HV; 10% 3HV; 11% 3HV; 12% 3HV 13% 3HV; 14% 3HV; 15% 3HV.

[0056] PHB3HP is a Type 1 PHB copolymer where the 3HP content is in the range of 3% to 15% by weight of the copolymer and preferably in the range of 4% to 15% by weight of the copolymer for example: 4% 3HP; 5% 3HP; 6% 3HP; 7% 3HP; 8% 3HP; 9% 3HP; 10% 3HP; 11% 3HP; 12% 3HP, 13% 3HP; 14% 3HP; 15% 3HP.

[0057] PHB4HB is a Type 1 PHB copolymer where the 4HB content is in the range of 3% to 15% by weight of the copolymer and preferably in the range of 4% to 15% by weight of the copolymer for example: 4% 4HB; 5% 4HB; 6% 4HB; 7% 4HB; 8% 4HB; 9% 4HB; 10% 4HB; 11% 4HB; 12% 4HB; 13% 4HB; 14% 4HB; 15% 4HB.

[0058] PHB4HV is a Type 1 PHB copolymer where the 4HV content is in the range of 3% to 15% by weight of the copolymer and preferably in the range of 4% to 15% by weight of the copolymer for example: 4% 4HV; 5% 4HV; 6% 4HV; 7% 4HV; 8% 4HV; 9% 4HV; 10% 4HV; 11% 4HV; 12% 4HV; 13% 4HV; 14% 4HV; 15% 4HV.

[0059] PHB5HV is a Type 1 PHB copolymer where the 5HV content is in the range of 3% to 15% by weight of the copolymer and preferably in the range of 4% to 15% by weight of the copolymer for example: 4% 5HV; 5% 5HV; 6% 5HV; 7% 5HV; 8% 5HV; 9% 5HV; 10% 5HV; 11% 5HV; 12% 5HV; 13% 5HV; 14% 5HV; 15% 5HV.

[0060] PHB3HH is a Type 1 PHB copolymer where the 3HH content is in the range of 3% to 15% by weight of the copolymer and preferably in the range of 4% to 15% by weight of the copolymer for example: 4% 3HH; 5% 3HH; 6% 3HH; 7% 3HH; 8% 3HH; 9% 3HH; 10% 3HH; 11% 3HH; 12% 3HH; 13% 3HH; 14% 3HH; 15% 3HH.

[0061] PHB3HX is a Type 1 PHB copolymer where the 3HX content is comprised of 2 or more monomers selected from 3HH, 3HO, 3HD and 3HDd and the 3HX content is in the range of 3% to 12% by weight of the copolymer and preferably in the range of 4% to 10% by weight of the copolymer for example: 4% 3HX; 5% 3HX; 6% 3HX; 7% 3HX; 8% 3HX; 9% 3HX; 10% 3HX by weight of the copolymer.

[0062] Type 2 PHB copolymers have a 3HB content of between 80% and 5% by weight of the copolymer, for example: 80%, 75%, 70%, 65%, 60%, 55%, 50%, 45%, 40%, 35%, 30%, 25%, 20%, 15%, 10%, 5% by weight of the copolymer.

[0063] PHB4HB is a Type 2 PHB copolymer where the 4HB content is in the range of 20% to 60% by weight of the copolymer and preferably in the range of 25% to 50% by weight of the copolymer for example: 25% 4HB; 30% 4HB; 35% 4HB; 40% 4HB; 45% 4HB; 50% 4HB by weight of the copolymer.

[0064] PHB5HV is a Type 2 PHB copolymer where the 5HV content is in the range of 20% to 60% by weight of the copolymer and preferably in the range of 25% to 50% by weight of the copolymer for example: 25% 5HV; 30% 5HV; 35% 5HV; 40% 5HV; 45% 5HV; 50% 5HV by weight of the copolymer.

[0065] PHB3HH is a Type 2 PHB copolymer where the 3HH is in the range of 35% to 95% by weight of the copolymer and preferably in the range of 40% to 80% by weight of the copolymer for example: 40% 3HH; 45% 3HH; 50% 3HH; 55% 3HH; 60% 3HH; 65% 3HH; 70% 3HH; 75% 3HH, 80% 3HH by weight of the copolymer.

[0066] PHB3HX is a Type 2 PHB copolymer where the 3HX content is comprised of 2 or more monomers selected from 3HH, 3HO, 3HD and 3HDd and the 3HX content is in the range of 30% to 95% by weight of the copolymer and preferably in the range of 35% to 90% by weight of the copolymer for example: 35% 3HX; 40% 3HX; 45% 3HX; 50% 3HX; 55% 3HX; 60% 3HX; 65% 3HX; 70% 3HX; 75% 3HX; 80% 3HX; 85% 3HX; 90% 3HX by weight of the copolymer.

[0067] PHAs for use in the methods, compositions and pellets described in this invention are selected from: PHB or a Type 1 PHB copolymer; a PHA blend of PHB with a Type 1 PHB copolymer where the PHB content by weight of PHA in the PHA blend is in the range of 5% to 95% by weight of the PHA in the PHA blend; a PHA blend of PHB with a Type 2 PHB copolymer where the PHB content by weight of the PHA in the PHA blend is in the range of 5% to 95% by weight of the PHA in the PHA blend; a PHA blend of a Type 1 PHB copolymer with a different Type 1 PHB copolymer and where the content of the first Type 1 PHB copolymer is in the range of 5% to 95 % by weight of the PHA in the PHA blend; a PHA blend of a Type 1 PHB copolymer with a Type 2 PHA copolymer where the content of the Type 1 PHB copolymer is in the range of 30% to 95% by weight of the PHA in the PHA blend; a PHA blend of PHB with a Type 1 PHB copolymer and a Type 2 PHB copolymer where the PHB content is in the range of 10% to 90% by weight of the PHA in the PHA blend, where the Type 1 PHB copolymer content is in the range of 5% to 90% by weight of the PHA in the PHA blend and where the Type 2 PHB copolymer content is in the range of 5% to 90% by weight of the PHA in the PHA blend.

[0068] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB3HP where the PHB content in the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 3HP content in the PHB3HP is in the range of 7% to 15% by weight of the PHB3HP.

[0069] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB3HV where the PHB content of the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 3HV content in the PHB3HV is in the range of 4% to 22% by weight of the PHB3HV.

[0070] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB4HB where the PHB content of the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 4HB content in the PHB4HB is in the range of 4% to 15% by weight of the PHB4HB.

[0071] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB4HV where the PHB content of the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 4HV content in the PHB4HV is in the range of 4% to 15% by weight of the PHB4HV.

[0072] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB5HV where the PHB content of the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 5HV content in the PHB5HV is in the range of 4% to 15% by weight of the PHB5HV.

[0073] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB3HH where the PHB content of the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 3HH content in the PHB3HH is in the range of 4% to 15% by weight of the PHB3HH.

[0074] The PHA blend of PHB with a Type 1 PHB copolymer can be a blend of PHB with PHB3HX where the PHB content of the PHA blend is in the range of 5% to 90 % by weight of the PHA in the PHA blend and the 3HX content in the PHB3HX is in the range of 4% to 15% by weight of the PHB3HX.

[0075] The PHA blend can be a blend of a Type 1 PHB copolymer selected from the group PHB3HV, PHB3HP, PHB4HB, PHBV, PHV4HV, PHB5HV, PHB3HH and PHB3HX with a second Type 1 PHB copolymer which is different from the first Type 1 PHB copolymer and is selected from the group PHB3HV, PHB3HP, PHB4HB, PHBV, PHV4HV, PHB5HV, PHB3HH and PHB3HX where the content of the First Type 1 PHB copolymer in the PHA blend is in the range of 10% to 90 % by weight of the total PHA in the blend.

[0076] The PHA blend of PHB with a Type 2 PHB copolymer can be a blend of PHB with PHB4HB where the PHB content in the PHA blend is in the range of 30%

to 95 % by weight of the PHA in the PHA blend and the 4HB content in the PHB4HB is in the range of 20% to 60% by weight of the PHB4HB.

[0077] The PHA blend of PHB with a Type 2 PHB copolymer can be a blend of PHB with PHB5HV where the PHB content in the PHA blend is in the range of 30% to 95 % by weight of the PHA in the PHA blend and the 5HV content in the PHB5HV is in the range of 20% to 60% by weight of the PHB5HV.

[0078] The PHA blend of PHB with a Type 2 PHB copolymer can be a blend of PHB with PHB3HH where the PHB content in the PHA blend is in the range of 35% to 95 % by weight of the PHA in the PHA blend and the 3HH content in the PHB3HH is in the range of 35% to 90% by weight of the PHB3HX.

[0079] The PHA blend of PHB with a Type 2 PHB copolymer can be a blend of PHB with PHB3HX where the PHB content in the PHA blend is in the range of 30% to 95 % by weight of the PHA in the PHA blend and the 3HX content in the PHB3HX is in the range of 35% to 90% by weight of the PHB3HX.

[0080] The PHA blend can be a blend of PHB with a Type 1 PHB copolymer and a Type 2 PHB copolymer where the PHB content in the PHA blend is in the range of 10% to 90 % by weight of the PHA in the PHA blend, the Type 1 PHB copolymer content of the PHA blend is in the range of 5% to 90% by weight of the PHA in the PHA blend and the Type 2 PHB copolymer content in the PHA blend is in the range of 5% to 90% by weight of the PHA in the PHA blend.

[0081] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HV content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HV content in the PHB3HV is in the range of 3% to 22% by weight of the PHB3HV, and a PHBHX content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 3HX content in the PHBHX is in the range of 35% to 90% by weight of the PHBHX.

[0082] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HV content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HV content in the PHB3HV is in the range of 3% to 22% by weight of the PHB3HV, and a PHB4HB content in the PHA blend in the range of

5% to 90% by weight of the PHA in the PHA blend where the 4HB content in the PHB4HB is in the range of 20% to 60% by weight of the PHB4HB.

[0083] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HV content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HV content in the PHB3HV is in the range of 3% to 22% by weight of the PHB3HV, and a PHB5HV content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 5HV content in the PHB5HV is in the range of 20% to 60% by weight of the PHB5HV.

[0084] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB4HB content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 4HB content in the PHB4HB is in the range of 4% to 15% by weight of the PHB4HB, and a PHB4HB content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 4HB content in the PHB4HB is in the range of 20% to 60% by weight of the PHB4HB.

[0085] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB4HB content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 4HB content in the PHB4HB is in the range of 4% to 15% by weight of the PHB4HB, and a PHB5HV content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend and where the 5HV content in the PHB5HV is in the range of 30% to 90% by weight of the PHB5HV.

[0086] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB4HB content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 4HB content in the PHB4HB is in the range of 4% to 15% by weight of the PHB4HB, and a PHB3HX content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend and where the 3HX content in the PHB3HX is in the range of 35% to 90% by weight of the PHB3HX.

[0087] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB4HV content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA

blend, where the 4HV content in the PHB4HV is in the range of 3% to 15% by weight of the PHB4HV, and a PHB5HV content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 5HV content in the PHB5HV is in the range of 30% to 90% by weight of the PHB5HV.

[0088] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HH content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HH content in the PHB3HH is in the range of 3% to 15% by weight of the PHB3HH, and a PHB4HB content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 4HB content in the PHB4HB is in the range of 20% to 60% by weight of the PHB4HB.

[0089] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HH content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HH content in the PHB3HH is in the range of 3% to 15% by weight of the PHB3HH, and a PHB5HV content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 5HV content in the PHB5HV is in the range of 20% to 60% by weight of the PHB5HV.

[0090] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HH content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HH content in the PHB3HH is in the range of 3% to 15% by weight of the PHB3HH, and a PHB3HX content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 3HX content in the PHB3HX is in the range of 35% to 90% by weight of the PHB3HX.

[0091] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HX content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HX content in the PHB3HX is in the range of 3% to 12% by weight of the PHB3HX, and a PHB3HX content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 3HX content in the PHB3HX is in the range of 35% to 90% by weight of the PHB3HX.

[0092] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HX content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HX content in the PHB3HX is in the range of 3% to 12% by weight of the PHB3HX, and a PHB4HB content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 4HB content in the PHB4HB is in the range of 20% to 60% by weight of the PHB4HB.

[0093] For example, a PHA blend can have a PHB content in the PHA blend in the range of 10% to 90% by weight of the PHA in the PHA blend, a PHB3HX content in the PHA blend in the range 5% to 90% by weight of the PHA in the PHA blend, where the 3HX content in the PHB3HX is in the range of 3% to 12% by weight of the PHB3HX, and a PHB5HV content in the PHA blend in the range of 5% to 90% by weight of the PHA in the PHA blend where the 5HV content in the PHB5HV is in the range of 20% to 60% by weight of the PHB5HV.

[0094] The PHA blend can be a blend as disclosed in U.S. Published Application No. US 2004/0220355, by Whitehouse, published November 4, 2004, which is incorporated herein by reference in its entirety.

[0095] Microbial systems for producing the PHB copolymer PHBV are disclosed in U.S. Patent No. 4,477,654 to Holmes. PCT Patent Publication No. WO 02/08428, by Skraly and Sholl describes useful systems for producing the PHB copolymer PHB4HB. Useful processes for producing the PHB copolymer PHB3HH have been described (Lee *et al.*, *Biotechnology and Bioengineering*, 67: 240-244 (2000); Park *et al.*, *Biomacromolecules*, 2: 248-254 (2001)). Processes for producing the PHB copolymers PHB3HX have been described by Matsusaki *et. al.*, (*Biomacromolecules*, 1: 17-22(2000)).

[0096] In determining the molecular weight techniques such as gel permeation chromatography (GPC) can be used. In the methodology, a polystyrene standard is utilized. The PHA can have a polystyrene equivalent weight average molecular weight (in daltons) of at least 500, at least 10,000, or at least 50,000 and/or less than 2,000,000, less than 1,000,000, less than 1,500,000, and less than 800,000. In certain embodiments, preferably, the PHAs generally have a weight-average molecular weight in the range of 100,000 to 700,000. For example, the molecular weight range for PHB and Type 1 PHB copolymers for use in this application are in

the range of 400,000 daltons to 1.5 million daltons as determined by GPC method and the molecular weight range for Type 2 PHB copolymers for use in the application 100,000 to 1.5 million daltons.

