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| <b>(21) International Application Number:</b> PCT/US92/00229<br><b>(22) International Filing Date:</b> 23 January 1992 (23.01.92)<br><b>(30) Priority data:</b><br>645,995                      25 January 1991 (25.01.91)      US<br><b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).<br><b>(72) Inventors:</b> HYUNKOOK, Shin ; 134 Hitching Post Drive, Wilmington, DE 19803 (US). TIETZ, Raymond, Frank ; 213 Stone Crop Road, Wilmington, DE 19810 (US).<br><b>(74) Agents:</b> HIGGS, W., Victor et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).                                                                                                                                                                              |           | <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).<br><br><b>Published</b><br><i>With international search report.</i><br><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| <b>(54) Title:</b> NOVEL POLYESTERS AND THEIR USE IN COMPOSTABLE PRODUCTS SUCH AS DISPOSABLE DIAPERS<br><br><b>(57) Abstract</b><br><br><p>The invention provides novel polyesters, fibers and films, nonwovens from the fibers and disposable products of the polyesters such as diapers. The products are degradable under the conditions typically existing in waste composting processes, have low ingredient costs and yet provide strength and toughness properties adequate for end uses such as in disposable diapers. The copolyesters are based upon polyethylene terephthalate copolymerized with a monomer containing an alkali metal or alkaline earth metal sulfo group, a polyethylene ether, such as diethylene glycol, and include units from aliphatic hydroxyacids selected for their melting points being lower than their decomposition temperatures.</p> |           |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |

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TITLE

Novel Polyesters and Their Use in Compostable Products Such as Disposable  
Diapers

This invention relates to novel polyesters and products  
5 therefrom. The products include fibers, films, foams, coated papers,  
extruded nets, molded objects and nonwovens and disposable products such  
as diapers from such products. The products are degradable to innocuous  
materials under conditions used in municipal solid waste composting systems.

The inadequate treatment of municipal solid waste which is  
10 being put in landfills and the increasing addition of nondegradable materials,  
including plastics, to the municipal solid waste streams are combining to  
reduce drastically the number of landfills available and to increase the costs  
of municipal solid waste disposal. While the recycling of reusable  
components of the waste stream is desirable in many instances, there are  
15 some products which do not readily fit into this framework, e.g. disposable  
personal absorbents such as diapers and sanitary napkins, garbage bags, and  
numerous other products. The composting of non-recyclable solid waste is a  
recognized and growing method of reducing solid waste volume for  
landfilling and/or making a useful product from the waste to improve the  
20 fertility of fields and gardens. One of the limitations to marketing such  
compost is the visible contamination by undegraded plastic such as film and  
fiber fragments.

As related in US B 5,053,482, there was a desire to achieve  
several objectives, as follows:

25 1 - to provide components which are useful in disposable  
products and which are degraded into less contaminating forms under the  
conditions typically existing in waste composting processes. These conditions  
may involve temperatures no higher than 70 C, and averaging more nearly  
55-60 C, humid conditions as high as 100% relative humidity, and exposure  
30 times which range from two weeks to more than three months.

2 - to provide disposable components which will not only

degrade aerobically/anaerobically in composting, but will continue to degrade in the soil or landfill. As long as water is present, they will continue to break down into low molecular weight fragments which can be ultimately biodegraded by microorganisms completely into biogas, biomass and liquid  
5 leachate, as for natural organics like wood.

3 - to provide novel polyesters for making the aforementioned fibers, films, coatings and nonwoven sheets of the polyesters, and disposable diapers containing the nonwoven sheets.

4 - to provide polyesters and derivative products which have  
10 low ingredient costs and yet provide strength and toughness properties adequate for end uses such as in disposable diapers.

Accordingly, Tietz US B 5,053,482 provided useful novel polyesters consisting essentially of recurring structural units of the formula

15 
$$-\text{C}(\text{O})-\text{R}-\text{C}(\text{O})-\text{OGO}-$$
  
wherein R is about 97.5 to 99.9 mole % para-phenylene (abbreviation T) and about 0.1 to 2.5 mole % of an alkali metal or alkaline earth metal 5-sulfoisophthalate radical (abbreviation 5SI) and wherein G is about 60 to 80 mole %  $-\text{CH}_2-\text{CH}_2-$  (abbreviation 2G) and about 20 to 40 mole %  
20  $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$  (abbreviation DEG), and especially wherein R is about 98 mole % para-phenylene (T) and about 2% of the sulfonate radical (5SI) and G is about 80 mole %  $-\text{CH}_2-\text{CH}_2-$  (2G) and about 20 mole %  $-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$  (DEG), and fibers, non-woven sheet, films and combinations thereof, and disposable diapers comprising such materials.  
25 Such polyesters are useful for some end uses, e.g., as described by Tietz. For other end uses, however, it would be desirable to provide degradable materials having properties better adapted for such different end uses. In particular, it is sometimes desirable to provide polyesters that can be formed into products that have still further improved rate of hydrolysis, but with  
30 similar advantageous properties in many respects, as regards the polyesters that were specifically disclosed by Tietz.

Abbreviations and nomenclature herein, except as otherwise indicated, are as described in aforesaid US B 5,053,482, (PCT/US91/03117, WO 91/18036) which is hereby incorporated herein by reference, as is copending PCT application (QP4690A) filed simultaneously herewith.

