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pH-MODIFIED POLYMER COMPOSITIONS WITH ENHANCED BIODEGRADABILITY

TECHNICAL FIELD

10 The present invention relates to biodegradable polymeric compositions and, more particularly, polymeric compositions having enhanced biodegradability relative to the polymer itself. Films prepared from such compositions are particularly suitable for use as backsheets in disposable absorbent articles designed for absorbing various bodily fluids, such as diapers, training pants, sanitary napkins, pantliners, and the like.

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BACKGROUND OF THE INVENTION

20 A wide variety of disposable absorbent structures designed for the absorption of bodily fluids, such as urine and menses, are known. Such products generally comprise some sort of fluid-permeable topsheet material, an absorbent core, and a fluid-impermeable backsheet material. The bulk of such products is often the absorbent core component, such that a typical disposable diaper having an absorbent core consisting primarily of wood pulp fibers consists of about 80% biodegradable materials. However, the remaining components generally comprise materials which are typically considered to be non- or marginally- biodegradable. For example, topsheet and backsheet
25 materials are often prepared from polypropylene or polyethylene.

The biodegradability of disposable absorbent products has recently been emphasized. Although these disposable products typically largely comprise materials that would be expected to ultimately biodegrade, and although such products contribute only a very small percentage of the total solid waste
30 materials generated by consumers each year, there is nevertheless a currently perceived need to devise such disposable products from materials that biodegrade relatively quickly, thereby lessening their bulk. There is a particular need to replace polyethylene backsheets with liquid impervious, biodegradable films since the backsheet is typically the largest non-
35 biodegradable component of an absorbent article. To avoid a buildup of man-made materials in the soil, it is desirable that such materials be fully biodegradable, i.e., biodegradation is complete to carbon dioxide, water,

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not describe the incorporation of the acids or bases into a polymer film. Indeed, the incorporation of such water-soluble acids and bases is believed to be unsuitable for forming polymer films and, more particularly, polymeric films for use in absorbent products intended for applications involving human contact, such as diapers. This is because such water-soluble acids and bases are strong acids and bases. It is believed that the incorporation of such materials into film products would present problems in manufacturing such as equipment corrosion, safety concerns, and moisture sensitivity. It is also believed that the incorporation of such materials into a polymer may result in premature hydrolysis of the polymer composition due to the hygroscopic character of such materials combined with their inherent acidity or basicity. Thus, such a composition may not be sufficiently stable for its intended use. This may be a particular problem in applications where the composition is exposed to moisture for extended periods, such as may occur with the overnight wearing of diapers. Such products may not retain sufficient integrity to satisfy consumer needs. In addition, the presence of strong acids and bases in components of absorbent articles wherein contact with human skin may occur presents toxicity concerns.

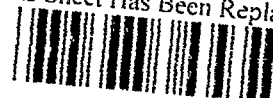
Thus there remains a need for film-processable polymers which are suitable for use in disposable absorbent articles and which have enhanced biodegradability. It is therefore an object of the present invention to provide biodegradable polymers which have increased rates of biodegradability. Another object of the invention is to provide such polymers which are fully biodegradable to carbon dioxide, water, biomass, and minerals. An additional object is to provide such materials which are non-toxic to humans and which remain sufficiently stable during use. Another object is to provide polymer materials which are compostable. Additional objects include providing disposable absorbent articles having enhanced biodegradability.

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SUMMARY OF THE INVENTION

The present invention is directed to polymer compositions having enhanced biodegradability. The polymer compositions comprise a polymer containing hydrolyzable bonds and a substantially water-insoluble, pH-modifying compound such as a substantially water-insoluble acid or base. In a preferred embodiment the polymer composition comprises a polymer containing base-hydrolyzable bonds and a substantially water-insoluble, pH-

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respectively. A bond may be both acid and base hydrolyzable. In addition, both types of bonds may be present in the polymer. The functional group containing hydrolyzable bonds may be present in the linear portions of the polymer chain (i.e., internal groups) or may be pendant to the polymer chain.

5 Exemplary functional groups which contain acid-hydrolyzable bonds include ortho-ester and amide groups. Exemplary functional groups which contain base-hydrolyzable bonds include α -ester and anhydride groups. Functional groups which contain both acid- and base- hydrolyzable bonds include carbonate, ester, and iminocarbonate groups. Thus, exemplary
10 polymers for use in the polymer compositions of the invention include polyesters, cellulose esters, polyester polyurethanes, polyamides, polycarbonates, and polyamino acids. For economic and functional reasons, the polymer is preferably a polyester.