[0097] In certain embodiments, when the nucleating agent additionally contains a polymer, the carrier polymer and/or base polymer or polymer if applicable is each independently PHB or a Type 1 PHB copolymer such as PHBP, PHB4HB, PHB3HV, PHB4HV, PHB5HV, PHB3HH or PHB3HX.

[0098] In more particular embodiments, the carrier polymer, and/or base polymer, or polymer if applicable is each independently PHB, PHB3HV where the 3HV content is in the range of 2% to 22% by weight of the polymer, PHB3HP where the 3HP content is in the range of 3% to 15% by weight of the polymer, PHB4HB where the 4HB content is in the range of 3% to 15% by weight of the polymer, PHB4HV where the 4HV content is in the range of 3% to 15% by weight of the polymer, PHB3HH where the 3HH content is in the range of 3% to 15% by weight of the polymer or PHB3HX where the 3HX content is in the range of 3% to 12% by weight of the polymer. The percent range indicated is the percent weight of monomer relative to the total weight of the polymer. For example, in PHB4HB with 3% to 15% 4HB content, 3% to 15 % of the total PHB4HB polymer weight is 4-hydroxybutyrate.

[0099] In certain embodiments, the carrier polymer, and/or base polymer or polymer if applicable is each independently PHB blended with a Type 1 PHB copolymer selected from the group: PHB3HV where the 3HV content is in the range of 2% to 22% by weight of the polymer, PHB3HP where the 3HP content is in the range of 3% to 15% by weight of the polymer, PHB4HB where the 4HB content is in the range of 3% to 15% by weight of the polymer, PHB4HV where the 4HV content is in the range of 3% to 15% by weight of the polymer, PHB3HH where the 3HH content is in the range of 3% to 15% by weight of the polymer or PHB3HX where the 3HX content is in the range of 3% to 12% by weight of the polymer.

[00100] In certain embodiments, the carrier polymer, and/or base polymer or polymer if applicable is each independently PHB blended with a Type 2 PHB copolymer selected from the group: PHB4HB where the 4HB content is in the range of 20% to 60% by weight of the polymer, PHB3HH where the 3HH content is in the range of 35% to 90% by weight of the polymer, PHB5HV where the 5HV content is

in the range 20% to 60% by weight of the copolymer or PHB3HX where the 3HX content is in the range of 30% to 90% by weight of the copolymer.

[00101] In more particular embodiments, the carrier polymer, and/or base polymer or polymer if applicable is each independently a) PHB blended with b) a PHB4HB with a 5% to 15% 4HB content; a) PHB blended with b) a PHB3HV with a 5% to 22% 3HV content; a) PHB blended with b) a PHB3HH with a 3% to 15% 3HH content; a) PHB blended with b) a PHB3HX with a 3% to 12% 3H content; a) PHB blended with b) a PHB5HV with a 3% to 15% 5HV content; a) a PHB4HB with a 5% to 15% 4HB content blended with b) a PHB3HV) with a 5% to 22% 3HV content; a) a PHB4HB with 5% to 15% 4HB content blended with b) a PHB3HH with a 3% to 15% 3HH content or a) a PHB3HV with a 5% to 22% 3-hydroxyvalerate content blended with b) a polyPHB3HV with a 3% to 15% 3HH content.

[00102] In other particular embodiments, the carrier polymer, and/or base polymer or polymer if applicable is each independently a) PHB blended with b) a PHB4HB and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) PHB blended with b) a PHB3HV and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) PHB blended to with b) PHB3HH and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) PHB4HB blended with b) a PHB3HV and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a PHB4HB blended with b) a PHB3HH and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); or a) a PHB3HV blended with b) a PHB3HH and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b).

[00103] In yet other particular embodiments, the carrier polymer, and/or base polymer or polymer if applicable is each independently a) PHB blended with b) a PHB4HB with a 20-60% 4-HB content; a) PHB blended with b) a PHB5HV with a 20% to 60% 5HH content; a) PHB blended with b) a PHB3HH having a 35%-95% 3-HH content; a) PHB4HB with a 3% to 15% 4HB content blended with b) a PHB4HB with a 20-60% 4HB; a) PHB4HB with a 3% to 15% 4-hydroxybutyrate content blended with b) a PHB5HV with a 20% to 60% 5HV content; a) a PHB4HB with 3% to 15% 4HB content blended with b) a PHB3HX having a 30%-90% 3HX

content; a) a PHB3HV with a 3% to 22% 3HV content blended with b) PHB4HB with a 20-60% 4HB content; a) a PHB3HV with a 3% to 22% 3HV content blended with b) PHB5HV with a 20% to 60% 5HV content; a) a PHB3HV with a 3% to 22% 3HV content blended with b) a PHB3HH having a 35%-90% 3-HH content; a) a PHB3HH with a 3% to 15% 3HH content blended with b) a PHB4HB with a 20-60% 4HB content; a) a PHB3HX with a 3% to 12% 3HX content blended with b) a PHB4HB with a 20-60% 4HB content; a) a PHB3HX with a 3% to 12% 3H content blended with b) a PHB5HV with a 20-60% 5HV content; a) a PHB3HH with a 3% to 15% 3HH content blended with b) a PHB5HV with a 20% to 60% 5-HV; a) a PHB3HH with a 3% to 15% 3HH content blended with b) a PHB3HX with a 30% to 90% 3HX content or a) a PHB3HH with a 3% to 15% 3HH content blended with b) a PHB3HH having a 3HH content of 35%-90%.

[00104] In more particular embodiments, the carrier polymer, and/or base polymer or polymer if applicable is each independently PHB blended with a Type 1 PHB copolymer and a Type 2 PHB copolymer where the PHB content in the PHA blend is in the range of 10% to 90 % by weight of the PHA in the PHA blend, the Type 1 PHB copolymer content of the PHA blend is in the range of 5% to 90% by weight of the PHA in the PHA blend and the Type 2 PHB copolymer content in the PHA blend is in the range of 5% to 90% by weight of the PHA in the PHA blend.

[00105] In the embodiments described in the immediately preceding paragraphs describing blends of polymer a) and b) or two polymer components, the copolymer blend comprises polymer a) and polymer b), wherein the weight of polymer a) is 20 % to 60% of the combined weight of polymer a) and polymer b) and the weight of polymer b is 40% to 80% of the combined weight of polymer a) and polymer b).

[00106] In other embodiments, the polymer blends described herein (*e.g.*, blends comprising polymer a) and polymer b) or which otherwise describe two polymer components) comprise a third polymer, polymer c) which is a PHB4HB with a 20% to 60% 4HB content.

[00107] In other embodiments the polymer blends described herein (*e.g.*, blends comprising polymer a) and polymer b) or which otherwise describe two polymer components) comprise a third polymer, polymer c) which is a PHB5HV with a 20% to 60% 5HV content.

[00108] In other embodiments, the polymer blends described herein (*e.g.*, blends comprising polymer a) and polymer b) or which otherwise describe two polymer components) comprise a third polymer, polymer c) which is a PHB3HH with a 5% to 50% 3HH content.

[00109] In other embodiments, the copolymer blend comprises polymer a), polymer b) and polymer c). In particular embodiments, wherein the weight of polymer c) is 5% to 95% of the combined polymer weight of polymer a), polymer b) and polymer c). In yet other embodiments, the weight of polymer c) is 5% to 40% of the combined polymer weight of polymer a), polymer b) and polymer c).

Biodegradable Aromatic-Aliphatic Polyesters

[00110] The PHA can be combined with another polymer, or several other polymers. For instance, the PHA can be combined with one or more biodegradable aromatic-aliphatic polyesters. Such blends are discussed in, for example, U.S. Provisional Application No. 61/050,896 ("Biodegradable Polyester Blends"), filed May 6, 2008, and PCT Patent Publication No. WO 2009/137058 the entire teachings of which are incorporated herein by reference.

[00111] Aromatic polyesters, which are not biodegradable, are synthesized by the polycondensation of aliphatic diols and aromatic dicarboxylic acids. The aromatic ring is resistant to hydrolysis, preventing biodegradability. Polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) are formed by the polycondensation of aliphatic glycols and terephthalic acid. The biodegradability of aromatic polyesters can be modified by the addition of monomers that are not resistant to hydrolysis, aliphatic diol or diacid groups. The addition of such hydrolysis-sensitive monomers creates weak spots for hydrolysis to occur.

[00112] Aromatic-aliphatic polyesters are also made by polycondensation of aliphatic diols, but with a mixture of aromatic and aliphatic dicarboxylic acids. For instance, modification of PBT by addition of aliphatic dicarboxylic acids can produce polybutylene succinate terephthalate (PBST) (butane diol as the aliphatic diol and succinic and terephthalic acid). Another example is the family of polyesters sold under the trade name BIOMAX[®] (du Pont), the members of which are polymerized from PET and a variety of aliphatic acid monomers such as dimethylglutarate and diethylene glycol. In the synthesis of polybutylene adipate

terephthalate (PBAT), butanediol is the diol, and the acids are adipic and terephthalic acids. Commercial examples include ECOFLEX[®] (BASF) and Eastar Bio (Eastman). ECOFLEX[®] has a melt temperature (T_M) of about 110°C to about 120°C, as measured by differential scanning calorimetry (DSC). Another example is polytetramethylene adipate terephthalate (PTMAT) is synthesized from tetramethylene glycol and adipic and terephthalic acids.

[00113] Biodegradable polymers therefore include polyesters containing aliphatic components. Among the polyesters are ester polycondensates containing aliphatic constituents and poly(hydroxycarboxylic) acid. The ester polycondensates can include diacids/diol aliphatic polyesters such as polybutylene succinate, polybutylene succinate co-adipate, aliphatic/aromatic polyesters such as terpolymers made of butylenes diol, adipic acid and terephthalic acid. The poly(hydroxycarboxylic) acids include lactic acid based homopolymers and copolymers, polyhydroxybutyrate (PHB), or other polyhydroxyalkanoate homopolymers and copolymers. Such polyhydroxyalkanoates include copolymers of PHB with higher chain length monomers, such as C₆-C₁₂, and higher.

[00114] Examples of biodegradable aromatic-aliphatic polyesters therefore include, but are not limited to, various copolyesters of PET and PBT with aliphatic diacids, diols, or hydroxy acids incorporated into the polymer backbone to render the copolyesters biodegradable or compostable; and various aliphatic polyesters and copolyesters derived from dibasic acids, *e.g.*, succinic acid, glutaric acid, adipic acid, sebacic acid, azealic acid, or their derivatives, *e.g.*, alkyl esters, acid chlorides, or their anhydrides; diols such as ethylene glycol, propylene glycol, 1,4-butanediol, 1,6-hexanediol, or 1,4-cyclohexanedimethanol.

[00115] An example of a suitable commercially available diacid/diol aliphatic polyester is the polybutylene succinate/adipate copolymers sold as BIONOLLE[®] 1000 and BIONOLLE[®] 3000 from the Showa High Polymer Company, Ltd. (Tokyo, Japan). An example of a suitable commercially available aromatic-aliphatic copolyester is the poly(tetramethylene adipate-co-terephthalate) sold as EASTAR BIO[®] Copolyester from Eastman Chemical or ECOFLEX[®] from BASF.

[00116] The biodegradable aromatic-aliphatic polyester can be a co-polyester. It can also itself be a blend of such polyesters or co-polyesters.

Blends of PHAs and Biodegradable Aromatic-Aliphatic Polyesters

[00117] PHAs and biodegradable aromatic-aliphatic polyesters can be combined to make blends of the polymers. Such blends are discussed in, for example, U.S. Provisional Application No. 61/050,896 ("Biodegradable Polyester Blends"), filed May 6, 2008 and PCT Patent Publication No. WO 2009/137058, the entire teachings of which are incorporated herein by reference.

[00118] The amount of PHA in the overall blend can be about 1% by weight, about 5%, about 10%, about 15%, about 20%, about 25%, about 30%, about 35%, about 40%, about 45%, about 50%, about 55%, about 60%, about 65%, about 70%, about 75%, about 80%, about 85%, about 90%, about 95%, or about 99% by weight. The selection and amount of each polymer will effect the softness, stiffness, texture, toughness, and other properties of the final product as will be understood by those of ordinary skill in the art. Typically, the PHA component is present in the blend in an amount of from about 10% to 95%, preferably from about 15% to about 85%, more preferably from about 20% to about 80%, by total weight of the total polymer components.

[00119] Each polymer component can contain a single polymer species or a blend of two or more species. For instance, and PHA component can in turn be a blend of PHA species as described above. Likewise, the biodegradable aromatic-aliphatic polyester component can be a mixture or blend of biodegradable aromatic-aliphatic polyesters.

[00120] Methods for making and using thermoplastic compositions are well known to those of skill in the art, and skilled practitioners will appreciate that the biodegradable blends of the present invention can be used in a wide range of applications and further, as is known to skilled practitioners, can contain one or more additive, *e.g.*, a plasticizer, nucleating agent, filler, antioxidant, ultraviolet stabilizer, lubricant, slip/antiblock, pigment, flame retardant, and/or antistatic agent.

Production and Processing of Biodegradable Blend Compositions

[00121] Biodegradable blend compositions can be produced using any art-known method that includes adding a biodegradable aromatic-aliphatic polyesters to a thermoplastic. The biodegradable aromatic-aliphatic polyesters can be added to a

thermoplastic as a dry biodegradable aromatic-aliphatic polyesters composition and/or as a biodegradable aromatic-aliphatic polyesters formulation.

[00122] Optimal amounts to be added will depend on various factors known to skilled practitioners, *e.g.*, cost, desired physical characteristics of the thermoplastic (*e.g.*, mechanical strength), and the type of processing to be performed (raising, *e.g.*, considerations of line speeds, cycle times, and other processing parameters). Also to be considered is whether the thermoplastic composition includes other additives, *e.g.*, plasticizers, stabilizers, pigments, fillers, reinforcing agents, and/or mold release agents. In general, however, a biodegradable aromatic-aliphatic polyesters can be included in a thermoplastic composition such that the composition contains about 5% to about 95%, *e.g.*, about 5% to about 90%, about 20% to about 80% biodegradable aromatic-aliphatic polyesters, based on the total weight of the composition. In certain embodiments of the present invention, the composition contains about 1% to about 10%, *e.g.*, about 1% to about 5% biodegradable aromatic-aliphatic polyesters.