5 In one embodiment of the invention there is, accordingly, provided a novel fiber and film forming polyester consisting essentially of recurring structural units of the formulae:



wherein R consists essentially of divalent aromatic radicals and at least about  
10 85 mole % of R is p-phenylene,  
wherein G is

about 20 to 40 mole % of a polyethylene ether radical selected from the group consisting of

15  $\text{-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-}$  and  $\text{-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-}$ ,  
and the remainder of G is a hydrocarbylene radical selected from the group consisting of

$\text{-(CH}_2\text{)}_2\text{-}$ ,  $\text{-(CH}_2\text{)}_3\text{-}$ , and  $\text{-(CH}_2\text{)}_4\text{-}$  radicals,

wherein Q is derived from an hydroxy acid of formula



where x is an integer, such hydroxy acid having a melting point at least 5 C below its decomposition temperature, and Q is selected from the group consisting of a chemical bond and hydrocarbylene radicals

25  $\text{-(CH}_2\text{)}_n\text{-}$ , where n is an integer from 1 to 5,  $\text{-C(R')}_n\text{H-}$ , and  
 $\text{-C(R')}_n\text{HCH}_2\text{-}$ , wherein R' is selected from the group of  $\text{-CH}_3$  and  $\text{-CH}_2\text{CH}_3$ ,

and wherein "a" and "b" are mole fractions of the polymer, and the mole fraction "a" may be 60 to 98% and, correspondingly, mole fraction "b" may be 2 to 40%,

30 provided, however, that about 0.1 to about 2.5 mole % of the polymer contains alkali metal or alkaline earth metal sulfo groups.

According to a further aspect of the invention, a process is provided whereby the polyesters may be copolymerized carefully to provide said copolyesters containing, by weight of the copolyester, about 60-98% of

- (1) the above polyester with about 2 to 40% consisting essentially of structural units (2) of the formula  $[-C(O)-Q-O-]_b$ , wherein Q is such that the hydroxy acid  $HO-C(O)-Q-OH$  and/or the polyhydroxy acid  $HO[-C(O)-Q-O-]_xH$  has a melting point at least 5 C below its decomposition temperature, and wherein the temperature of preparation is carefully controlled so as not to exceed such decomposition temperature.

Other embodiments of the invention include fibers, films, foams and coatings of the above polyesters and nonwovens of the fibers. The invention also contemplates disposable products, such as diapers, which contain an absorbent body portion, with, on at least one surface, a water permeable nonwoven sheet composed of the polyester fibers, a water impermeable film of the polyester, or a combination thereof.

It is a finding of the invention that such polyesters derived from terephthalic acid (abbreviation T), ethylene glycol (abbreviation 2G), a polyethylene ether radical (abbreviation DEG), with a metal salt of a 5-sulfoisophthalic acid (abbreviation 5SI) in amount about 0.1 to 2.5 mole%, undergo degradation when subjected to the conditions of high humidity and temperature that typically characterize composting operations, and that the inclusion of hydroxyacid recurring units increases the rate of hydrolysis of these polyesters. It is significant that the bulk of the monomers resulting from degradation, i.e. terephthalic acid, the hydroxyacid and the glycols, are readily digested by organisms in solid waste or compost to create carbon dioxide and water.

A preferred polyester is indicated by the abbreviation 2G/DEG(80/20)-T/5SI(98/2)//2E[66//34], where the numbers in parentheses connote the mole percentages of the glycol and diacid monomeric units in the polyester, and the numbers in square brackets connote the molar proportions of glycol/diacid recurring units to hydroxyacid recurring units (2E being glycolic acid units). Such abbreviations to connote compositions on a mole % basis will be used throughout this specification.

These provide useful material having applications in end uses where containment of body fluids is necessary and disposability is desirable in a degradable film or a fabric coated with a film which will conform easily

to body contours yet act as an effective barrier to penetration of body fluids. It is especially preferred that such a film or coated fabric should have a reduced tendency to rattle and rustle when flexed during body movements. Such a film or fabric must have adequate strength and toughness to allow its survival during use. In order that it not leave objectionable residues when disposed of, it should disintegrate quickly when placed in proper waste disposal facilities and, ultimately, degrade substantially completely to innocuous materials, such as carbon dioxide and water.

Many copolyesters which are copolymerized with 5-sulfoisophthalic acid (5SI) will hydrolyze readily. Not all such copolymers are acceptable in the end uses contemplated. The polymers should exhibit the desired physical properties, and be processable under practical conditions, but the products of hydrolysis should desirably have the potential to be digested by the organisms likely to be found in waste disposal facilities and compost. This cannot be achieved by all monomers used in preparing other copolyesters. We have found, for example, that terephthalic acid is decomposed substantially completely in such a test over 28 days, and that ethylene glycol and polyethylene ether glycols are also satisfactorily digested by organisms typical of those found in waste disposal systems. Sodium dimethyl 5-sulfoisophthalate has shown slower degradation in these tests, and constitutes only a very small proportion of the copolymers. 4-sulfophthalic acid (4SP) has been used instead of 5SI in related compositions and has shown complete decomposition in certain tests, and may sometimes be preferred, if this is an important consideration. In this regard, it should be recognised that the rate and extent of decomposition is affected significantly by selection of particular organisms and other specifics during composting.

As indicated, the polyesters of the invention consist essentially of recurring structural units of formulae :



Of the R radicals, at least about 85 mole % should be T (para-phenylene), with optional inclusion of up to about 15% mole % of I (meta-phenylene).

Of the G radicals, about 20 to 40 mole % are DEG and/or

TEG (i.e., polyethylene ether radicals  $-(CH_2)_2-O-(CH_2)_2-$  and  $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$ , respectively).