Polyesters for use as the base polymer in the present invention may be
15 aliphatic, aromatic, or mixed aliphatic and aromatic. Typically the polyester will be aliphatic or mixed aliphatic and aromatic.

Exemplary aliphatic polyesters include polycaprolactone, polyesters derived from the reaction of an aliphatic dicarboxylic acid and a diol, polyhydroxyalkanoates, and oxidized ethylene/carbon monoxide polymers.

20 Polycaprolactone can be produced, e.g., via the ring-opening polymerization of epsilon-caprolactone. Such polymers are available from the Union Carbide Corporation under the tradename TONE in a variety of molecular weight (hereinafter MW) grades. For example, TONE polymer P-300, P-700, P-767 and P-787 have average molecular weights of about 10,000;
25 about 40,000; about 43,000; and about 80,000 grams per mole, respectively. These polymers are described in Union Carbide Brochure F-60456 entitled "Tone Polymers," incorporated herein by reference. Polycaprolactone polymers having molecular weights of at least about 40,000 grams per mole can be melt processed into strong, water resistant films and are therefore
30 generally preferred for use in disposable film applications. Polycaprolactone polymers having an average molecular weight of about 80,000 grams per mole are especially preferred.

Block copolymers of polycaprolactone with polydienes such as polyisoprene and polybutadiene are also suitable for use in the present
35 invention. Such polyesters are described in U.S. Patent 3,585,257, issued to Mueller et al., incorporated herein by reference. The block copolymers can have various architectures, for example, an A-B diblock copolymer, an A-B-A triblock copolymer, and $-(A-B)_n-$ multiblock copolymers where $n = 2, 3$, etc.

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- diethylene glycol and 5-sulfoisophthalic acid. International Patent Application WO 91/02015, published February 21, 1991, discloses hydrodegradable, random copolymers comprised of aromatic polyesters such as PET or PBT randomly interrupted with aliphatic hydrodegradable link polymers such as
- 5 polyglycolic acid, polylactic acid, polycaprolactone, polyhydroxybutyrate, polyhydroxybutyrate/valerate, polybutylene oxalate, polyethylene adipate, polyethylene carbonate, polybutylene carbonate, and other polyesters containing silyl ethers, acetals, or ketals. Each of these references is incorporated herein by reference.
- 10 Other mixed aliphatic and aromatic polyesters include copolymers derived from aromatic monomers and aliphatic monomers such as oxalates, malonates, succinates, glutarates, adipates, pimelates, suberates, azelates, sebacates, nonanedioates, glycolates, and mixtures thereof. Such copolymers may contain PET or PBT.
- 15 Cellulose esters represent another type of polymer suitable for use in the present invention. Such esters are described in Modern Plastics Encyclopedia, p.p. 23-24 (McGraw Hill, 1990), incorporated herein by reference. The cellulose esters useful in the present invention can be prepared using techniques known in the art or are commercially available, e.g.,
- 20 from the Eastman Chemical Company, Inc., Kingsport, TN, U.S.A. The cellulose esters which are particularly useful in the present invention have degrees of substitution (DS) in the range of from about 1.6 to about 3.0. Preferred cellulose esters include cellulose acetate (CA), cellulose propionate (CP), cellulose butyrate (CB), cellulose acetate propionate (CAP), cellulose
- 25 acetate butyrate (CAB), cellulose propionate butyrate (CPB), and the like. More preferably, the cellulose ester is CAP or CAB, and is most preferably CAP. These cellulose esters are described in U.S. Patent Nos. 1,698,049; 1,683,347; 1,880,808; 1,880,560; 1,984,147; 2,129,052; and 3,617,201; each being incorporated herein by reference.
- 30 Polyester polyurethanes suitable for use herein include, for example, biodegradable polyurethanes prepared from low molecular weight aliphatic polyesters derived from epsilon-caprolactone or the reaction products of a diol-dicarboxylic acid condensation. For example, biodegradable polyester urethanes derived from polyethyleneglycol adipate, poly (1,3-propanediol
- 35 adipate) and poly (1,4-butanediol adipate) are disclosed in "The Prospects for Biodegradable Plastics", F. Rodriguez (Chem Tech, July - 1971), incorporated herein by reference. Exemplary aliphatic polyester urethanes are available from Morton International, Inc. under the tradename MORTHANE.



compound is preferably calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, or any mixture thereof.