Branched Polyhydroxyalkanoates

[0010] Branched compositions of PHA used in the methods and compositions described herein improve the melt strength of PHAs, a desirable property for many polymer product applications. Melt strength is a rheological property that can be measured a number of ways. One measure is G' . G' is the polymer storage modulus measured at melt processing temperatures. Exemplary branched PHAs and methods of making them are provided in U.S. Patent Nos. 6,096,810 and 6,201,083, and in International Application Nos. PCT/US09/003687 and PCT/US09/003675, both filed on June 19, 2009, all of which are incorporated by reference herein in their entirety.

[00123] In certain embodiments, branched polyhydroxyalkanoate polymers are used to make the non-woven materials as described herein. Such branched polyhydroxyalkanoates have better thermal stability than unbranched polyhydroxyalkanoate polymers.

[00124] Polyhydroxyalkanoate polymers are branched using a cross-linking agent, also referred to as co-agents containing two or more reactive functional groups such as epoxides or double bonds. These cross-linking agents modify the

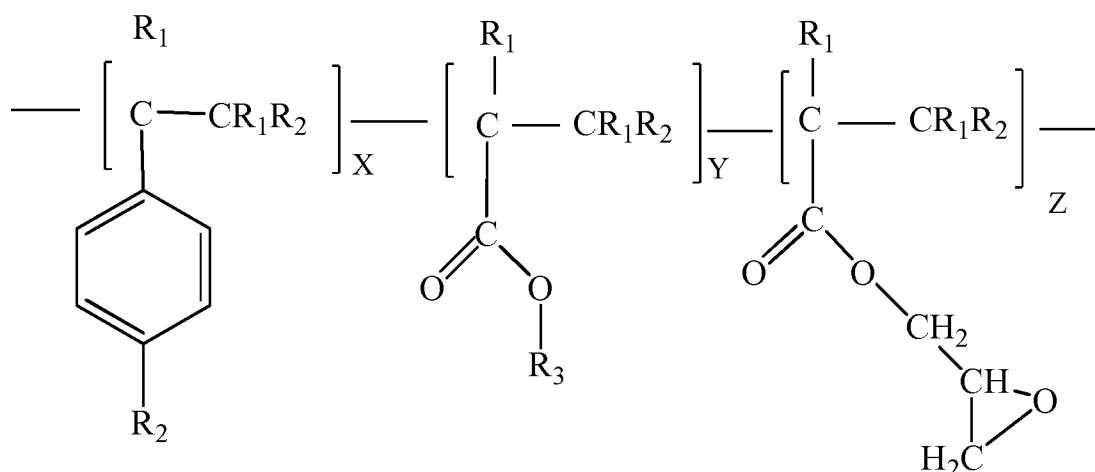
properties of the polymer. These properties include, but are not limited to, melt strength or toughness.

[00125] One type of cross-linking agent is an “epoxy functional compound.” As used herein, “epoxy functional compound” is meant to include compounds with two or more epoxide groups capable of increasing the melt strength of polyhydroxyalkanoate polymers by branching, *e.g.*, end branching as described above. When an epoxy functional compound is used as the cross-linking agent in the disclosed methods, a branching agent is optional. As such one embodiment of branching includes reacting a starting polyhydroxyalkanoate polymer (PHA) with an epoxy functional compound. Alternatively, another method of branching includes reacting a starting polyhydroxyalkanoate polymer, a branching agent and an epoxy functional compound. Alternatively, another branching method includes reacting a starting PHA, and an epoxy functional compound in the absence of a branching agent.

[00126] Such epoxy functional compounds can include epoxy-functional, styrene-acrylic polymers (such as, but not limited to, *e.g.*, JONCRYL[®] ADR-4368 (BASF), or MP-40 (Kaneka)), acrylic and/or polyolefin copolymers and oligomers containing glycidyl groups incorporated as side chains (such as, but not limited to, *e.g.*, LOTADER[®] (Arkema), poly(ethylene-glycidyl methacrylate-co-methacrylate)), and epoxidized oils (such as, but not limited to, *e.g.*, epoxidized soybean, olive, linseed, palm, peanut, coconut, seaweed, cod liver oils, or mixtures thereof, *e.g.*, MERGINAT[®] ESBO (Hobum, Hamburg, Germany) and EDENOL[®] B 316 (Cognis, Dusseldorf, Germany)).

[00127] For example, reactive acrylics or functional acrylics cross-linking agents are used to increase the molecular weight of the polymer in the branched polymer compositions described herein. Such cross-linking agents are sold commercially. BASF, for instance, sells multiple compounds under the trade name “JONCRYL[®]”, which are described in U.S. Patent No. 6,984,694 to Blasius *et al.*, “Oligomeric chain extenders for processing, post-processing and recycling of condensation polymers, synthesis, compositions and applications”, incorporated herein by reference in its entirety. One such compound is JONCRYL[®] ADR-4368CS, which is styrene glycidyl methacrylate and is discussed below. Another is MP-40 (Kaneka). And still another is “Petra” line from Honeywell, see for example, U.S.

Patent No. 5,723,730. Such polymers are often used in plastic recycling (*e.g.*, in recycling of polyethylene terephthalate) to increase the molecular weight (or to mimic the increase of molecular weight) of the polymer being recycled. Such polymers often have the general structure:



R_1 and R_2 are independently H or alkyl

R_3 is alkyl

X and Y are 1-20

Z is 2-20

alkyl is $\text{C}_1\text{-C}_8$

[00128] Without wishing to be bound by theory, it is believed that the epoxy-functional polymeric acrylics are capable of branching polyesters, and effectively repair the damage (in particular, loss of melt strength G') that occurs to the molecular weight of the polyester in the extruder. The epoxy-functional compounds may also improve thermal stability of polyhydroxyalkanoate polymers by preventing beta scission.

[00129] E.I. du Pont de Nemours & Company sells multiple reactive compounds under the trade name Elvaloy[®], which are ethylene copolymers, such as acrylate copolymers, elastomeric terpolymers, and other copolymers. One such compound is Elvaloy PTW, which is a copolymer of ethylene-n-butyl acrylate and glycidyl methacrylate. Omnova sells similar compounds under the trade names "SX64053," "SX64055," and "SX64056." Other entities also supply such compounds commercially.

[00130] Specific polyfunctional polymeric compounds with reactive epoxy groups are the styrene-acrylic copolymers and oligomers containing glycidyl groups incorporated as side chains. Several useful examples are described in U.S. Patent

No. 6,984,694 to Blasius *et al.*, “Oligomeric chain extenders for processing, post-processing and recycling of condensation polymers, synthesis, compositions and applications”, which is incorporated herein by reference in its entirety. These materials are based on oligomers with styrene and acrylate building blocks that have glycidyl groups incorporated as side chains. A high number of epoxy groups per oligomer chain can be used, for example at least 10, greater than 15, or greater than 20. These polymeric materials generally have a molecular weight greater than 3000, specifically greater than 4000, and more specifically greater than 6000. These are commercially available from Johnson Polymer, LLC (now owned by BASF) under the trade name JONCRYL[®], ADR 4368 material. Other types of polyfunctional polymer materials with multiple epoxy groups are acrylic and/or polyolefin copolymers and oligomers containing glycidyl groups incorporated as side chains. A further example of a such polyfunctional carboxy-reactive material is a co- or terpolymer including units of ethylene and glycidyl methacrylate (GMA), available under the trade name LOTADER[®] resin, sold by Arkema. These materials can further comprise methacrylate units that are not glycidyl. An example of this type is poly(ethylene-glycidyl methacrylate-co-methacrylate).

[00131] Fatty acid esters or naturally occurring oils containing epoxy groups (epoxidized) can also be used. Examples of naturally occurring oils are olive oil, linseed oil, soybean oil, palm oil, peanut oil, coconut oil, seaweed oil, cod liver oil, or a mixture of these compounds. Particular preference is given to epoxidized soybean oil (*e.g.*, Merginat[®] ESBO from Hobum, Hamburg, or Edenol[®] B 316 from Cognis, Dusseldorf), but others may also be used.

[00132] As used herein, “epoxy functional compound” is meant to include compounds with epoxide groups capable of increasing the melt strength of polyhydroxyalkanoate polymers by end chain branching as described above. Such epoxy functional compounds can include epoxy-functional, styrene-acrylic polymers (such as, but not limited to, *e.g.*, JONCRYL[®] ADR-4368 (BASF), or MP-40 (Kaneka)), acrylic and/or polyolefin copolymers and oligomers containing glycidyl groups incorporated as side chains (such as, but not limited to, *e.g.*, LOTADER[®] (Arkema), poly(ethylene-glycidyl methacrylate-co-methacrylate)), and epoxidized oils (such as, but not limited to, *e.g.*, epoxidized soybean, olive, linseed, palm,

peanut, coconut, seaweed, cod liver oils, or mixtures thereof, *e.g.*, Merginat® ESBO (Hobum, Hamburg, Germany) and Edenol® B 316 (Cognis, Dusseldorf, Germany)).

[00133] In general, it appears that compounds with terminal epoxides may perform better than those with epoxide groups located elsewhere on the molecule.

Nucleating Agents

[00134] The nucleating agent of the methods and compositions herein is selected from boron nitride, cyanuric acid or related compounds, carbon black, mica talc, silica, clay, calcium carbonate, synthesized silicic acid and salts, metal salts of organophosphates, kaolin, and possibly other materials. In particular compositions and methods, the nucleating agent is boron nitride.

[00135] In preferred embodiments, the nucleating agent is wet-milled. Wet milling the nucleating agent in a liquid carrier produces a nucleating agent with a particle size well below that obtained via standard air jet milling. In certain embodiments, the nucleating agent is wet-milled to an average particle size of less than 20 microns.

[00136] Wet grinding can be done, for instance, in a model KD5 Dyno Mill, which is a horizontal mill with a 1.5 liter mixing volume capacity. Any equivalent mill can be used. The KD5 Dyno Mill can be used in either a batch cycle or continuous loop mode. The mixing horizontal chamber contains a central horizontal shaft onto which are attached 5-7 polyurethane paddles stators which provided the circumventional driving velocity to agitate the grinding media (typically from, *e.g.*, 0.4mm to 1.2mm ceramic beads, with narrow size distribution range). As described herein, the mixing chamber can be filled with 0.6-0.8mm zirconia beads to about 80-85% volume fill capacity. The shaft speed can be set to, *e.g.*, 2400 rpm. The liquid media (carrier) can be pumped through the chamber while the beads are agitated. This effects a grinding action. The residence time is controlled by the external flow rate of the liquid media. Grinding efficiency is controlled by the size of the beads, shaft rpm and residence time of the material in the chamber (*i.e.*, as a function of flow rate). The liquid exits the mill through a angular slot die which is small enough to retain the grinding media (the beads) while allowing the liquid to flow through the gap, typically, *e.g.*, <50% -25% of the grinding media diameter.

[00137] Nucleating agents for various polymers can include simple substances, metal compounds including composite oxides, for example, carbon black, calcium carbonate, synthesized silicic acid and salts, silica, zinc white, clay, kaolin, basic magnesium carbonate, mica, talc, quartz powder, diatomite, dolomite powder, titanium oxide, zinc oxide, antimony oxide, barium sulfate, calcium sulfate, alumina, calcium silicate, metal salts of organophosphates, and boron nitride; low-molecular organic compounds having a metal carboxylate group, for example, metal salts of such as octylic acid, toluic acid, heptanoic acid, pelargonic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, cerotic acid, montanic acid, melissic acid, benzoic acid, p-tert-butylbenzoic acid, terephthalic acid, terephthalic acid monomethyl ester, isophthalic acid, and isophthalic acid monomethyl ester; high-molecular organic compounds having a metal carboxylate group, for example, metal salts of such as: carboxyl-group-containing polyethylene obtained by oxidation of polyethylene; carboxyl-group-containing polypropylene obtained by oxidation of polypropylene; copolymers of olefins, such as ethylene, propylene and butene-1, with acrylic or methacrylic acid; copolymers of styrene with acrylic or methacrylic acid; copolymers of olefins with maleic anhydride; and copolymers of styrene with maleic anhydride; high-molecular organic compounds, for example: alpha-olefins branched at their 3-position carbon atom and having no fewer than 5 carbon atoms, such as 3,3 dimethylbutene-1, 3-methylbutene-1, 3-methylpentene-1, 3-methylhexene-1, and 3,5,5-trimethylhexene-1; polymers of vinylcycloalkanes such as vinylcyclopentane, vinylcyclohexane, and vinylnorbornane; polyalkylene glycols such as polyethylene glycol and polypropylene glycol; poly(glycolic acid); cellulose; cellulose esters; and cellulose ethers; phosphoric or phosphorous acid and its metal salts, such as diphenyl phosphate, diphenyl phosphite, metal salts of bis(4-tert-butylphenyl) phosphate, and methylene bis-(2,4-tert-butylphenyl)phosphate; sorbitol derivatives such as bis(p-methylbenzylidene) sorbitol and bis(p-ethylbenzylidene) sorbitol; and thioglycolic anhydride, p-toluenesulfonic acid and its metal salts. The above nucleating agents may be used either alone or in combinations with each other. In certain embodiments, the nucleating agent can also be another polymer (e.g., polymeric nucleating agents such as PHB).

[00138] The amount of nucleating agent in liquid carrier is from 5% to 50% by weight of the nucleating agent-liquid carrier composition, preferably from 20% to

45% by weight, more preferably 30% to 40% by weight, and most preferably 40% by weight of the combined weight of the nucleating agent and liquid carrier.

[00139] A liquid carrier is typically used in combination with the nucleating agent. The liquid carrier allows the nucleating agent to be wet milled.

[00140] Once the nucleating agent has been wet milled in the liquid carrier, and an appropriate amount of the liquid carrier plus nucleating agent is then added to the polymer to be processed. One of ordinary skill in the art of polymer compounding can therefore plan the nucleant and liquid carrier ratio to suit their specific needs, knowing by experience what amount of nucleant and liquid carrier (*i.e.*, plasticizer, surfactant, lubricant, etc.) are appropriate to use.

[00141] Choice of the liquid carrier is important as the carrier becomes an integral component in the polymer formulation when the nucleant is added. In poly-3-hydroxybutyrate compositions, for example, plasticizers are often used to change the glass transition temperature and modulus of the composition, but surfactants may also be used. Lubricants may also be used, *e.g.*, in injection molding applications.