Importantly, the polymer contains sulfo groups, such as are described in U. S. Patent No. 3,018,272 (Griffing and Remington), the disclosure of which is hereby incorporated by reference. The amount of sulfo groups in the polymer should be about 0.1 to 2.5 mole %. Thus, about 0.1 to 2.5 mole % of the R may be 5SI and/or 4SP radicals, as described herein, or may be another sulfo group suggested by Griffing et al. Or, if desired, about 0.1 to 2.5 mole % of the G may be the sulfo group. Thus the content of sulfo group-containing radical is calculated with respect to the recurring structural units of the formula  $[-C(O)-R-C(O)-OGO-]$ . Such radicals may, however, be contained in other units, i.e., other than in the R or G units, for instance in end groups or in hydroxyacid units, if desired. The radicals containing sulfo groups need not necessarily be aromatic, although 5SI and 4SP have given good results. Preferred amounts are about 1.5 to 2 mole %.

The copolyesters of the invention are water-insoluble, unlike other polyesters which might be derived from the same constituents but which contain very much higher mole percentages of 5SI. They also have relatively low glass transition temperatures, Tg.

Thus advantageously the Tg of the copolyester fibers or films should be no higher than approximately the temperature at which degradation will take place. Since the temperatures in composting operations are often no higher than about 70 C, it is desired that the Tg of the copolyester be no more than about 70 C, preferably about 65 C or below. Commercial unmodified polyethylene terephthalate (abbreviation 2GT) polyester fibers have a Tg of about 80 C. Even a 2GT polyester containing 2.5 mole % of 5SI has a Tg value of 76 C.

It will be understood that, with minor variations in composition, it is possible for the copolyesters of the invention to have a further significant reduction in their Tg values. For example, the replacement of up to 5 mole % of the terephthalic acid with an aliphatic acid such as azelaic, succinic, adipic, sebacic or glutaric acid, and the replacement of some ethylene glycol with a polyethylene ether, such as DEG or TEG



(triethylene glycol) can lower the T<sub>g</sub> even below 65 C. Such amounts will not otherwise materially alter the degradation characteristics of the copolyesters, hence their inclusion is contemplated by the term "consisting essentially" used to describe the polyesters and other products of the invention.

5                   Minor amounts of polyfunctional branching agents, such as trimellitic acid residues, may be incorporated to modify melt rheology and film processing, if desired.

                  The polyesters may be prepared by conventional  
polycondensation techniques using, for example, as the glycol component, a  
10   combination of about 20 to 40 mole% of the diethylene glycol, with a  
complemental molecular amount of ethylene glycol, and, as the acid  
component, a combination of about 97.5 to 99.9 mole % of terephthalic acid  
with about 0.1 to 2.5 mole % of a metal salt of 5-sulfoisophthalic acid.  
Optionally up to about 5 mole % of the ethylene glycol or terephthalic acid  
15   can be replaced, respectively, by another glycol or by an aliphatic acid. In  
lieu of the mentioned dicarboxylic acids, ester forming derivatives such as the  
dimethyl esters of the acids may be used.

                  The glycol component advantageously contains the  
polyethylene ether radical, such as DEG or TEG, as well as the 2G to  
20   achieve an optimum level of degradability without a major sacrifice to fiber  
and film physical properties such as tensile strength. Above about 40 mole  
% DEG such properties are adversely affected, as indicated in my parent  
application.

                  The acid component preferably includes about 1.5 to 2 mole %  
25   SSI. This component is not only relatively costly but also excessively large  
amounts can render the polyesters water soluble and thus affect the fiber and  
film physical properties such as shrinkage. As little as 0.1 mole % of SSI  
contributes significantly to the degradability characteristics of the resultant  
fibers and films. Alternatively, as indicated, other sulfo group-containing  
30   units may be included, as taught in U. S. Patent No. 3,018,272. As indicated  
in some of the aforementioned copending cases, 4-sulfophthalic acid (4SP)  
gives excellent degradability in related polyesters. In such monomeric units,  
the metal ion is preferably an alkali metal such as sodium, potassium or

lithium. However, alkaline earth metals such as magnesium are also useful. The sodium salt of 5SI has given very good results.

A relative viscosity of at least 16, preferably at least about 18, is generally acceptable for melt spinning performance.

5                    In the Examples herein, the various monomeric components are charged to a polymerization vessel along with an antimony or other catalyst and subjected to polycondensation conditions to produce a linear polyester in which the units are randomly distributed along the molecular chain. It will be understood that it is also possible, however, to first react two  
10 or more of the monomeric components to a prepolymer stage followed by addition of the remaining components which may be polymeric such as polylactide, polyglycolide or polycaprolactone and completion of the polymerization. When carrying out polymerizations in this sequential manner, the melting point of the initially formed polymer should preferably  
15 be below the decomposition temperature of the subsequently added hydroxy acid, oligomer or polymer; otherwise the reaction time must generally be shortened to minimize the extent of decomposition and then transesterification will likely be incomplete. Complete transesterification is not generally required, however, for the benefits of this invention.

20                    The copolyesters of the invention are very hydrolytically sensitive, having a higher equilibrium moisture content than 2GT resin and a faster moisture regain rate. It is desirable that isolated flake be dried thoroughly, preferably to a moisture content below 400 ppm before reextrusion, and to maintain a nitrogen atmosphere around all possible air in  
25 leakage points, and to transfer polymer in warm condition (e.g., above about 50 C) from the dryer to the extruder.

                    The copolyesters as isolated from the reactor usually have multiple melting points by DSC analysis. These are seen at temperatures which overlap those which might be used in drying 2GT flake, making it  
30 difficult to dry these polymers without fusing the flake into a solid mass when they are rapidly heated to get fast economical drying rates. Slower heating to allow crystallization, after which heating at higher temperatures for fast drying, is desirable.