Suitable acidic compounds have a room temperature (i.e., 25°C) solubility in water of less than 10 g/l. Suitable acidic compounds include, for example, organic acids such as aliphatic, aromatic, and mixed aliphatic/aromatic acids (e.g., aliphatic, aromatic, and mixed aliphatic/aromatic carboxylic acids), and inorganic acids such as acid phosphates. Exemplary organic acids are valeric, isovaleric, caproic, heptanoic, lauric, palmitic, adipic, citric (monohydrate), benzoic, 2-acetoxybenzoic, and phthalic acid. Inorganic acids include, for example, mono-, di-, and tri- acid phosphates. The acidic compound is preferably citric acid, adipic acid, phthalic acid, an acid phosphate, or any mixture thereof.

The level of pH-modifying compound used in the polymer composition may be varied by one of ordinary skill in the art to minimize or eliminate any potential skin sensitivity or to maximize hydrolytic activity. Typically, the pH-modifier will be used at a level of from about 1 to about 15 percent based on the weight of the polymer containing hydrolyzable bonds. Hydrolytic activity tends to increase with increasing levels of the pH-modifying compound.

Any combination of an acidic compound and a polymer having acid-hydrolyzable bonds, or a basic compound with a polymer having base-hydrolyzable bonds may be used. However, the combination should provide both sufficient stability of the polymer in storage and in the intended application, and an improved rate of biodegradability under disposal conditions such as in a landfill or in a composter. Thus, the particular blend is preferably chosen such that the polymer composition does not prematurely decompose while in its intended use, for example, when in contact with bodily fluids. The particular selection should also provide an increased rate of biodegradability relative to the unmodified polymer. In general, the components should be selected such that hydrolysis does not occur to a significant extent under the normal storage and use conditions of the composition. These conditions may range, for example, between the extremes of hot and arid, hot and humid, exposure to urine for extended times (e.g., greater than 16 hours), and the extremes of cold and arid or cold and humid. In general, hydrolysis of the polymer composition under normal storage and use conditions should not occur in less than about 1 day, preferably less than about 1 week. Upon later exposure to more extreme hydrolysis conditions, e.g., as may be encountered in a municipal solid waste composting process (typically relatively high

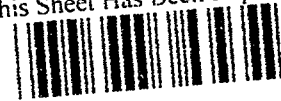


hydrolysis will increase with an increase in moisture in the polymer environment. It is also believed that for a given polymer composition and environmental moisture level, the rate and extent of hydrolysis tends to increase with an increase in temperature, most likely with an increase in temperature to at least the glass transition temperature of the polymer containing hydrolyzable bonds.

Typically, significant microbial degradation will only occur when a polymer or fragment thereof has a molecular weight which is sufficiently low to allow internal enzymatic microbial degradation. Thus, the rate and extent of the microbial degradation step generally depends on the average molecular weight of the polymer between hydrolyzable bonds and the rate and extent of hydrolysis occurring in the hydrolytic step. The lower the molecular weight fragments of the polymer resulting from hydrolysis, the more susceptible the fragments are to microbial attack and thus biodegradation. Typically, to achieve enhanced biodegradability in accordance with the present invention, the average molecular weight of the polymer chain between hydrolyzable bonds is less than about 1000 grams per mole, preferably less than about 500 grams per mole. Without intending to be bound by theory, it is believed that the rate and extent of microbial degradation for these polymers will increase with the rate and extent of hydrolysis. In addition, without intending to be bound by theory, it is expected that for a given degree of hydrolysis of these polymers, the rate and extent of microbial degradation increases as the average molecular weight between hydrolyzable bonds decreases.

The pH-modifying compound may be incorporated into the polymer by any known method of incorporating particulate materials into polymer materials. Such methods are well-known to those skilled in the art and include solution slurries, pre-compounding, and co-extrusion. The resultant compositions are typically dried soon after compounding in order to prevent or minimize any premature hydrolysis. In addition, the composition is preferably dried after any subsequent steps in which significant moisture contamination may occur. Drying conditions are dependent on polymer type and are readily available from the base resin manufacturer. Typically, drying is performed by subjecting the polymer or polymer composition to elevated temperatures (e.g., about 40°C - 60°C) for a period of about 4-12 hours under vacuum or under low moisture air (dew point below about 0°F (18°C)). Drying temperatures are preferably selected to avoid softening and subsequent coalescence of resin particles.