[00142] Plasticizers, surfactants and lubricants may all therefore be used as the liquid carrier for the milling of the nucleating agent.

[00143] The liquid carrier for wet milling the nucleant can be a plasticizer. Examples of plasticizers include but are not limited to phthalic compounds (including, but not limited to, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, di-n-octyl phthalate, di-2-ethylhexyl phthalate, diisooctyl phthalate, dicapryl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diundecyl phthalate, dilauryl phthalate, ditridecyl phthalate, dibenzyl phthalate, dicyclohexyl phthalate, butyl benzyl phthalate, octyl decyl phthalate, butyl octyl phthalate, octyl benzyl phthalate, n-hexyl n-decyl phthalate, n-octyl phthalate, and n-decyl phthalate), phosphoric compounds (including, but not limited to, tricresyl phosphate, trioctyl phosphate, triphenyl phosphate, octyl diphenyl phosphate, cresyl diphenyl phosphate, and trichloroethyl phosphate), adipic compounds (including, but not limited to, dibutoxyethoxyethyl adipate (DBEEA), dioctyl adipate, diisooctyl adipate, di-n-octyl adipate, didecyl adipate, diisodecyl adipate, n-octyl n-decyl adipate, n-heptyl adipate, and n-nonyl adipate), sebacic compounds (including, but not limited to, dibutyl sebacate, dioctyl sebacate, diisooctyl sebacate, and butyl benzyl sebacate), azelaic compounds, citric

compounds (including, but not limited to, triethyl citrate, acetyl triethyl citrate, tributyl citrate, acetyl tributyl citrate, and acetyl trioctyl citrate), glycolic compounds (including, but not limited to, methyl phthalyl ethyl glycolate, ethyl phthalyl ethyl glycolate, and butyl phthalyl ethyl glycolate), trimellitic compounds (including, but not limited to, trioctyl trimellitate and tri-n-octyl n-decyl trimellitate), phthalic isomer compounds (including, but not limited to, dioctyl isophthalate and dioctyl terephthalate), ricinoleic compounds (including, but not limited to, methyl acetyl, recinoleate and butyl acetyl recinoleate), polyester compounds (including, but not limited to, polypropylene adipate and polypropylene sebacate), epoxidized soy bean oil, epoxidized butyl stearate, epoxidized octyl stearate, chlorinated paraffins, chlorinated fatty acid esters, fatty acid compounds, plant oils, pigments, and acrylic compounds. The plasticizers may be used either alone respectively or in combinations with each other.

[00144] In certain embodiments, the liquid carrier for wet milling the nucleating agent can be a surfactant. Surfactants are generally used to de-dust, lubricate, reduce surface tension, and/or densify. Examples of surfactants include, but are not limited to mineral oil, castor oil, and soybean oil. One mineral oil surfactant is Drakeol 34, available from Penreco (Dickinson, Texas, USA). Maxsperser W-6000 and W-3000 solid surfactants are available from Chemax Polymer Additives (Piedmont, South Carolina, USA). Surfactants can also include detergents such as Triton X-100, TWEEN[®]-20, TWEEN[®]-65, Span-40 and Span 86.

[00145] Anionic surfactants include: aliphatic carboxylic acids such as lauric acid, myristic acid, palmitic acid, stearic acid, and oleic acid; fatty acid soaps such as sodium salts or potassium salts of the above aliphatic carboxylic acids; N-acyl-N-methylglycine salts, N-acyl-N-methyl-beta-alanine salts, N-acylglutamic acid salts, polyoxyethylene alkyl ether carboxylic acid salts, acylated peptides, alkylbenzenesulfonic acid salts, alkyl naphthalenesulfonic acid salts, naphthalenesulfonic acid salt-formalin polycondensation products, melaminesulfonic acid salt-formalin polycondensation products, dialkylsulfosuccinic acid ester salts, alkyl sulfosuccinate disalts, polyoxyethylene alkylsulfosuccinic acid disalts, alkylsulfoacetic acid salts, (alpha-olefinsulfonic acid salts, N-acylmethyltaurine salts, sodium dimethyl 5-sulfoisophthalate, sulfated oil, higher alcohol sulfuric acid ester salts, polyoxyethylene alkyl ether sulfuric acid

salts, secondary higher alcohol ethoxysulfates, polyoxyethylene alkyl phenyl ether sulfuric acid salts, monoglylsulfate, sulfuric acid ester salts of fatty acid alkylolamides, polyoxyethylene alkyl ether phosphoric acid salts, polyoxyethylene alkyl phenyl ether phosphoric acid salts, alkyl phosphoric acid salts, sodium alkylamine oxide bistridecylsulfosuccinates, sodium dioctylsulfosuccinate, sodium dihexylsulfosuccinate, sodium dicyclohexylsulfosuccinate, sodium diamylsulfosuccinate, sodium diisobutylsulfosuccinate, alkylamine guanidine polyoxyethanol, disodium sulfosuccinate ethoxylated alcohol half esters, disodium sulfosuccinate ethoxylated nonylphenol half esters, disodium isodecylsulfosuccinate, disodium N-octadecylsulfosuccinamide, tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinamide, disodium mono- or didodecyl diphenyl oxide disulfonates, sodium diisopropyl naphthalenesulfonate, and neutralized condensed products from sodium naphthalenesulfonate.

[00146] In other embodiments, the liquid carrier is a lubricant. For example, a lubricant normally used in polymer processing can also be used as the liquid carrier for wet milling the nucleant. Lubricants are normally used to reduce sticking to hot processing metal surfaces and can include polyethylene, paraffin oils, and paraffin waxes in combination with metal stearates. Other lubricants include stearic acid, amide waxes, ester waxes, metal carboxylates, and carboxylic acids. Lubricants are normally added to polymers in the range of about 0.1 percent to about 1 percent by weight, generally from about 0.7 percent to about 0.8 percent by weight of the compound. Solid lubricants can be warmed and melted during the wet milling.

[00147] In yet other embodiments, the liquid carrier is a volatile or organic solvent. In these embodiments, a volatile solvent will flash off during subsequent compounding of the polymer, leaving behind the nucleating agent. Volatile liquid carriers that can be used in the invention include, alcohols (*e.g.*, ethanol, propanol, isopropanol, etc.

[00148] Examples of organic solvents for use in the methods and compositions of the invention include but are not limited to: n-pentane, n-hexane, isohexane, n-heptane, n-octane, isooctane, n-decane, 2,2-dimethylbutane, petroleum ether, petroleum benzene, ligroin, gasoline, kerosene, petroleum spirit, petroleum naphtha, 2-pentene, mixed pentene, cyclohexane, methylcyclohexane, benzene, toluene, xylene, ethylbenzene, diethylbenzene, isopropylbenzene, amylbenzene,

diamylbenzene, triamylbenzene, tetraamylbenzene, dodecylbenzene, didodecylbenzene, amyltoluene, coal tar naphtha, solvent naphtha, p-cymene, naphthalene, tetralin, decalin, biphenyl, dipentene, turpentine oil, pinene, p-menthane, pine oil, camphor oil, methyl chloride, methylene chloride, chloroform, carbon tetrachloride, ethyl chloride, ethylene chloride, ethylidene chloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, pentachloroethane, hexachloroethane, vinylidene chloride, 1,2-dichloropropane, butyl chloride, amyl chloride, mixed amyl chloride, dichloropentane, hexyl chloride, 2-ethylhexyl chloride, methyl bromide, ethyl bromide, ethylene bromide, tetrabromoethane, chlorobromomethane, ethylene chlorobromide, chlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, bromobenzene, o-dibromobenzene, o-chlorotoluene, p-chlorotoluene, alpha-chloronaphthalene, chlorinated naphthalene, fluorodichloromethane, dichlorodifluoromethane, fluorotrichloromethane, trifluoromonobromomethane, difluorochloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, ethyl ether, dichloroethyl ether, isopropyl ether, n-butyl ether, diisoamyl ether, n-hexyl ether, methyl phenyl ether, ethyl phenyl ether, n-butyl phenyl ether, amyl phenyl ether, o, m, p-cresyl methyl ether, p-t-amylphenyl n-amyl ether, ethyl benzyl ether, 1,4-dioxane, trioxane, furan, furfural, dioxolane, 2-methylfuran, tetrahydrofuran, cineol, methylal, diethyl acetal, acetone, methylacetone, methyl ethyl ketone, methyl n-propyl ketone, methyl n-butyl ketone, methyl isobutyl ketone, methyl n-amyl ketone, methyl n-hexyl ketone, diethyl ketone, ethyl n-butyl ketone, di-n-propyl ketone, diisobutyl ketone, 2,6,8-trimethylnonanone-4, acetone oil, acetonylacetone, mesityl oxide, phorone, isophorone, cyclohexanone, methylcyclohexanone, acetophenone, dypnone, camphor, methyl formate, ethyl formate, propyl formate, n-butyl formate, isobutyl formate, methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, sec-butyl acetate, n-amyl acetate, isoamyl acetate, methylisoamyl acetate, methoxybutyl acetate, sec-hexyl acetate, 2-ethylbutyl acetate, methylisobutylcarbinol acetate, 2-ethylhexyl acetate, cyclohexyl acetate, methylcyclohexyl acetate, benzyl acetate, methyl propionate, ethyl propionate, n-butyl propionate, isoamyl propionate, methyl butyrate, ethyl butyrate, n-butyl butyrate, isoamyl butyrate, ethyl oxyisobutyrate, butyl stearate, amyl stearate, methyl acetoacetate, ethyl acetoacetate, isoamyl isovalerate, methyl lactate, ethyl

lactate, butyl lactate, amyl lactate, methyl benzoate, ethyl benzoate, propyl benzoate, butyl benzoate, isoamyl benzoate, benzyl benzoate, ethyl cinnamate, methyl salicylate, octyl adipate, diethyl oxalate, dibutyl oxalate, diamyl oxalate, diethyl malonate, dibutyl tartrate, tributyl citrate, dioctyl sebacate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, dioctyl phthalate, nitromethane, nitroethane, nitropropane, nitrobenzene, nitroanisole, monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, aniline, toluidine, acetoamide, acetonitrile, benzonitrile, pyridine, picoline, lutidine, quinoline, morpholine, carbon disulfide, dimethyl sulfoxide, propanesulfone, triethyl phosphate, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and polyepichlorohydrin. These organic solvents may be used either alone respectively or in combinations with each other.

[00149] An advantage of using a volatile liquid is that the liquid will flash off during processing in the extruder, and can be removed. This can be advantageous for applications where little plasticizer or surfactant is desired in the finished polymer product.

[00150] In still another embodiments, the liquid carrier for wet milling the nucleating agent is water. An advantage of using water is that it, like the volatile solvents, will also flash off during processing. Additionally, no residue behind is left behind, and minimal or no effect on the chemistry of the polymer itself is found.

[00151] In yet other embodiments, the liquid carrier for wet milling the nucleating agent can be a mixture of any of the above. For instance, the liquid carrier can be a mixture of one or more plasticizers, one or more surfactants, one or more volatile liquid carriers, or water. The liquid carrier can also be a mixture of one or more plasticizers, surfactants, volatile liquid carriers, or water.

[00152] One of ordinary skill in the polymer processing arts can therefore compose the overall liquid carrier with consideration for the later processing of the polymer. For instance, if the polymer application calls for only a small amount of plasticizer or surfactant, then one can compose a liquid carrier with a small amount of plasticizer or surfactant, with the balance of the carrier being a volatile liquid that will flash off during processing.

[00153] In certain embodiments, the nucleating agent is wet-milled as described in PCT Patent Publication No. WO 2009/129499, incorporated herein by reference in its entirety.

[00154] In certain embodiments, the nucleating agent further include a polymer and is then referred to as a nucleating composition. In these embodiments, the polymer in the nucleating composition is referred to a “carrier polymer” to differentiate from the polymer in the fiber or web, referred to as a “base polymer” when the carrier polymer is also present in the composition. A carrier polymer is a polymer included in compositions for dispersing a nucleating agent. In certain aspects, the carrier polymer is combined with the nucleating agent and a liquid carrier under conditions to form a nucleating pellet. A nucleating pellet is a composition distributed within a base polymer to facilitate crystallization. A base polymer or polymer as used in the methods and compositions of the invention is a polymer used in compositions for making the fibers and non-wovens.

[00155] In certain embodiments, a base polymer and a carrier polymer is the same polymer. In other embodiments, the base polymer and the carrier polymer are different.

Melt Viscosity of Polymer Compositions

[00156] In general, it has been found that the melt viscosity of the polyhydroxyalkanoate polymer should be maintained. Preferably the melt viscosity of the starting material is about 800 to about 1100 Pa.sec. Melt viscosity, as the term is used herein, is measured by test ASTM D3835 (ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA).

[00157] While it may be preferable to having starting material with a melt viscosity of about 800 to about 1100 Pa/second, the weight average molecular weight of the fibers after extrusion is also highly critical to achieving a non-woven material with soft fibers, *i.e.*, fibers with reduced brittleness. Extruded fibers with a molecular weight under 100 kg/mol were found to be brittle. Preferably, the fibers after extrusion have a molecular weight of at least about 150 kg/mol, more preferably at least about 180 kg/mol, even more preferably at least about 200 kg/mol, and most preferably at least about 250 kg/mol.

[00158] For instance, polyhydroxybutyrate, combined with plasticizer, was found to have the following “hand” (a subjective determination of softness) in relation to the following degrees of molecular weight retention:

Table 1. Hand of Polyhydroxyalkanoate Non-Wovens as a Function of Molecular Weight

Mw, g/mol	Percent Mw Retention	Hand
81,936	18.6	very brittle
83,047	18.9	very brittle
101,874	23.2	brittle
123,682	29.1	not very soft
157,045	35.7	softer
167,148	38.0	soft
158,795	36.1	soft

[00159] The relationship between the molecular weight of the starting material and the extruded fibers can also be expressed in terms of molecular weight retention, *i.e.*, the weight-average molecular weight of the extruded fibers as a percentage of the weight average molecular weight of the starting material, *e.g.*, extruded fibers with a molecular weight of 235 kg/mol, which were made from starting material with a molecular weight of 420 kg/mol, can be said to have a molecular weight retention of 56%. However, starting material with a very high molecular weight can have a low molecular weight retention and still produce soft fibers, if the molecular weight of the extruded fibers is sufficiently high. Likewise, if the starting material has a relatively low molecular weight, the molecular weight retention would need to be relatively high in order to produce fibers with a sufficiently high molecular weight. Understanding the relationship between these variables is necessary for one to understand how much “play” one has in controlling the residence time and temperature in the extruder. The wet-milled nucleating agent does not change the fiber retained molecular weight.