A desirable procedure for preparing high molecular weight resins from rapidly polymerized lower molecular weight ones may be to use solid phase polymerization of low molecular weight flake. This procedure may desirably be carried out after or in combination with the crystallization  
5 procedure mentioned above so that temperatures high enough for rapid polymerization can be attained without fusing of the flaked resin. In addition, as known from U.S. Patent No. 3,544,523, anticaking agents may be useful to prevent sticking, such as Cab-o-sil grade MS-75D, and other finely divided inert solids, like  $\text{TiO}_2$ , talc, carbon black and clay.

10 If it is desired, for environmental or other reasons, to avoid use of a catalyst that comprises antimony or another heavy metal, then this may be achieved, for instance, by using a crystalline sodium aluminosilicate molecular sieve such as Linde Molecular Sieve 13X, type 9356, with a nominal pore size of 10A, obtained from Union Carbide Corporation. Such  
15 procedure is more fully described in commonly assigned U.S. application Serial No. 07/497,069 filed March 20, 1990 in the name of Jackson, but other methods of avoiding antimony may be used, if desired.

In any event, the particular mole percentages of the aforementioned components are desirably selected to provide a polyester  
20 which in fiber or film form has a Tg of 70 C or less, preferably of about 65 C or less.

As will be understood, while the copolyesters of the invention are well suited for use as fibers or filaments in nonwoven sheets, they can be used to particular advantage in the form of cast and blown films, coatings, or  
25 molded articles wherever polyesters with such properties are desired.

Fibers and filaments herein are interchangeable terms in the general sense, but where a more specific acknowledgement of length is appropriate, the term "fibers" is intended to refer to short filaments as in "staple fibers". Hereafter only one of the terms may be used.

30 The polyesters of the invention may be converted to fibers or filaments by conventional melt spinning techniques. Deniers of 2 to 15 dpf are most common. The filaments may be used as-spun(undrawn) or in a

stretched (drawn or oriented) condition. Drawing to reduce denier or for increasing orientation can be accomplished by the usual procedures.

The polymer compositions of the invention can be formed into nonwoven fabrics via a number of processes. These may be roughly divided  
5 into spunbonded fabrics and those fabrics using staple fibers. These are discussed in "Encyclopedia of Textiles, Fibers and Nonwoven Fabrics", Ed. Martin Grayson, John Wiley and Sons, New York, 1984, pp 252-304. The compositions described herein can be used in many such products. Spunbonded nonwovens can be prepared by spinning and laying down  
10 simultaneously into webs of continuous filaments using known methods of distributing the threadline in the desired orientation in the web plane. Such webs can be thermally bonded under suitable conditions of time, temperature and pressure to strong fabrics with tensile properties which are usually superior to those obtained with staple webs. Bonding can also be  
15 carried out by using suitable adhesives and both these methods may be used to make point bonded or area bonded fabrics. Needle punching may also be used to give the webs stability and strength. Spunbonded fabrics can also be made by melt blowing wherein a stream of molten polymer is extruded into a high velocity stream of heated air and a bonded web formed directly on a  
20 screen conveyor from the resultant fibers. Nonwoven fabrics can also be made by direct extrusion through a rotating die into a netlike product (US 3,959,057 J.J. Smith) or by stretching and drawing embossed films of the thermoplastic polymers (British Patent 914,489 and 1,548,865 to Smith and Nephew Research Ltd.).

25               Staple fibers can be made into nonwovens by several processes. Most of these can be classified into (1) web preparation and (2) reinforcing ("Manual of Nonwovens", Dr. Radko Krcma, Textile Trade Press, Manchester, England, pp 74-76, 1971). During web preparation, bales of staple fiber are opened and formed into a web having either a random  
30 orientation (via air, water or electrostatic deposition) or parallel or crosslaid orientation (via carding and plying). Reinforcement to impart physical integrity and useful mechanical properties can be accomplished by mechanical means such as needlepunching or hydroentanglement (where water jets move fibers out of the plane of the web and entangle them) as in

the spunlaced fabrics (US 3,485,706 to Du Pont) or by stitchbonding where a reinforcing thread is sewn through the web. (See "Principles of Stitch Through Technology" Nonwovens Fabrics Forum, Clemson University, Clemson, S C 1978 by J.D. Singelyn). Reinforcement can also be

5 accomplished by adhesive bonding which includes impregnation of the web by a water based resin binder solution or dispersion and subsequent evaporation of the water leaving a fabric which is composed typically of 60-70% by weight fiber and 30-40% by weight binder. Dry adhesive powders may also be applied to the staple web prior to a heating step to produce a

10 powder-bonded nonwoven. Webs of thermoplastic staple fibers may also be reinforced by thermal bonding in which use is made of the ability of the fibers to soften and adhere to each other upon application of heat. As with the spunbonded fabrics these may be point bonded or area bonded. Heat may be applied by hot air (known as through air bonding) or by a pair of

15 patterned and/or flat heated rollers which form a nip through which the web passes to achieve bonding. This process may be carried out with 100% thermoplastic fibers or with blends of thermoplastic fibers with fibers which do not thermally bond in the 100% form, i.e. cotton and rayon.

In addition, useful articles can also be made by laminating,

20 extrusion melt coating or adhesively combining the above types of nonwoven fabrics with each other, with films or with staple webs in such a way as to confer desired properties on the combined fabric.

In particular, a fabric made by extrusion melt coating a thin, pinhole free film of the compositions of this invention on a nonwoven, made

25 by the spunbonded process or by thermally bonding staple from fibers of this invention alone or in combination with other compostable fibers such as cotton or rayon, is aesthetically pleasing and non-fluid permeable.