The polymer compositions may optionally contain other components conventionally used in plastics compounding, including pigments and

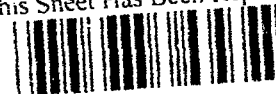


the like. In a preferred embodiment, the films are used as components of disposable absorbent articles, e.g., in the form of backsheets or fastener tabs.

As used herein, the term "absorbent article" refers to devices which absorb and contain bodily fluids (e.g., urine, menses, feces), and, more specifically, refers to devices which are placed against or in proximity to the body of the wearer to absorb and contain the various fluids discharged from the body. The term "disposable" is used herein to describe absorbent articles which are not intended to be laundered or otherwise restored or reused as an absorbent article (i.e., they are intended to be discarded after a single use and, preferably, to be recycled, composted or otherwise disposed of in an environmentally compatible manner). A "unitary" absorbent article refers to absorbent articles which are formed of separate parts united together to form a coordinated entity so that they do not require separate manipulative parts like a separate holder and liner. As used herein, the term "diaper" refers to an absorbent article generally worn by infants and incontinent persons that is worn about the lower torso of the wearer. It should be understood, however, that the present invention is also applicable to other absorbent articles such as incontinent briefs, incontinent undergarments, diaper holders and liners, feminine hygiene garments, sanitary napkins, pantliners, and the like.

Disposable diapers typically comprise a liquid pervious topsheet; a liquid impervious backsheet joined with the topsheet, an absorbent core positioned between the topsheet and the backsheet, and a fastening system. In addition, these diapers may comprise various elastic components such as elasticized side panels, elasticized leg cuffs, or an elastic waist feature. The diaper of the present invention may be assembled in a variety of well known configurations. Preferred diaper configurations are described generally in U.S. Patent 3,860,003, issued to Buell on January 14, 1975; and U.S. Patent 5,152,092, issued to Buell, et al. on September 29, 1992; each of which is incorporated herein by reference. Alternatively preferred configurations for disposable diapers herein are also disclosed in U.S. Patent 4,808,178, issued to Aziz, et al. on February 28, 1989; U.S. Patent 4,695,278, issued to Lawson on September 22, 1987; and U. S. Patent 4,816,025, issued to Foreman on March 28, 1989. These patents are incorporated herein by reference.

U.S. Patent No. 5,152,092 describes in detail various components which may be present in the diaper of the present invention. In order to enhance the biodegradability of the diaper, the diaper has at least one component containing the polymer composition of the present invention. The composition can be incorporated in any form, including film, particulate (including fiber), or



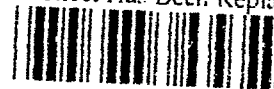
water, biomass, and minerals (under aerobic conditions), and optionally also methane (under anaerobic conditions).

Biodegradation, and thus any enhancements thereof, can be established by a modified Sturm test or by an Organic Waste System (i.e., OWS) method.

- 5 The modified Sturm test is a dilute, aqueous, aerated test. The OWS method is a controlled composting biodegradation test. Both tests are based on the fact that during the aerobic biodegradation of organic materials, carbon dioxide is the primary carbon-containing decomposition product which is generated. The cumulative CO₂ production can be determined by monitoring and
10 integrating the evolved CO₂ in the exhaust stream from a test reactor. The percentage biodegradation can then be calculated as the percentage of carbon in the test material (determined by standard physico-chemical methods) which is converted to CO₂. The Sturm test employs an inoculum derived from the supernatant of a settled, activated sludge from a waste water treatment facility.
15 The inoculum in the OWS test consists of a mature, stabilized fraction of municipal solid waste. Details of these techniques are found in "Ready Biodegradation: Modified Sturm Test," OECD Method #301B; and in "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials under Controlled Composting Conditions," ASTM Method #D5338-92; each test
20 method being incorporated herein by reference.

- A material may be biodegradable without being compostable. "Compostability," "compostable," and the like means the ability of a material to undergo physical, chemical, thermal, and/or biological degradation in a municipal solid waste (hereinafter "MSW") composting facility such that the
25 material will break down into, or otherwise become part of, usable finished compost. To be considered compostable, a material must also ultimately fully biodegrade in the environment in a manner similar to paper and yard waste.