[00160] It has been found that the viscosity is related to producing soft non-wovens with reduced brittleness. Others have attempted to decrease viscosity in order to be better able to push the polymer formulation through the fine holes in the

die. One way to do this is to decrease the molecular weight of the polymer, *e.g.*, by increasing the thermal degradation of the polymer.

[00161] However, it has been discovered that an increase in the thermal degradation, or a decrease in the molecular weight, while making it easier to extrude the polymer through the die, has the added effect of producing brittle fibers, or no fibers at all.

[00162] Instead, as described herein, addition of a plasticizer, and maintenance of melt viscosity (or, at least, reduction of thermal degradation) increases the viscosity, allowing for extrusion through a fine die, but still produces fibers that are soft, and reduces their brittleness.

[00163] In certain embodiments, the particular plasticizer is acetyl tri-n-butyl citrate (CITROFLEX[®] A4). Another plasticizer known to be useful in the invention is diisononyl adipate (DINA).

[00164] Examples of other plasticizers include those plasticizers described above. The plasticizers may be used either alone respectively or in combinations with each other.

[00165] The biodegradable non-woven materials described in the present invention can be produced using any art-known method for producing non-wovens.

[00166] For instance, the non-wovens can be made by melt blowing, as is described in Example 1, below. Operation and adjustment of such equipment is well within the knowledge of those of ordinary skill in the art of making non-woven materials.

[00167] For instance, screen packs can contribute to the back pressure and shear heat. For melt blown processes, it is common to use high mesh size screens. However, it has been found that coarser screens work better, *e.g.*, 60 mesh or 180 mesh, or 110 or 130 or even 90 mesh.

[00168] The die hole size can be around 250 μm . The compressed air can be heated, *e.g.*, to 220 °C. Line speed can be increased by heating the collector belt or take up roll. The machinery should be purged, *e.g.*, with polypropylene.

[00169] For instance, the polymeric composition can also include an optional nucleating agent to aid in crystallization of the polymeric composition. However, due to the small diameter of the fibers, a particulate nucleating agent should not be used.

[00170] In poly-3-hydroxybutyrate compositions, for example, plasticizers are often used to change the glass transition temperature and modulus of the composition, but surfactants, such as those described above may also be used.

Additives

[00171] The non woven compositions and fibers described herein can further included additives, for example, surfactants and clays. The polymeric composition can include one or more surfactants.

[00172] Surfactants are generally used to de-dust, lubricate, reduce surface tension, and/or densify. Examples of surfactants include, but are not limited to mineral oil, castor oil, and soybean oil. One mineral oil surfactant is Drakeol 34, available from Penreco (Dickinson, Texas, USA). Maxsperser W-6000 and W-3000 solid surfactants are available from Chemax Polymer Additives (Piedmont, South Carolina, USA). Nionic ionic surfactants with HLB values ranging from about 2 to about 16 can be used examples being TWEEN-20, TWEEN-65, Span-40 and Span 86.

[00173] Anionic surfactants include aliphatic carboxylic acids such as lauric acid, myristic acid, palmitic acid, stearic acid, and oleic acid; fatty acid soaps Another optional functional component is a nanoclay or organically modified clay. There are several types of clays used in polymeric compositions, including cationic or medium or high cation exchange capacity. The cation exchange capacity is generally reported as the number of milliequivalents of exchangeable base which can be exchanged per 100 grams of clay. The cation exchange capacity varies from about 50 to about 150 depending on the type of clay. Examples of clays which can be organically modified include sepiolite, attapulgite, montmorillonites, bentonites, saponite and nentronite.

[00174] Organically modified clays are known in the art and are also described in U.S. Patent No. 2,531,440. Examples include montmorillonite clay modified with ternary or quaternary ammonium salts. Nanoclays are commercially available from Southern Clay Products, Inc. of Gonzales, Texas, USA (such as, but not limited to, CLOISITE[®]NA⁺ (a natural montmorillonite), CLOISITE[®]93A & 30B (a natural montmorillonite modified with ternary ammonium salts), and

CLOISITE[®] 10A, 15A, 20A, and 25A (a natural montmorillonite modified with quaternary ammonium salts).

[00175] Montmorillonite clay is the most common member of the smectite family of nanoclays. Smectites have a unique morphology, featuring one dimension in the nanometer range. The montmorillonite clay particle is often called a platelet, which is a sheet-like structure where the dimensions in two directions far exceed the particle's thickness. The length and breadth of the particles range from 1.5 microns down to a few tenths of a micrometer. However, the thickness is only about a nanometer. These dimensions result in extremely high average aspect ratios (on the order of 200 - 500). Moreover, the very small size and thickness mean that a single gram of clay can contain over a million individual particles.

[00176] The clay initially comprises agglomerates of platelet layers. Nanoclay becomes commercially useful if processed into an intercalate, which separates (exfoliates) the platelets in the agglomerates. In an intercalate, the clay is mixed with an intercalate under conditions which cause the platelets to separate and the intercalate to enter into the spaces between the platelets. The intercalant is often an organic or semi-organic chemical capable of entering the montmorillonite clay gallery and bonding to the surface of the platelets. An intercalate is therefore a clay-chemical complex wherein the clay gallery spacing has increased, due to the process of surface modification by the substance (the intercalant). Under the proper conditions of temperature and shear, the platelet agglomerates are capable of exfoliating (separating), allowing the intercalant to enter between them, separating and exfoliating them.

[00177] The platelets can be exfoliated (separated) by a number of processes. In one exfoliation procedure, described in U.S. Patent No. 6,699,320, the process utilizes a dispersant to enter between the layers of clay platelets and separate them. In this process, the clay is mixed with a dispersant (*e.g.*, castor wax), and then heated in the barrel of an extruder to a temperature above the melting point of the dispersant (*e.g.*, 82° C – 104° C in the case of castor wax). The heated mixture is then agitated, *e.g.*, with a deep flighted screw. This heating and agitating disperses the platelet layers and delaminates the platelets from neighboring layers, by allowing molecules of dispersant to enter between the layers. The layers are considered “exfoliated” when the separation between the platelet layers is large enough such

that there is no longer sufficient attraction between layers to cause uniform spacing between the layers.

[00178] In the process described in U.S. Patent No. 6,699,320, the screw within the extruder moves the clay-wax mixture out of an extrusion die opening in the form of a hot slurry. Two chilled chrome-plated rollers are then used to calender the mixture to a predetermined thickness that is determined by the spacing between the rollers. The mixture is cooled to solidify the wax. The clay-wax mixture is then scraped off the rollers and falls as flakes onto a conveyer belt. The flakes can be tumbled to further reduce their size, and used immediately, or stored.

[00179] Because of the very small size of the clay particles, nanoclays are difficult to handle, and may pose health risks. They are therefore sometimes processed into “masterbatches,” in which the clay is dispersed into a polymer resin at a high concentration. Portions of the masterbatch are then added in measured quantities to polymer that does not contain nanoclay, to produce a polymer containing a precise amount of the nanoclay.

[00180] One montmorillonite clay is Cloisite® 25A, which can be obtained from Southern Clay Products of Gonzales, Texas, USA. A typical dry particle size distribution of Cloisite® 25A is 10% less than 2 microns, 50% less than 6 microns, and 90% less than 13 microns.

[00181] Other nanoclays are identified in U.S. Patent No. 6,414,070 (Kausch *et al.*), which is incorporated herein by reference in its entirety, and PCT Patent Publication Nos. WO 00/66657 and WO 00/68312.

Annealing

[00182] Post-fabrication heat treating (*e.g.*, annealing) of compositions described herein produces a composition with improved physical properties, such toughness.

[00183] For instance, the PHA compositions are treated for about 10 to about 120 minutes at temperatures of about 80°C to about 120°C. Such treatment improves the toughness of the fibers or nonwovens. Another physical property improved is that physical aging of the fiber is reduced by the annealing temperature as compared without the treatment.

[00184] Although various PHAs are capable of being processed on conventional processing equipment, many problems have been found with the polymers that

impede their commercial acceptance. These include brittleness and age-related brittleness. For instance the mechanical properties of articles made from polyhydroxyalkanoate polymers are known to change over time, during storage at ambient conditions. Specifically, the impact toughness and tensile elongation at break (ϵ_b) are known to decrease systematically over time. The exact reasons for this decrease are not known. This age-related increase in brittleness limits the commercial applications available for use of the polymer. In addition, the crystallization kinetics of the polymer are poorly understood, and longer cycle times (relative to polyethylene and polypropylene) are often required during processing of these polymers, further limiting their commercial acceptance. Post-fabrication heat treating (*e.g.*, annealing) provides benefits to the mechanical properties of the PHA compositions.

[00185] As disclosed herein, “annealing” and “heat treatment” means a treatment where the polyhydroxyalkanoate polymer processed to a product in is subsequently (*i.e.*, after the fiber or web is formed) heated for a period of time. This has been found to provide surprising and unexpected properties of toughness. Preferably the fiber or web is heated to about 80°C to about 140°C for about 5 seconds to about 90 minutes, more preferably to about 90°C to about 130°C for about 10 minutes to about 70 minutes, and most preferably to about 110°C to about 125°C for about 15 minutes to about 60 minutes.

[00186] This is accomplished, for instance, in-line by forming the fiber or web in any of a variety of ways, and then running the fiber or web through an oven that is maintained at the appropriate temperature. The oven is long enough so that between entering and exiting the oven, the composition is exposed to the heat for the appropriate amount of time. Alternatively, the composition is “snaked” through the oven, *e.g.*, back and forth on a series of rollers within the oven, so that the fiber or web is exposed to the heat for the appropriate amount of time before exiting the oven.

[00187] For the fabrication of useful articles, a polymeric composition described herein is created at a temperature above the crystalline melting point of the thermoplastic but below the decomposition point of any of the ingredients of the composition. Alternatively, a pre-made blend composition of the present invention

is simply heated to such temperature. Such processing can be performed using any art-known technique used to make non-woven materials.

[00188] The polymeric compositions of the present invention can be used to create, without limitation, a wide variety of useful products, *e.g.*, automotive, consumer, durable, construction, electrical, medical, and packaging products. For instance, the polymeric compositions can be used to make, without limitation, non-wovens and articles made from non-woven materials, such as filters, insulation materials and disposable clothing and wipes.

[00189] The invention will be further described in the following examples, which do not limit the scope of the invention defined by the claims.

EXAMPLES

TESTING METHODS

Measurement of Molecular Weight of Polymers

[00190] Molecular weight (either weight-average molecular weight (Mw) or number-average molecular weight (Mn)) of PHA is estimated by gel permeation chromatography (GPC) using, *e.g.*, a Waters Alliance HPLC System equipped with a refractive index detector. The column set is, for example, a series of three PLGel 10 micrometer Mixed-B (Polymer Labs, Amherst, MA) columns with chloroform as mobile phase pumped at 1 ml/min. The column set is calibrated with narrow distribution polystyrene standards. Unless otherwise indicated, "molecular weight," as used herein, refers to weight average molecular weight.

[00191] The PHA sample is dissolved in chloroform at a concentration of 2.0 mg/ml at 60°C. The sample is filtered with a 0.2 micrometer Teflon syringe filter. A 50 microliter injection volume is used for the analysis.

[00192] The chromatogram is analyzed with, for example, Waters Empower GPC Analysis software. Molecular weights and PD are reported as polystyrene equivalent molecular weights.

[00193] The GPC method become inaccurate when measuring molecular weights over about one million. For polymers with such high molecular weights, the weight average molecular weight is estimated by flow injection polymer analysis (FIPA) system (commercially available from, *e.g.*, Viscotek Corp, Houston, TX) The polymer solution is eluted through a single, low volume size exclusion to separate

polymer, solvent and impurities. The detection system consists of a refractive index, light scattering and viscosity group.

[00194] The polymer sample is dissolved in chloroform at a concentration of 2.0 mg/ml at 60°C. The sample is filtered with a 0.2 micrometer Teflon syringe filter. The FIPA unit operates at 45°C with tetrahydrofuran mobile phase at a flow rate of 1.0 ml/min. A 100 microliter injection volume is used for the analysis.

[00195] The chromatogram is analyzed with, *e.g.*, Viscotek Omni-Sec software. The absolute Mw is reported in grams/mole.

[00196] For PHA polymers, the absolute Mw (as measured by FIPA) is related to the Mw (as measured by GPC in polystyrene equivalents) by dividing the GPC value by approximately 1.3.

Measurement of Thermal Stability

[00197] The thermal stability of a polymer sample is measured in two different ways. The thermal stability is represented herein by a sample's "k," which shows the change in Mw over time. It can also be measured by melt capillary stability (MCS), which shows the change in the capillary shear viscosity over time.

[00198] To measure the thermal stability ("k") of a sample, a polymer specimen (*e.g.*, 2 mg) is exposed to 170° C in a DSC test chamber (*e.g.*, a TA Instrument Q-2000), and the specimen heated for 0, 5 and 10 minutes. The cooled sample cup is unsealed and the sample dissolved in chloroform to the concentration required for gel permeation chromatography (GPC). GPC is used to measure Mw, Mn and Mz molecular weight averages of polymers, relative to a 900K polystyrene control.

[00199] The slope of the best-fit straight line of reciprocal weight-average molecular weight ($1/M_w$) versus time is the thermal stability of the sample in moles per gram per minute. A smaller "k" translates to better thermal stability.

[00200] The thermal stability of a sample is measured using a capillary rheometry test. Capillary rheometers are generally used to measure the melt viscosity of plastics as a function of shear rate (typically from about 0.1 to 10,000 sec⁻¹). However, measuring the melt viscosity of PHA polymers is complicated, because the molecular weight degradation reaction occurs at the test conditions themselves, which results in decreasing viscosity as a function of melt dwell time.