The compostable polyester fibers described herein may be used in all these methods of preparing nonwovens to yield fabrics which

30 when subjected to composting conditions will be substantially degraded. Thus staple webs of the polyester fibers, as well as blends of these fibers with cotton and rayon, may be bonded by hydro-entanglement, by needle punching, by wet resin bonding and by dry adhesive bonding. (The adhesives

used should be chosen to allow the desired degradation under composting conditions.)

Thermally bonded staple webs of the described compostable polyester fibers can be made in the 100% form or webs containing a significant proportion of these fibers together with cotton and/or rayon may be thermally bonded to fabrics having useful mechanical properties.

Continuous or spun yarns prepared from the compositions described herein may be used to stitch bond webs of fibers such as cotton, rayon or blends of these fibers, or wood pulp, with the compostable polyester fibers of this invention resulting in fabrics which will degrade under composting conditions.

Spunbonded fabrics can be made by thermally bonding webs of continuous fibers or of melt blown fibers, prepared from the compostable compositions described herein, to directly extruded nets, or to nets formed by drawing of embossed films, prepared from the compostable compositions.

The compostable compositions described herein can be melt extruded as films to coat spunlaced nonwoven fabrics which themselves may be composed of compostable fibers alone or in combination with wood pulp, rayon or cotton.

A process for preparing ultramicrocellular and plexifilamentary products is disclosed in U. S. Patent 3,227,784 (Blades et al) and durable plexifilamentary and microcellular products are described in U. S. Patents 3,227,664 (Blades et al) and U.S. Patent 3,081,519 (Blades et al).

Extrusion of foamed plastics has also been described, for example in Modern Plastics Encyclopedia Oct 1990 Vol 67 #11 pp 291-2. In foam extrusion, molten polymer is first mixed with a relatively small amount (e.g. 1 to 15 wgt %) of a blowing agent. The blowing agent used does not have to be a true solvent for the polymer. When the mixture is extruded, the blowing agents expand due to depressurization and/or volatilization to form a microcellular structure. Unlike in flash spinning, most of the blowing agents used do not leave but stay inside the foam. Most commonly used

blowing agents are: 1). gaseous materials such as nitrogen and carbon dioxide, 2). low boiling organic solvents such as hydrofluorocarbons (e.g. HFC-134a, 152a, 125), hydrochlorofluorocarbons (e.g. HCFC-22, 123, 141b, 142b, 124), and hydrocarbons (e.g. isobutane, pentane). In addition to these  
5 types of physical blowing agents, chemical blowing agents are also used to make foams. Chemical blowing agents decompose at elevated temperatures or through chemical reaction to generate gases. Nucleating agents which are finely divided powders such as fumed silica are usually added to encourage the formation of small uniform cells.

10 Nonwoven webs of the compostable compositions made by the melt blowing process may also be used as an adhesive layer between other nonwoven fabrics.

It is apparent that the fiber, film, foam, and sheet products made from compositions described herein have a great number of  
15 applications in products which are disposed of or potentially may be disposed of in composting systems. In addition the compositions have utility in objects made by injection molding, injection blow molding, thermal forming of sheets, rotational molding of powder, extrusion, and pultrusion, which desirably can be disposed of and degraded in composting systems. The  
20 following is a nonexclusive list of such end uses:

- Agricultural mulch
- Agricultural mats containing seeds
- Nutrients
- Adhesive tape substrate
- 25 Baby pants
- Bags
- Bag closures
- Bed sheets
- Bottles
- 30 Cartons
- Disposable diapers
- Dust bags
- Fabric softener sheets
- Garment bags

5                    Garbage and lawn waste bags  
                     Industrial bags  
                     Labels, tags  
                     Monofilaments  
                     Packaging materials and structures  
                     Pillow cases  
                     Protective clothing  
                     Surgical drapes  
                     Surgical gowns  
10                   Surgical sheets  
                     Surgical sponges  
                     Tampon applicators  
                     Temporary enclosures  
                     Temporary siding  
15                   Toys  
                     Wipers.

                     The invention can provide fluid impermeable sheets which are  
compostable in typical waste disposal facilities. Preferably these sheets  
should not rattle or rustle objectionably and should have strength and  
20                   toughness adequate for use in personal absorbent products, such as  
disposable diapers.

                     The fibers, films, foams and nonwoven fabrics prepared from  
the compositions of the present invention are of particular utility in  
disposable diapers since in that use they have an enhanced capability of  
25                   being degraded in a composting operation. Typical examples of disposable  
diaper constructions are given in U.S. Patents 3,860,003 (Buell) and  
4,687,477 (Suzuki et al.), the disclosures of which are incorporated herein by  
reference. Items which can be made of the compostable compositions of this  
invention include:-

30

(1) the backsheet film, i.e., the water-impermeable outside layer,  
which may be a film which is 100% of the compostable composition or it may  
be a laminated sheet with a nonwoven or web of compostable fibers  
including cotton or rayon adhered to the film, or it may be a film adhered to



a suitable grade of paper,

(2) the topsheet, i.e., the water permeable or inner layer, which is a film of a composition of the invention or a nonwoven fabric of the  
5 compostable fiber composition or a blend of the compostable fiber of this invention with cotton or rayon fiber, having a porosity suitable for passing urine quickly to the fluid absorbing pad between the topsheet and backsheet,

(3) the fastening tapes which may optionally be made from films or  
10 nonwovens of the compositions of the invention; the fastening tapes are typically coated with a pressure sensitive adhesive,

(4) the frontal landing strip, which may be made from films of this invention; the frontal landing strip is typically printed with a decorative  
15 design and coated with a pressure sensitive adhesive,

(5) the flexible foam optionally inserted into the diaper under modest extension to gather the waist, leg openings, and/or barrier leg cuffs may be made from polymers of this invention,  
20