- Municipal solid waste (MSW) composting processes generally involve three sequential phases: waste preparation, active composting, and curing.
30 During the waste preparation phase, raw MSW is first sorted to remove recyclables and known non-compostable materials. The sorted materials are then reduced in physical size, generally via a grinder or rotating drum such as are known in the composting art. The goal is to obtain a consistent physical size, typically particles of about 2" diameter, which will maximize surface area
35 for microbial attack and allow effective air management during the subsequent active composting phase. Following size reduction, materials are usually screened through a 1.5" - 2" screen. In order to be compostable by this process, a material must be capable of being reduced in size such that it



compostable by this process, the material must form an integral part of the usable finished compost and ultimately completely biodegrade in the environment in a manner and at a rate consistent with materials such as paper and yard waste.

- 5 "Enhanced compostability" means either rendering a previously non-compostable material compostable as defined herein, or decreasing the time required to compost an already compostable material. Enhancements in compostability of the polymer compositions of the present invention can be determined by a direct comparison of the composting processes for different
10 materials.

The following example illustrates the practice of the present invention but is not intended to be limiting thereof.

EXAMPLE

- 15 A polymer composition which is a 95%/5% by weight blend of (a) a polyester polymer such as described in U.S. Patent 5,171,308 or International Publication No. WO 92/09654 and (b) calcium hydroxide as the pH-modifying compound may be prepared as follows:

- 20 The polyester polymer is dried in a vacuum oven so as to minimize molecular weight loss of the polyester due to hydrolysis in the elevated temperature of the extruder. Sufficient drying depends on the specific polyester involved, as would be understood by the skilled artisan. Typically sufficient drying is achieved after 4 hours at 140°F (60°C). In 200 gram batches, 190 grams of the dried polyester and 10 grams of $\text{Ca}(\text{OH})_2$ are melt
25 compounded in a Rheomix TW-100 twin screw extruder (available from Haake) equipped with conical barrels, two partially intermeshing counter-rotating screws and a horizontal rod die having a 0.125 inch (0.3175 cm) diameter nozzle. The temperature of the extruder is varied from 284°F (140°C) in the first heating zone, to 302°F (150°C) in the second zone, and to 320°F (160°C)
30 at the discharge end near the die. The die is maintained at 266°F (130°C). The screw speed is held constant at 30 rpm. The resultant, extruded molten strand is then cooled and solidified in a water bath prior to entering a Berlyn Model PEL-2 pelletizer (available from the Berlyn Co.) where it is chopped into pellets approximately 0.125 inches (0.3175 cm) long. Successive 200 gram
35 batches are melt compounded until a total of about 1600 grams of pellets is



What is claimed is:

1. A polymer composition having enhanced biodegradability, comprising a blend of:
 - (i) a polymer containing base-hydrolyzable bonds, preferably selected from the group consisting of polyesters, cellulose esters, polyester polyurethanes, polyamides, polycarbonates, polyamino-acids, and mixtures thereof, more preferably a polyester; and
 - (ii) a substantially water-insoluble, pH-modifying basic compound, said compound being capable of accelerating the hydrolysis of said base-hydrolyzable bonds, preferably having a 25°C solubility product constant in water of from about 1×10^{-6} to about 1×10^{-13} , more preferably selected from the group consisting of alkaline earth metal salts, alkaline earth metal oxides, alkali metal salts of organic acids, basic mono-, di-, and tri- phosphates, conjugate bases of organic acids, and mixtures thereof, most preferably selected from the group consisting of calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, basic mono-, di-, and tri- phosphates, the conjugate bases of organic acids, and mixtures thereof.
2. A film comprising the polymer composition of Claim 1.
3. A method of enhancing the biodegradability of a polymer containing base-hydrolyzable bonds, comprising the step of adding a substantially water-insoluble, pH-modifying basic compound to the polymer, the compound being capable of accelerating the hydrolysis of said base-hydrolyzable bonds, more preferably selected from the group consisting of alkaline earth metal salts, alkaline earth metal oxides, alkali metal salts of organic acids, basic mono-, di-, and tri- phosphates, conjugate bases of organic acids, and mixtures thereof, most preferably selected from the group consisting of calcium oxide, calcium hydroxide, magnesium oxide, magnesium hydroxide, basic mono-, di-, and tri- phosphates, the conjugate bases of organic acids, and mixtures thereof, and the polymer preferably being selected from the group consisting of polyesters, cellulose esters, polyester polyurethanes, polyamides, polycarbonates, polyamino-acids, and mixtures thereof, more preferably a polyester.

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