[00201] This obstacle is overcome by measuring the melt viscosity at various dwell times and extrapolating back to zero time (this is described in ASTM D3835-08, ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA). In the tests used herein, measurements are performed at 180°C. The material is preheated for 240 seconds (4 minutes) before the testing is commenced, and a capillary die of 0.75 mm diameter and 30 mm length is used. The measured apparent viscosity (as calculated from pressure and rate) decreases with increasing dwell time in the rheometer. When measured apparent viscosity (at an apparent shear rate of 100 sec⁻¹) is plotted as a function of time, the slope of this best-fit straight line is used as another indicator of thermal stability. This slope is referred to as “melt capillary stability,” or MCS. The MCS number is negative, because viscosity decreases with time, and a larger magnitude (*i.e.*, a smaller number) corresponds to poorer thermal stability. In other words, a negative number closer to zero is more desirable, and a larger negative number is less desirable.

Measuring G' Using Torsional Melt Rheometry

[00202] Torsional rheometry is used to measure the melt strength of a polymer. For purposes of simplicity, G' will be used herein, measured at an imposed frequency of 0.25 rad/s as a measure of “melt strength” (unless otherwise indicated). Higher G' translates to higher melt strength.

[00203] All oscillatory rheology measurements are performed using a TA Instruments AR2000 rheometer employing a strain amplitude of 1%. First, dry pellets (or powder) are molded into 25 mm diameter discs that are about 1200 microns in thickness. The disc specimens are molded in a compression molder set at about 165° C, with the molding time of about 30 seconds. These molded discs are then placed in between the 25 mm parallel plates of the AR2000 rheometer, equilibrated at 180° C, and subsequently cooled to 160° C for the frequency sweep test. A gap of 800-900 microns is used, depending on the normal forces exerted by the polymer. The melt density of PHB is determined to be about 1.10 g/cm³ at 160° C; this value is used in all the calculations.

[00204] Specifically, the specimen disc is placed between the platens of the parallel plate rheometer set at 180° C. After the final gap is attained, excess material

from the sides of the platens is scraped. The specimen is then cooled to 160° C where the frequency scan (from 625 rad/s to 0.10 rad/s) is then performed; frequencies lower than 0.1 rad/s are avoided because of considerable degradation over the long time it takes for these lower frequency measurements. The specimen loading, gap adjustment and excess trimming, all carried out with the platens set at 180° C, takes about 2½ minutes. This is controlled to within ±10 seconds to minimize variability and sample degradation. Cooling from 180° C to 160° C (test temperature) is accomplished in about four minutes. Exposure to 180° C ensures a completely molten polymer, while testing at 160° C ensures minimal degradation during measurement.

[00205] During the frequency sweep performed at 160° C, the following data are collected as a function of measurement frequency: $|\eta^*|$ or complex viscosity, G' or elastic modulus (elastic or solid-like contribution to the viscosity) and G'' or loss modulus (viscous or liquid-like contribution to the viscosity).

[00206] As used herein, G' measured at an imposed frequency of 0.25 rad/s (unless otherwise indicated) is used as a measure of “melt strength.” Higher G' translates to higher melt strength.

[00207] Melt viscosity is measured by ASTM D3835 (ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA).

[00208] Tensile properties were measure according to ASTM D412-Test Method A-Standard Test Method for Vulcanized Rubber and Thermoplastic Elastomers (ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA).

Example 1. Production of Soft Non-Woven Fibers From PHB and CITROFLEX[®] A4 Plasticizer

[00209] A 6 inch melt blowing line that was used to produce in general PHA fabrics was used to produce the PHB non-woven materials in this example. The line used a die with 0.025 inch die hole diameter (120 holes).

Table 2. Other parameters of the melt blowing line.

Design	horizontal line
Die-to collector distance	23-25 inches
Extruder screw compression ratio	3
Extruder screw metering section channel depth ratio to barrel diameter	10
Extruder screw diameter	1.25"
Extruder screw design	3 zones
Typical material usage	8 lb/hr
Typical melt residence time	7 minutes
Melt filtration	No
Take up speed	Can vary from 5 sec to 2 min

[00210] A resin formulation of 90% PHB and 10% of plasticizer CITROFLEX[®] A4 (acetyl tri-n-butyl citrate) was fed into the extruder. The resin formulation had a melt viscosity after 5 minutes exposure at 180° C of 924 Pa.s as measured by D3835 (ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA), and a weight-average molecular weight of 420 kg/mol. Two screen packs of 60 and 180 mesh sizes were used and the die was a 121 hole die of 0.010 inch (250 μ m) holes. The air gap was set to 0.060 inch.

[00211] The conditions used are shown in Table 3, below.

Table 3. Conditions used to make non-woven web.

Control Point	Settings*	Running conditions
Screw Zone 1	150° C	170° C
Screw Zone 2	155° C	165° C
Screw Zone 3	120° C	145° C
C Zone	145° C	150° C
Die Zone 1	NA	NA
Die Zone 2	155° C	160° C
Die Zone 3	155° C	160° C
Die Zone 4	155° C	160° C
Screw Speed (rpm)		26-30
Pressure (psi)		350-400

Air Temp	400-415° F (204-213° C)
Air Rate	5-8 psi
Throughput	4.5 g/min
Distance die/collector belt	85 cm

[00212] A soft continuous web was obtained with the fiber diameter ranging from 2 to 5 microns and basis weight from 20 to 160 GSM. The residual Mw of the polymer was 235 kg/mol, providing a molecular weight retention of 56%. The residual crystallinity was 51%.

[00213] Samples from six identical runs were tested for strength, and the tensile/elongation curve is presented in FIG. 2. A summary of the mechanical properties is presented in Table 4.

Table 4. Mechanical Properties of Six Samples of Non-Wovens.

Thickness (millimeters)	Mean	1.52
	SD	0.08
Air Permeability (cfm)	Mean	25.90
	SD	2.70
PMI (microns)	Bubble	29.91
	Mean	15.71
Basis Weight (grams/sq. meter)	Mean	141.20
	SD	8.42
Fiber diameter (microns)	Mean	2.14
	SD	5.11
Penetration by alcohol	Rating No.	1
Peak Force (machine direction)	Lbs.	1.98
Peak Elongation (machine direction)	%	3.39

[00214] A photograph of the fiber structure is presented in FIG. 3.

Example 2. Effect of Increased Temperature Exposure on Production of Non-Woven Fibers From PHB and CITROFLEX[®] A4 Plasticizer

[00215] A resin formulation of 90% polyhydroxybutyrate and 10% of CITROFLEX[®] A4 (acetyl tri-n-butyl citrate) was used to make non-wovens. The formulation had a melt viscosity of 924 Pa.s after 5 minutes at 180° C, and a weight-

average molecular weight of 420 kg/mol. The onset of crystallization was 102°C and the temperature of peak crystallization was 93.5°C.

[00216] The material was fed into the same extruder as used in Example 1. Two screen packs of 60 and 180 mesh sizes were used and the die was a 121-hole die with 0.010 inch (250 μ m) holes. The air gap was set to 0.060 inch. The processing conditions used are provided in Table 5, below.

Table 5. Processing conditions for 90% PHB : 10% CITROFLEX[®] A4.

Control Point	Settings	Run Conditions
Screw Zone 1	160°C	161°C
Screw Zone 2	160°C	160°C
Screw Zone 3	155°C	170°C
C Zone	155°C	157°C
Die Zone 1	NA	169°C
Die Zone 2	155°C	154°C
Die Zone 3	155°C	156°C
Die Zone 4	160°C	162°C
Screw Speed (rpm)		18
Pressure (psi)		312
Air Temp		395°F
Air Rate		8 psi
Throughput		4.5 g/min

[00217] These higher temperature exposure and longer residence time (the screw rpm was 18), the fibers started to become much rougher and more brittle. Molecular weight retention dropped to less than 40%. The molecular weight of three samples of the extruded fibers was 167, 159 and 157 kg/mol.

[00218] Samples from six identical runs were tested for strength, and the tensile/elongation curve is presented in FIG. 4. The basis weight for the tested samples is 30 GSM. The peak force in the machine direction was 0.77 lbs., and the peak elongation was 1.65%. The mean fiber diameter was 2 microns, with a standard deviation of 9 microns. The fiber felt rough.

Example 3. Production of Non-Woven Fibers From PHB and DINA

[00219] A formulation of 85% polyhydroxybutyrate and 15% DINA (diisononyl adipate) was used to make non-wovens. The formulation had a melt viscosity after 5 minutes at 180° C of 1058 Pa.s. The peak crystallization of this formulation at 10°C per minute was 83°C, and the temperature of onset of crystallization was 98°C.

[00220] Two screen packs of 60 and 180 mesh sizes were used and the die was a 121-hole die with 0.010 inch (250 µm) holes and an air gap of 0.060 inch. The processing conditions used were as follows.

Table 6. Processing Conditions for 85% PHB : 15% DINA.

Control Point	Settings	Run Conditions
Screw Zone 1	150°C	148°C
Screw Zone 2	1550°C	154°C
Screw Zone 3	120°C	128°C
C Zone	145°C	147°C
Die Zone 1	NA	128°C
Die Zone 2	155°C	158°C
Die Zone 3	155°C	153°C
Die Zone 4	145°C	145°C
Screw Speed (rpm)		30
Pressure (psi)		182
Air Temp		420°F
Air Rate		5 psi

[00221] The fibers made from this formulation were more brittle, and lost their softness.

Example 4. Effect of Processing Conditions on Production of Non-Woven Fibers From PHB Copolymer and CITROFLEX[®] A4 Plasticizer

[00222] A resin formulation of 90% polyhydroxyalkanoate copolymer and 10% of CITROFLEX[®] A4 (acetyl tri-n-butyl citrate) was used to make non-wovens. The polyhydroxyalkanoate copolymer was 60% polyhydroxybutyrate and 40% poly(3-hydroxybutyrate-co-4-hydroxybutyrate). The formulation had a weight-average molecular weight of 92.855 kg/mol.

[00223] The material was fed into the same extruder as used in Example 1. One 200 mesh screen packs and the die was a 121-hole die with 0.025 inch holes. The air gap was set to 0.030 inch. The processing conditions used are provided in Table 7, below.

Table 7. Processing conditions for 90% PHB : 10% CITROFLEX[®] A4.

Control Point	Settings	Run Conditions
Screw Zone 1	170°C	179°C
Screw Zone 2	170°C	168°C
Screw Zone 3	170°C	181°C
C Zone	170°C	169°C
Die Zone 1	NA	NA
Die Zone 2	170°C	171°C
Die Zone 3	170°C	170°C
Die Zone 4	170°C	171°C
Screw Speed (rpm)		200
Pressure (psi)		107
Air Temp		330°F
Air Rate		11 psi

[00224] The processing temperatures and back pressure were very high, relative to Examples 1 and 2. Coarse and brittle fibers were produced. The molecular weight retention was 22%.

Example 5. PHA blend with Wet-Milled Nucleating agent and Plasticizer

[00225] The compound was based on PHA resin with the following composition: 36% P3HB, 24% (3HB-11%4HB), 40% (3HB-30%4HB). The wet milled boron nitride (BN) (dispersion D218, 18% BN in acetyl tri-n-butyl citrate, Citraflex A4, Vertellus) was mixed with acetyl tri-n-butyl citrate, Citraflex A4, dryblended and added to the resin. The average particle size of the BN were found to be below 20 microns (based on optical microscopy data).

[00226] The compound's formulation is presented in Table 8.

Table 8. Composition of the compound for the non-woven material.

Ingredients	%
PHA	86
acetyl tri-n-butyl citrate	9
Wet milled Boron Nitride (BN) dispersed in acetyl tri-n-butyl citrate, 18% BN	5

[00227] The compounding was done on a 27 mm MAXX Leistritz twin-screw extruder using the following temperature profile: 10 zones set at 170 / 170 / 165 / 165 / 165 / 160 / 160 / 160 / 160 / 155° C. The extrusion rate was set at 60 lbs/hr and the extruder was operated at 200 rpm.

[00228] The compound had the following melt viscosity at 180° C: after 5 minutes 284 Pa sec, after 10 minutes 198 Pa sec, melt stability -0.0723 (see FIG. 5).

[00229] To prepare the melt blown non-woven, the compound was extruded on a single screw extruder with the screw diameter of 50mm and L/D ratio of 30. The die holes were of 300 micron in diameter. The screw temperatures were 185° C, transition temperature was 180° C and the die temperature was 180° C. The attenuation was done with hot air at the temperatures 200-220° C under the pressure of 0.37 kg/cm². The distance from the die to the collector was 60-65 cm, the throughput was 70g/minute. The fiber network is found to be less brittle and embrittlement is not noticeable after 4 months of ambient storage. The fibers were not annealed.

[00230] At these conditions, a fiber network was built (average fiber diameter 45 microns) (see FIG. 6).

Example 6. P3HB polymer with Wet-Milled Nucleating Agent and Plasticizer.

[00231] The compound was based on P3HB resin. The wet milled boron nitride (dispersion D218, 16% BN in acetyl tri-n-butyl citrate, Citraflex A4, Vertellus, average particle size below 20 microns in diameter) was mixed with acetyl tri-n-butyl citrate, Citraflex A4, dryblended and added to the resin.

[00232] The formulation is presented in Table 9, below.

Table 9. Composition of the compound for the non-woven material.

Ingredients	%
PHB	75
acetyl tri-n-butyl citrate	20
Wet milled BN dispersed in acetyl tri-n-butyl citrate, 16% BN	5

[00233] The compounding was done on a 27 mm MAXX Leistritz twin-screw extruder using the following temperature profile: 10 zones set at 175 / 175 / 175 / 175 / 170 / 170 / 170 / 170 / 180 / 180° C. The extrusion rate was set at 60 lbs/hr and the extruder was operated at 100 rpm.

[00234] The compound had the following melt viscosity at 180C: after 5 minutes 517 Pa sec, after 10 minutes 278 Pa sec, melt stability -0.124.

[00235] The melt blowing conditions were identical to those described in Example 5. The fibers were much stiffer and more brittle than in Example 5.

RESULTS

[00236] The improvement of the melt blown fibers was due to the combination of the newly developed wet milling and dispersion of boron nitride particles in a citrate based plasticizer. The incorporation of the nucleating agent enabled lower crystallinity PHA polymers to be introduced to the melt blown process. These PHA resins provided better physical properties to the fibers and their networks. The improvements included that they were shown to become less stiff, less prone to the aging related embrittlement, were more elastic and much stronger (tougher).