(6) hot melt adhesives used to bond the diaper components to one another may be formulated to incorporate polymers of this invention,

(7) the leakage shield used at the diaper waist, in front and back, may  
25 be made from films of this invention, and may be glued, thermally bonded, or sonically bonded to the topsheet or the topsheet and backsheet,

(8) additives to the absorbent cellulose pulp core, which may be short fibers, fibrils, synthetic pulp prepared by flash spinning, or some other  
30 mechanically dispersable and finely divided form made from polymers or fibers of this invention, and which serve to increase wet strength of the core, particularly when superabsorbent polymers have been incorporated and pulp content subsequently reduced,

35 (9) other minor components of the diaper which require the

combination of compostability and thermoplastic fabrication and/or processing, and

- 5 (10) diaper packaging, which may comprise a bag made of film of compositions of this invention, or paper or cardboard coated with film of compositions of this invention.

It will be apparent that the products of the invention may contain additives such as dyes, fillers, pigments, plasticizers, etc. Indeed, use of appropriate fillers or other additives may be helpful, as an acceptable way to enhance disintegratability. Use of starch is particularly helpful, as taught in Application (QP-4850). Also for instance, microporous films are taught by Moss in U. S. Patent No. 4,698,372, and similar techniques may be followed with products of the present invention. The addition of low molecular weight polyethylene adipate (Rucoflex Mn=2000) has been shown to reduce rattle or rustle of films of related polymers, and would be expected to be advantageous for these polymers.

### TEST METHODS

Polyester glass transition temperatures, T<sub>g</sub>, are obtained by using a Du Pont model 2910 Differential Scanning Calorimeter. Samples are heated under a nitrogen atmosphere at a rate of 20 C/min. to a temperature 10 - 20 C above the melting point, then the melt is cooled using the rapid air quench capability of the instrument. The T<sub>g</sub> is determined from the second cycle scan done at 20 C/min. using the internal software to determine the inflection point of the baseline shift.

25 Polymer melting point, m.p., is determined on the first heating cycle as described in T<sub>g</sub> determination. The temperature at which the highest endothermic peak occurs is reported as the polymer melting point.

Number average molecular weight, Mn, is determined by gel permeation chromatography (gpc) versus a standard polyethylene terephthalate sample with an Mn of 22000 and a weight average molecular weight of 44000. Polymers are dissolved in and the analysis is run using HFIP (hexafluoroisopropanol) containing 0.01M sodium trifluoroacetate as

the solvent. A Waters model 150 C ALC/GPC instrument, or its equivalent, is used with two Zorbax PSM-S biomodal columns (sold by E. I. du Pont de Nemours and Company) (or equivalent) in series at 30 C. A refractive index detector was used and data collected at 100 intervals and analyzed via  
5 software provided by the instrument supplier.

Carboxyl end groups are determined by titration of an o-cresol solution of the polymer at 115 C with KOH in benzyl alcohol to a colorimetric endpoint using bromophenol blue as the indicator. Results are reported in eq./10<sup>6</sup> grams of polymer.

10 Inherent viscosity is defined in "Preparative Methods of Polymer Chemistry", W. R. Sorenson and T. W. Campbell, 1961, p. 35. It is determined at a concentration of 0.5 g/100 ml of the indicated solvent at the indicated temperature, usually HFIP at 30 C.

Relative viscosity is the ratio of the viscosity of a solution of  
15 0.8 gram of polyester dissolved in 10 ml of hexafluoroisopropanol (HFIP) containing 80 ppm H<sub>2</sub>SO<sub>4</sub> to the viscosity of H<sub>2</sub>SO<sub>4</sub>-containing HFIP itself, both measured at 25 C in a capillary viscometer and expressed in the same units.

Stress/Strain properties of fibers are given as T/E/M for  
20 Tenacity/Elongation/Modulus, in the dimensions of Ksi (kilo pounds per square inch) for Tenacity and Modulus, and, as a percentage, Elongation.

The "Hydrolysis" results are generally after boiling in water at 100 C, for the indicated period, to show any reductions in molecular weight (Mn), as a percentage, except as indicated, e.g. at 60 C.

25 This invention will be further illustrated by the following Examples. Parts and percentages are by weight unless otherwise indicated. The 2G/DEG-T/5SI proportions are by mole % of that polymer. The following commercially available materials are used for the indicated hydroxyacid monomer components: (1) the polyglycolide is of inherent  
30 viscosity 1.3 dl/g (as measured in hexafluoroisopropanol, HFIP, at 30 C) and is commercially available as MEDISORB® Bioresorbable Polymer 100 PGA;

(2) the polylactide is of intrinsic viscosity 7.93 (as measured in chloroform,  $\text{CHCl}_3$ ), and commercially available from CCA Biochem b.v. GORINCHEM, Holland; (3) the polycaprolactone is available from Aldrich 18,160-9).

5

### Example 1

This Example shows the preparation of a copolyester of the invention containing about 10% by weight (34 mole %) of a polyglycolide, spinning of fibers from this composition, and how readily these fibers can hydrolyse.

10

The copolyester is made by mixing the polyglycolide with 2G/DEG(80/20)-T/5SI (98.5/1.5) bearing in mind the fact that there may have been some small deviation in glycol content, as some DEG may have been distilled off during the polymerization.

15

In a one liter 3-necked flask fitted with a stirrer,  $\text{N}_2$  inlet and distillation head are placed:

20

334.8 g ethylene glycol (2G)  
0.407 g  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$   
0.218 g  $\text{Sb}_2\text{O}_3$   
0.278 g NaOAc.