Example 7. Comparison of PHA Compositions: Soft non-woven described in Example 1.

[00237] Compound A containing 90% PHB and 10% of Citraflex A4 (acetyl tri-n-butyl citrate) was fed into the extruder with L/D=27, screw compression ratio of 3, 2 screen packs of 60 and 180 mesh sizes and the die containing 121 holes of 0.010 inch (250 μ m) in diameter. Air gap was set to 0.060 inch.

Table 10. Conditions of extrusion.

Control Point	Settings*	Running conditions
Screw Zone 1	150° C	170° C
Screw Zone 2	155° C	165° C
Screw Zone 3	120° C	145° C
C Zone	145° C	150° C
Die Zone 1	NA	NA
Die Zone 2	155° C	160° C
Die Zone 3	155° C	160° C
Die Zone 4	155° C	160° C
Screw Speed rpm		26-30
Pressure psi		350-400
Air Temp		400-415° F (204-213° C)
Air Rate		5-8 psi
Throughput		4.5 g/min
Distance die/collector belt		85 cm

[00238] The tensile data for original fiber vs 3.5 month aged fiber is presented in Table 11, below.

Table 11. Tensile data for fresh vs. aged fiber.

	fresh	aged, 3.5 mo
thickness, mean mm	1.52+/- 0.08	
basis weight, GSM	141.2+/- 8.42	
Fiber d, um	2.14 +/- 5.11	
Peak force MD, lbs	1.98	1.66-1.28
Peak elongation, MD, %	3.39	2.41-1.9

[00239] The data shows that the peak force required to break the fiber network decreases up to 35% after 3.5 months of ambient aging. The peak % of elongation also decreases up to 44%.

[00240] Compound B was prepared with PHA resin with the following composition: 36% P3HB, 24% (3HB-11%4HB), 40% (3HB-30%4HB). The wet milled boron nitride (dispersion D218, 18% BN in acetyl tri-n-butyl citrate, CITROFLEX[®] A4, Vertellus) was mixed with acetyl tri-n-butyl citrate, CITROFLEX[®] A4, dryblended and added to the resin. The average particle size of the BN were found to be below 20 microns (optical microscopy data).

[00241] Compound A is the softest with the smallest fiber diameter (a mean of 2 microns). This compound also formed thick non-wovens of about 1.52mm thickness. Tensile retention is sufficient for such thick materials. These fibers would be useful for applications where softness is a key property, such as wipes.

[00242] The compound's formulation is presented in Table 12.

Table 12 Composition of the compound for the non-woven material.

Ingredients	%
PHA	86
acetyl tri-n-butyl citrate	9
Wet milled BN dispersed in acetyl tri-n-butyl citrate, 18% BN	5

[00243] The compounds below were produced as described in Example 6:

Table 13. Characteristics of fibers produced from Compounds A and B.

	PHB, Compound A- 1, aged 4 mo	Compound B, aged 4 mo
thickness, mean mm	0.26	0.35
basis weight, GSM	100	164
Fiber d, um	40	40
Peak force MD, lbs	0.6	1.9
Peak elongation, MD, %	1.74	8.6

Max load, N	2.67	8.61
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[00244] These fibers have diameters of about 40 microns and are stiffer non-wovens compared to the fibers in Table 12. These fibers would have applications for use in filers, thermal or sound insulators, erosion control and mulch control materials. these fibers form much thinner networks and because they are thicker may be more susceptible to brittleness with aging.

[00245] This data demonstrates that after similar aging and with the same fiber geometry, the Compound B fibers were capable to withstand 8.6 N or force while Compound A-1 breaks at 2.67N. Tensile properties are measured according to ASTM D412, Test method A-Standard Test Method for Vulcanized Rubber and Thermoplastic Elastomers (ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959 USA). Tension Die C-half. The rate of extention was 10mm/min. These fibers were made on the same equipment for comparison. The fibers of Compounds A-1 and B are much coarser and much more sensitive to embrittlement.

Example 8: Copolymer Wet-milled Nucleating Compositions for making melt-blown fibers and non-wovens.

[00246] The following formulations and blends of two or more formulations can be useful for producing fibers according the present invention for use in fiber and non-woven applications. The extruded non-woven fibers can be produced by the methods described herein or known in the art.

Table 14. Polymer blends for non-wovens.

Formulation	Copolymer	Wet-milled Nucleating agent in acetyl tri-n-butyl citrate (18% BN)
1a	poly(3-hydroxybutyrate-co-4-hydroxybutyrate) 8% 4-hydroxybutyrate content	1-10% of wet-milled boron nitride
1b	poly(3-hydroxybutyrate-co-4-hydroxybutyrate) 11% 4-hydroxybutyrate content	1-10% of wet-milled boron nitride
1c	poly(3-hydroxybutyrate-co-4-	1-10% of wet-

	hydroxybutyrate) 15% 4-hydroxybutyrate content	milled boron nitride
2a	poly(3-hydroxybutyrate-co-5-hydroxyvalerate) 8 % 5-hydroxyvalerate content	1-10% of wet-milled boron nitride
2b	poly(3-hydroxybutyrate-co-5-hydroxyvalerate) 11% 5-hydroxyvalerate content	1-10% of wet-milled boron nitride
2c	poly(3-hydroxybutyrate-co-5-hydroxyvalerate) 15% 5-hydroxyvalerate content	1-10% of wet-milled boron nitride
3a	poly(3-hydroxybutyrate-co-3-hydroxyvalerate) 8 % 3-hydroxyvalerate content	1-10% of wet-milled boron nitride
3b	poly(3-hydroxybutyrate-co-3-hydroxyvalerate) 11% 3-hydroxyvalerate content	1-10% of wet-milled boron nitride
3c	poly(3-hydroxybutyrate-co-3-hydroxyvalerate) 15% 3-hydroxyvalerate content	1-10% of wet-milled boron nitride
4a	poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) 8 % 3-hydroxyhexanoate content	1-10% of wet-milled boron nitride
4b	poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) 11% 3-hydroxyhexanoate content	1-10% of wet-milled boron nitride
4c	poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) 15% 3-hydroxyhexanoate content	1-10% of wet-milled boron nitride

[00247] Each formulation additionally can contain a plasticizer such as acetyl tri-n-butyl citrate. In addition to the above, two or more component blends of each copolymer of the recited formulations can also be made, for example : the copolymer of 1a can be blended with poly (3-hydroxybutyrate) or the copolymer of 2a, 2b, 2c, 3a, 3b, 3c, 4a, 4b, or 4c or combinations thereof and the resultant composition further includes 1-10% of wet-milled boron nitride dispersed in acetyl tri-n-butyl citrate (18% BN).

[00248] Other than in the examples herein, or unless otherwise expressly specified, all of the numerical ranges, amounts, values and percentages, such as those for amounts of materials, elemental contents, times and temperatures of reaction, ratios of amounts, and others, in the following portion of the specification and attached claims may be read as if prefaced by the word “about” even though the term “about” may not expressly appear with the value, amount, or range.

Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[00249] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains error necessarily resulting from the standard deviation found in its underlying respective testing measurements. Furthermore, when numerical ranges are set forth herein, these ranges are inclusive of the recited range end points (*i.e.*, end points may be used). When percentages by weight are used herein, the numerical values reported are relative to the total weight.

[00250] Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of “1 to 10” is intended to include all sub-ranges between (and including) the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10. The terms “one,” “a,” or “an” as used herein are intended to include “at least one” or “one or more,” unless otherwise indicated.

[00251] Any patent, publication, or other disclosure material, in whole or in part, that is said to be incorporated by reference herein is incorporated herein only to the extent that the incorporated material does not conflict with existing definitions, statements, or other disclosure material set forth in this disclosure. As such, and to the extent necessary, the disclosure as explicitly set forth herein supersedes any conflicting material incorporated herein by reference. Any material, or portion thereof, that is said to be incorporated by reference herein, but which conflicts with existing definitions, statements, or other disclosure material set forth herein will only be incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material.

[00252] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

[00253] While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS**WHAT IS CLAIMED IS:**

1. An extruded and melt-blown fiber, comprising a polyhydroxyalkanoate polymer, a wet milled nucleating agent and a plasticizer, wherein the average particle size of the wet-milled nucleating agent is below about 20 microns and is dispersed in the polymer.
2. The fiber of Claim 1, wherein the nucleating agent is boron nitride.
3. The fiber of Claim 1 or 2, wherein the fiber comprises about 75% to about 95% by weight polyhydroxyalkanoate polymer.
4. The fiber of Claim 1, 2 or 3 wherein the fiber has a weight-average molecular weight of at least about 150 kg/mol.
5. The fiber of any one of Claims 1 - 4, wherein the plasticizer is acetyl tri-n-butyl citrate.
6. The fiber of any one of Claims 1 - 5, wherein the fiber diameter is about 0.1 to about 50 microns.
7. The fiber any one of Claims 1 - 6, wherein the fiber diameter is about 2 to about 5 microns.
8. The fiber any one of Claims 1 - 7, wherein the nucleating agent is between about 1% to 10 % weight of the total composition.
9. The fiber of claim any one of Claims 1 - 8, wherein the basis weight is from about 20 to about 160 GSM.
10. The fiber of any one of Claims 1 - 9, wherein, the polyhydroxyalkanoate polymer is a poly(3-hydroxybutyrate) homopolymer, a poly(3-

hydroxybutyrate-co-4-hydroxybutyrate), a poly(3-hydroxybutyrate-co-3-hydroxyvalerate), a poly(3-hydroxybutyrate-co-5-hydroxyvalerate), or a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).

11. The fiber of any one of Claims 1 - 9, wherein the polyhydroxyalkanoate polymer is a poly(3-hydroxybutyrate) homopolymer, a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with 5% to 15% 4-hydroxybutyrate content, a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with 5% to 22% 3-hydroxyvalerate content, a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with 5% to 15% 5-hydroxyvalerate content, or a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with 3% to 15% 3-hydroxyhexanoate content.
12. The fiber of any one of Claims 1 - 9, wherein the polyhydroxyalkanoate is a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate); a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate); a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) or a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).
13. The fiber of any one of Claims 1 - 9, wherein the polyhydroxyalkanoate is a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-hydroxybutyrate content; a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content; a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content; a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-

hydroxybutyrate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content; a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with 5% to 15% 4-hydroxybutyrate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content or a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content.

14. The fiber of Claim 12 or 13, wherein the polyhydroxyalkanoate is a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); or a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b).
15. The fiber of Claim 12, 13 or 14, wherein the weight of polymer a) is 20 % to 60% of the combined weight of polymer a) and polymer b) and the weight of polymer b) is 40% to 80% of the combined weight of polymer a) and polymer b).

16. The fiber of Claims 1 - 9, wherein the polyhydroxyalkanoate is a) poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content; a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate content; a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content; a) poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-hydroxybutyrate content blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content; a) poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-hydroxybutyrate content blended with b) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate content; a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with 5% to 15% 4-hydroxybutyrate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content; a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content blended with b) poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content; a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content blended with b) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate content; a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content; a) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content; a) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content blended with b) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate; or a) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

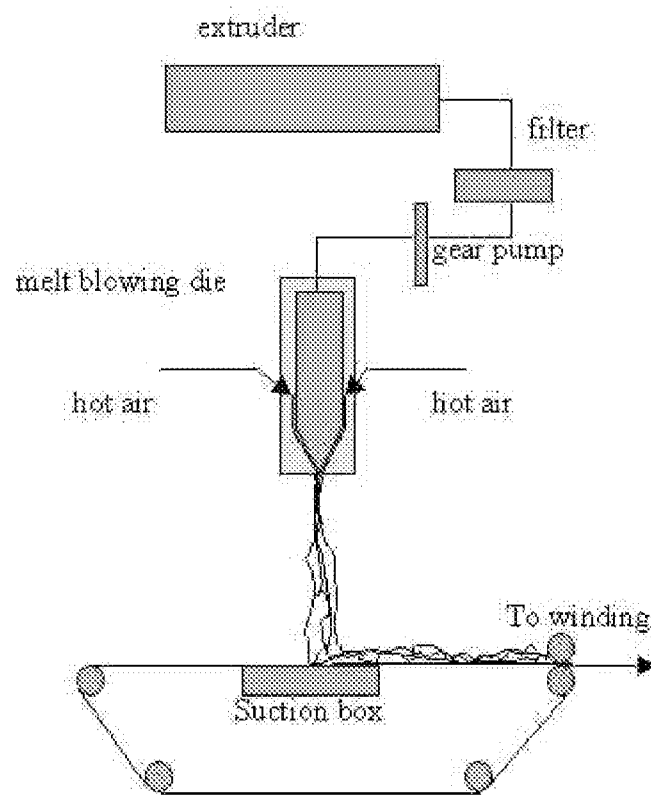
with a 3% to 15% 3-hydroxyhexanoate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content.

17. The fiber of any one of Claims 1 - 9, wherein the polyhydroxyalkanoate is a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate) homopolymer blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-hydroxybutyrate content blended with b) poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-hydroxybutyrate content blended with b) poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 5% to 15% 4-hydroxybutyrate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content blended with b) poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate

content blended with b) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with a 5% to 22% 3-hydroxyvalerate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content blended with b) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20-50% 4-hydroxybutyrate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); a) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content blended with b) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b); or a) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 3% to 15% 3-hydroxyhexanoate content blended with b) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) having a 5%-50% 3-hydroxyhexanoate content and the weight of polymer a) is 5% to 95% of the combined weight of polymer a) and polymer b).

18. The fiber of Claim 16 or 17, wherein the weight of polymer a) is 20 % to 60% of the combined weight of polymer a) and polymer b) and the weight of polymer b is 40% to 80% of the combined weight of polymer a) and polymer b).
19. The fiber of any one of Claims 12 - 18, wherein the polyhydroxyalkanoate is further blended with polymer c) a poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with a 20% to 50% 4-hydroxybutyrate content.
20. The fiber of any one of Claims 12 - 18, wherein the polyhydroxyalkanoate is further blended with c) a poly(3-hydroxybutyrate-co-5-hydroxyvalerate) with a 20% to 50% 5-hydroxyvalerate content.