This is heated to 160 C in an oil bath until all components are dissolved. Then there are added:

25

63.6 g diethylene glycol (DEG)  
571.2 g dimethyl terephthalate (DMT)  
14.04 g sodium dimethyl 5-sulfo-isophthalate (5SI)

The temperature of the oil bath is slowly increased. Distillate (methanol) in the amount of 238 ml is collected between 180-220 C. Then 2 ml of a  $\text{H}_3\text{PO}_4$  solution in ethylene glycol is added (4.79 g 85%  $\text{H}_3\text{PO}_4$  diluted to 50 ml with ethylene glycol) and the mixture is stirred for 5 min.

The resultant molten monomer is then used to fill a polymer tube about two-thirds full.

30

Polymerization is continued by attaching a filter flask to the side arm of the polymer tube and inserting a capillary inlet tube drawn finely so as to reach to the bottom of the molten monomer pool. Nitrogen gas is bled in as the tubes are heated in a dimethyl phthalate vapor bath (284 C),  
5 first under laboratory vacuum for 1 hour, then at 0.3 mm Hg using a vacuum pump for 6 hours.

The capillary tube is removed from the molten polymer and the polymer is allowed to cool.

The polymer is recovered and ground into small particles in a  
10 Thomas mill. The resulting flake is dried at about 130 C overnight under laboratory vacuum to give the desired 2G/DEG(80/20)-T/5SI(98.5/1.5)polymer.

50 g of this polymer is mixed with 5.8 g of the indicated polyglycolide in a medium size polymer tube fitted with a drawn-out  
15 capillary tube supplied with N<sub>2</sub> which reaches to the bottom of the polymer tube. The tube is evacuated and flushed twice with N<sub>2</sub> before it is heated to 231 C in the vapor from a bath of boiling n-decyl alcohol. After the polymers are melted, laboratory vacuum is applied for 15 minutes, then a 0.2 mm Hg vacuum is applied for 2.5 hours while N<sub>2</sub> is bubbled through the melt. After  
20 cooling, the copolymer is recovered from the broken tube and ground in a Thomas mill. After drying for 48 hrs at 90 C under laboratory vacuum, the copolymer is molded into a 7/8 inch diameter plug, which is placed in a press spinning apparatus and spun through a 5 hole-(0.015 inch x 0.045 inch) spinneret at 213 C into fiber that is wound up at 500m/min. The fiber is  
25 hand drawn 2X over an 85 C hot pin. T/E/M is 9 Ksi/116%/214 Ksi. The filaments are about 2 dpf. The carboxyl end group concentration is 183 eq/10<sup>6</sup> g.

The Mn (molecular weight) of this fiber was 10,800. After boiling for 2 hours in deionized water, the Mn was reduced to only 5,650. By  
30 immersion of the fiber in 60 C water, the Mn was reduced to 4,575 after 4 weeks; after 8 weeks, it was reduced to 4330.

For comparison, a fiber having a composition of

2G/DEG(80/20)-T/5SI(98/2) and a molecular weight (Mn) of 28,360 had an Mn of 21,100 after 4 weeks in 60 C water and 18,520 after 8 weeks at 60 C. The copolymer of the present invention was hydrolysed more readily.

### Example 2

5                    This Example shows the preparation of a copolymer from 90 wt% of 2G/DEG(80/20)-T/5SI(98.5/1.5) and about 10 wt % (25 mole %) poly L-lactide, its spinning into fibers and hydrolysis of the fibers. The polymer is made and spun similarly to Example 1 except that 5.8 g of the indicated poly L-lactide is used, the polymer is spun at 205-210 C and wound  
10 up at 70 m/min. This fiber is drawn 3.5X on an 80 C hot pin. The fiber had an Mn of 16,100, and a carboxyl end group concentration of 125.5 eq/10<sup>6</sup> g. The T/E/M is 26 Ksi/14%/943 Ksi. The filaments are about 8 dpf. After boiling 2 hrs in deionized water, the Mn is 15,900; after 8 hours, it is 11,200; and after 24 hrs, it is 5,230.

15

### Example 3

                    This Example shows the preparation of a copolymer containing 16.4 % by weight (25 mole %) of polycaprolactone with 83.6 wt % of 2G-T/5SI(98/2), and its hydrolysis. A comparison without 5SI was also hydrolysed.

20

                    The 2G-T/5SI(98/2) polymer was made essentially as described in Example 1 with;

                                         74.4 g ethylene glycol (2G)  
                                         0.124 g Sb<sub>2</sub>O<sub>3</sub>  
                                         0.100 g Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O  
25                                        114.0 g dimethyl terephthalate (DMT)  
                                         3.79 g sodium dimethyl 5-sulfoisophthalate (5SI)

                    After removal of methanol at temperature up to 225 C, 22.8 g of the polycaprolactone was added and stirring continued for 30 min. The molten product was transferred to a polymer tube, as described in Example 1, and  
30 polymerization was continued while the tube was heated with a glycol vapor bath (198 C) for 1 hour under laboratory vacuum, and then for 5 hours under

0.3mm Hg pressure. The polymer was cooled, ground and dried as in Example 1, then spun using a press spinning apparatus fitted with a 9 mil x 12 mil single hole spinneret at a temperature of 203 C with a delivery rate of 0.7 cc/min and a windup speed of 38 m/min. The fibers had a Mn of 13,300.

5 Hydrolysis at 100 C for 8 hrs in deionized water reduced the Mn to 4,500. After 24 hours, the Mn was 3,700.

For comparison, when a similar polymer was made without any 5SI and spun under the same conditions to give a fiber of molecular weight (Mn) 13,550, hydrolysis at 100 C for 8 hours and even 24 hours hardly

10 reduced the Mn at all, the values being 13,000 and 12,600, respectively.

When a copolymer containing 25 wt% polycaprolactone is made by the same method described above, spun and hydrolyzed in 60 C water, initial Mn is 10960, after 3 days it is 7510, after 7 days 4400, and after 12 days 3630.

15

#### EXAMPLE 4

This Example demonstrates that hydroxyacetic acid can be used in the melt polymerization instead of polyglycolide.

In a 500 ml reaction kettle fitted with a stirrer, N<sub>2</sub> inlet and distillation head are placed:

20 67.0 g ethylene glycol (2G)  
0.081 g Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O  
0.044 g Sb<sub>2</sub>O<sub>3</sub>  
0.056 g NaOAc

These are dissolved by heating to 160 C then

25 12.7 g diethylene glycol (DEG)  
114.2 g dimethyl terephthalate (DMT)  
2.80 g sodium dimethyl 5-sulfoisophthalate (5SI)

are added and the solution heated gradually to 220 C while methanol is distilled off. At this point 19.7 g of hydroxyacetic acid (95% pure) is added

30 and the mixture stirred for 30 minutes.

The molten prepolymer is transferred to a polymer tube as described in Example 1 and polymerization is carried out with the tube

22

immersed in an ethylene glycol vapor bath (198 C) for 2 hours under laboratory vacuum and 23 hours under about 0.3 mm Hg pressure. The molten polymer forms fibers when the capillary tube is withdrawn.



What is claimed is:-

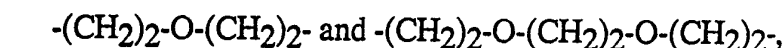
1. A fiber and film forming polyester consisting essentially of recurring structural units of the formulae:-



wherein R consists essentially of divalent aromatic radicals and at least about 85 mole % of R is p-phenylene,

wherein G is

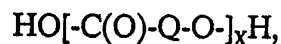
10 about 20 to 40 mole % of a polyethylene ether radical selected from the group consisting of



and the remainder of G is a hydrocarbylene radical selected from the group consisting of

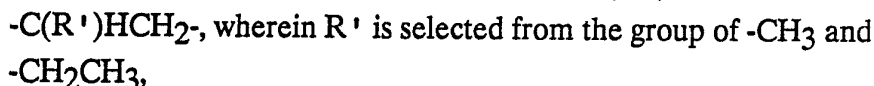
15  $-(\text{CH}_2)_2\text{--}$ ,  $-(\text{CH}_2)_3\text{--}$ , and  $-(\text{CH}_2)_4\text{--}$  radicals,

wherein Q is derived from an hydroxy acid of formula



where x is an integer, such hydroxy acid having a melting point at least 5 C below its decomposition temperature, and Q is selected from the

20 group consisting of a chemical bond and hydrocarbylene radicals



and wherein "a" and "b" are mole fractions of the polymer, and the mole

25 fraction "a" may be 60 to 98% and, correspondingly, mole fraction "b" may be 2 to 40%,

provided that about 0.1 to about 2.5 mole % of the polymer contains alkali metal or alkaline earth metal sulfo groups.

2. A polyester according to Claim 1, wherein at least about 97.5  
30 mole % of R is p-phenylene.

3. A fiber of the polyester of Claim 1 or 2.

4. A non-woven sheet of the polyester of Claim 1 or 2.

5. A film of the polyester of Claim 1 or 2.
6. A foam of the polyester of Claim 1 or 2.
7. A composite of the film of Claim 5 and of a layer of nonwoven sheet or of paper.
- 5 8. A disposable diaper which includes an absorbent body portion having on one surface thereof a water permeable sheet of the polyester of Claim 1 or 2.
9. A disposable diaper which includes an absorbent body portion having on one surface thereof a water impermeable sheet of the polyester of  
10 Claim 1 or 2.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/00229

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1.5      C 08 G 63/688      C 08 G 63/66      A 61 L 15/00  
 D 01 F 6/86

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System

Classification Symbols

Int.C1.5

C 08 G  
A 61 L

D 01 F

C 08 J

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>

III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

| Category <sup>10</sup> | Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup> | Relevant to Claim No. <sup>13</sup> |
|------------------------|----------------------------------------------------------------------------------------------------------------|-------------------------------------|
| P,A                    | US,A,5053482 (R.F. TIETZ) 1 October 1991, see claims 1-11; example 1 (cited in the application)<br>---         | 1-5,7-9                             |
| P,A                    | WO,A,9102015 (THE PENNSYLVANIA RESEARCH CORP.) 21 February 1991, see page 3, line 23 - page 7, line 4<br>---   | 1,2                                 |
| A                      | EP,A,0311943 (AKZO N.V.) 19 April 1989, see abstract; claim 1<br>---                                           | 1,2,9                               |
| A                      | US,A,4335220 (C.H. CONEY) 15 June 1982, see claim 1; column 2, line 62 - column 4, line 56<br>---              | 1,2                                 |
| A                      | US,A,4052368 (W.K. LARSON) 4 October 1977, see claim 1; examples 24,25<br>-----                                | 1,2                                 |

<sup>10</sup> 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

"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

## IV. CERTIFICATION

|                                                             |                                                                                                                                             |
|-------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| Date of the Actual Completion of the International Search   | Date of Mailing of this International Search Report                                                                                         |
| 25-05-1992                                                  | 23 JUN 1992                                                                                                                                 |
| International Searching Authority<br>EUROPEAN PATENT OFFICE | Signature of Authorized Officer<br><br>MISS T. TAZELAAR |

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9200229

SA 56011

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/06/92. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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