21. The fiber of any one of Claims 12 - 18, wherein the polyhydroxyalkanoate further blended with c) a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) with a 5% to 50% 3-hydroxyhexanoate content.
22. The fiber of Claim 19, 20 or 21, wherein the weight of polymer c) is 5% to 95% of the combined polymer weight of polymer a), polymer b) and polymer c).
23. The fiber of Claim 21 wherein the weight of polymer c) is 5% to 40% of the combined polymer weight of polymer a), polymer b) and polymer c).
24. A non-woven web, comprising the fiber of any one of Claims 1 - 23.
25. A disposable article, comprising the fiber of any one of Claims 1 - 23.
26. An extruded melt-blown fiber comprising between about 85% and about 95% by weight biologically-produced polyhydroxybutyrate, between about 5% and about 15% acetyl tri-n-butyl citrate, wherein the fiber has a weight-average molecular weight of at least about 200 kg/mol.
27. An extruded fiber comprising a biologically-produced polyhydroxyalkanoate a plasticizer, and a wet milled nucleating agent wherein the fiber has a weight-average molecular weight of at least about 150 kg/mol.
28. A fiber comprising a polymer, a plasticizer and a nucleating agent, wherein the nucleating agent is dispersed in the polymer and wherein at least 5% of the cumulative solid volume of the nucleating agent exists as particles with a particle size of 5 microns or less.



Process layout for meltblown systems

FIG. 1

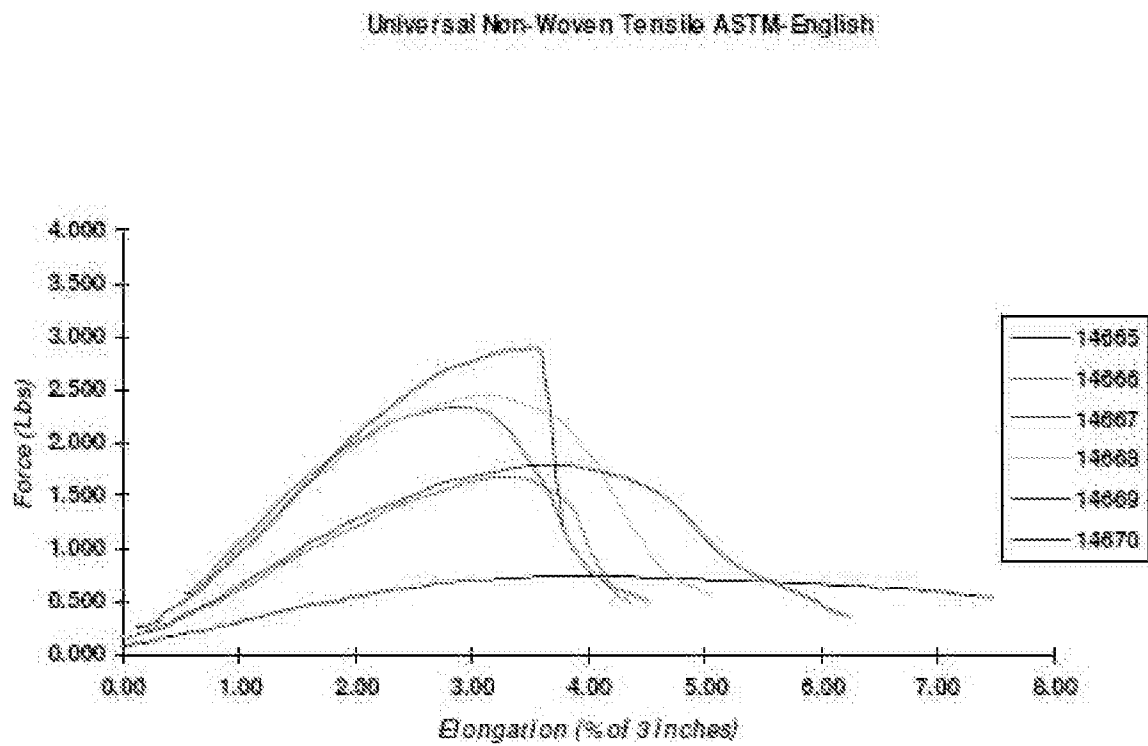


FIG. 2

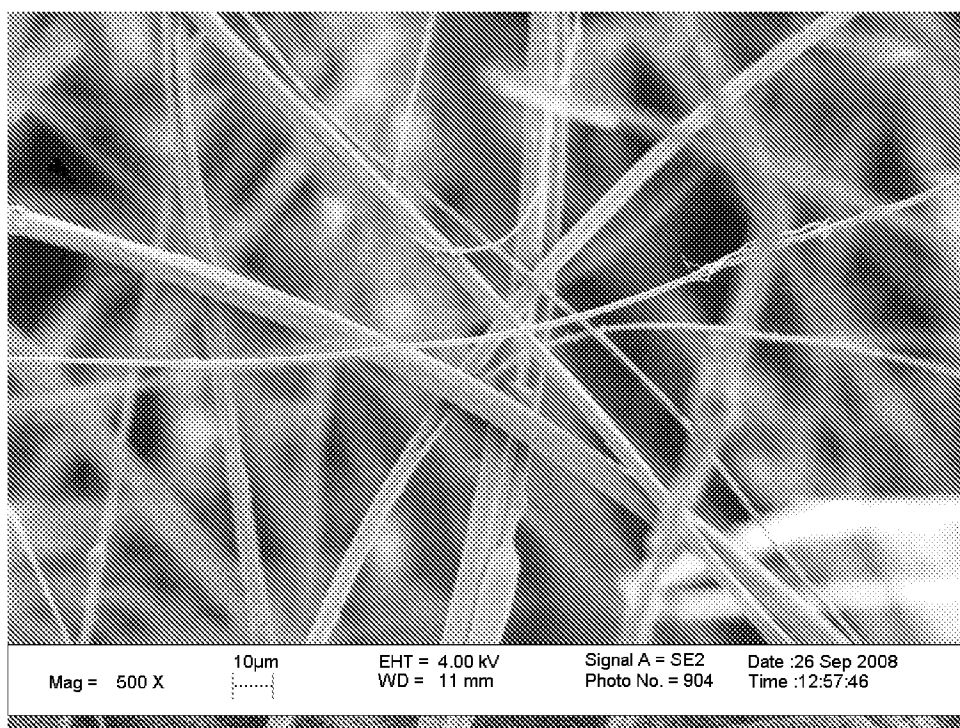


FIG. 3

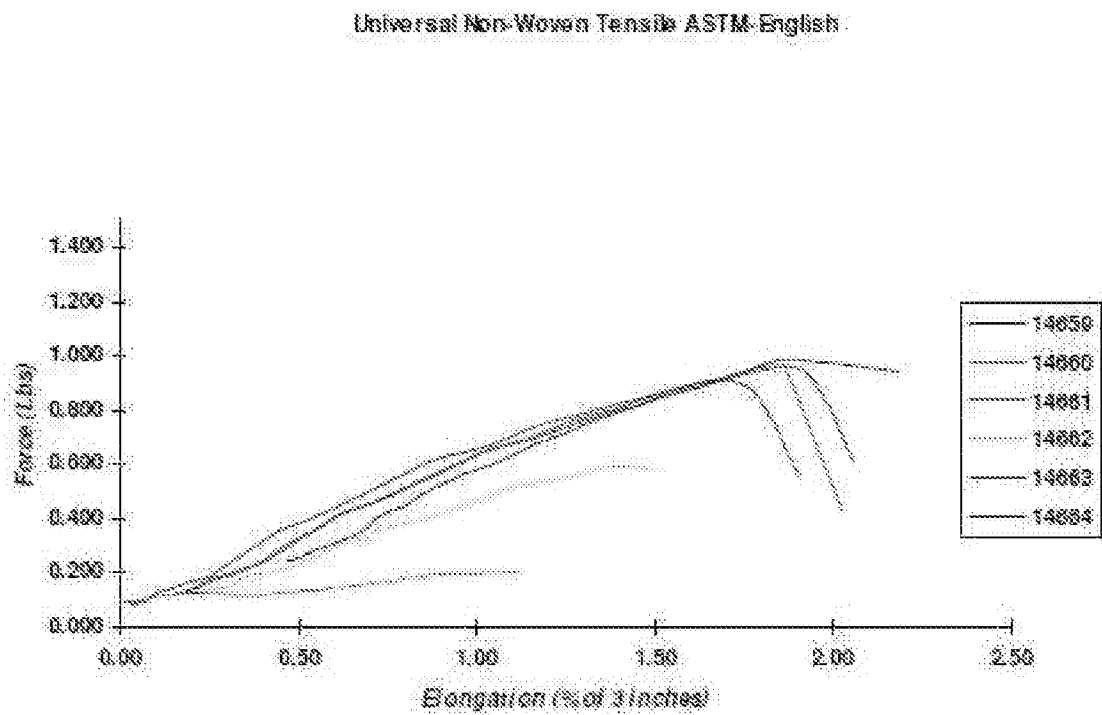


FIG. 4

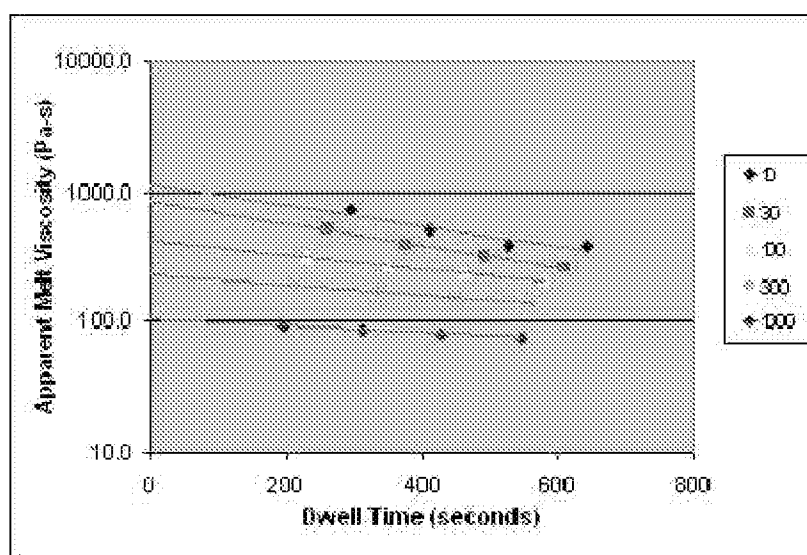


FIG. 5

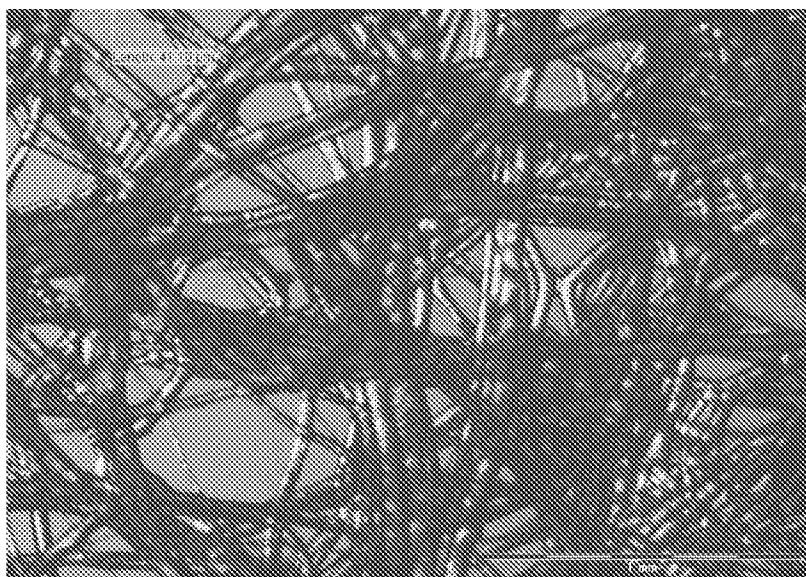


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/069444

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G63/00 D04H3/00 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G D04H C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 111 060 A (GRUBER PATRICK R [US] ET AL) 29 August 2000 (2000-08-29) claims 1,2,5 column 9, line 57 - line 66 column 11, line 22 - column 12, line 25 examples 3,4,6,25,26	1-25,28
Y	US 2002/143116 A1 (NODA ISAO [US] ET AL) 3 October 2002 (2002-10-03) claim 1 examples 1-3 paragraphs [0044], [0045] paragraph [0047]	1-25,28
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

22 March 2010

Date of mailing of the international search report

01/06/2010

Name and mailing address of the ISA/

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Authorized officer

Lauteschlaeger, S

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/069444

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95/20615 A (PROCTER & GAMBLE [US]) 3 August 1995 (1995-08-03) claim 1 example 15 page 31, paragraph 2 -----	1-25,28
Y	WO 2005/066256 A (METABOLIX INC [US]; PADWA ALLEN R [US]) 21 July 2005 (2005-07-21) claims 1,7-11,22 page 10, paragraph 3 page 11, paragraph 4 - page 13 page 15, paragraphs 1,2 page 16, paragraph 3 page 17, line 3, paragraph 1 page 17, paragraph 5 page 18, paragraph 3 table 1 -----	1-25,28
Y	US 5 789 536 A (LIGGAT JOHN JAMIESON [GB] ET AL) 4 August 1998 (1998-08-04) claims 1,2 column 5, paragraph 2 column 3, line 30 - column 4, line 34 examples 1-3 -----	1-25,28
Y	DATABASE WPI Week 200735 Thomson Scientific, London, GB; AN 2007-367776 XP002572615 & JP 2007 077232 A (KANEKA CORP) 29 March 2007 (2007-03-29) abstract -----	1-25,28
Y	DATABASE WPI Week 200720 Thomson Scientific, London, GB; AN 2007-195742 XP002574272 & JP 2007 021428 A (TORAY IND INC) 1 February 2007 (2007-02-01) abstract -----	1-25,28
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2009/069444

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-25, 28

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-25,28

Fibres comprising a polymer, a plasticizer and a nucleating agent the latter being characterized by particular particle size

2. claims: 26,27

Extruded fibres comprising PHA and a particular plasticizer, wherein the polymer contained in the final fibre is characterized by a high molecular weight; according to claim 26 no nucleating agent at all needs to be contained

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/069444

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