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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 therefrom.  
5 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 being  
10 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 some products which do not readily fit  
15 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 fertility of fields and gardens. One of the limitations to  
20 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:

1 - to provide components which are useful in disposable products and  
25 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 times which range from two weeks to more than three months.

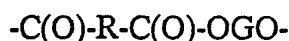
30 2 - to provide disposable components which will not only degrade aerobically/anaerobically in composting, but will continue to degrade in the soil

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 leachate, as for natural organics like wood.

5           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 low ingredient costs and yet provide strength and toughness properties adequate for  
10       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



          wherein R is about 97.5 to 99.9 mole % para-phenylene (abbreviation T) and  
15       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 %  $-CH_2-CH_2-$  (abbreviation 2G) and about 20 to 40 mole %  
 $-(CH_2)_2-O-(CH_2)_2-$  (abbreviation DEG), and especially wherein R is about 98  
mole % para-phenylene (T) and about 2% of the sulfonate radical (5SI) and G  
20       is about 80 mole % 2G and about 20 mole % DEG, and fibers, non-woven 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 %  $-CH_2-CH_2-$  (2G) and  
about 20 mole %  $-(CH_2)_2-$   $-(CH_2)_2-$  (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  
desirable to provide polyesters that can be formed into films that have still  
further improved toughness, but with similar advantageous properties in many  
30       respects, as regards the polyesters that have been 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, WO91/18036) which is hereby incorporated herein by reference, as is copending PCT application (QP4710A) filed simultaneously herewith.

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

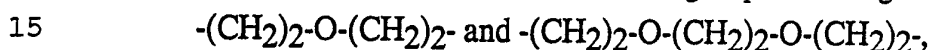


wherein R consists essentially of divalent aromatic radicals and at least about 85 mole % of R is p-phenylene, (T),

10 wherein G consists essentially of the following radicals:

a radical of a polyalkylene ether glycol of molecular weight at least about 250, in amount at least about 13% by weight of the total of the [C(O)-R-C(O)-OGO-] units,

a polyethylene ether radical selected from the group consisting of



in amount up to about 40 mole % of G,

and the remainder of G is a hydrocarbylene radical selected from the group consisting of  $\text{-(CH}_2\text{)}_2\text{-}$  (2G),  $\text{-(CH}_2\text{)}_3\text{-}$  (3G), and  $\text{-(CH}_2\text{)}_4\text{-}$  (4G) 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  $\text{-(CH}_2\text{)}_n\text{-}$ , where n is an integer from 1 to 5,  $\text{-C(R ' )H-}$ , and  $\text{-C(R ' )HCH}_2\text{-}$ , wherein R ' is selected from the group of

25  $\text{-CH}_3$  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%, provided that about 0.1 to about 2.5 mole % of the polymer contains alkali metal or alkaline earth metal sulfo groups.

30 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 [C(O)-R-C(O)-OGO-] units, with about 2 to 40% consisting essentially of structural units (2) of the formula [C(O)-Q-O-]<sub>b</sub>, and wherein Q is such that the

hydroxy acid HO-C(O)-Q-OH and/or the polyhydroxy acid HO[-C(O)-Q-O-]<sub>x</sub>H 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.

5 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  
10 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) or other lower alkylene glycol (such as 3G or 4G), polyethylene ether radical (abbreviations DEG or TEG), C<sub>2</sub>-C<sub>4</sub> polyalkylene ether glycol radical of the  
15 indicated molecular weight (PAG), and a metal salt of a sulfo derivative, such as 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. It is significant that the bulk of the monomers resulting from degradation, i.e.  
20 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/PEG(91-94/15-20W)-T/5SI(98-98.5/1.5-2), where PEG indicates the radical of a polyethylene ether glycol of the indicated molecular weight, and the numbers  
25 connote the mole percentages of the diacid monomeric units in the polyester, with the PEG content being denoted in weight (W)% of the total diacid/glycol polymer, and the 2G constitutes the remainder of the "G" content. Such abbreviations to connote compositions on a mole % basis (except for the polyalkylene glycol content) will be used throughout this specification.

30 As indicated, the molecular weight (MW) of the polyalkylene glycol should be relatively low, a polyethylene glycol of MW about 600 being satisfactory and generally preferred, as it is available at a reasonable cost, which is an important consideration for many end uses. Molecular weights that are

higher, such as 3500, are reputedly biodegradable, but are not so easy to handle, so are generally less preferred, and may not be so available. Polypropylene glycol is not as desirable as polyethylene glycol.

The desirable amount of polyalkylene glycol in the glycol/diacid polyester is generally at least 13% by weight. Depending on the MW of the polyalkylene glycol used, 13% by weight corresponds to about 6 mole % when the MW is 600, but the precise mole % will depend on the other components. Amounts of about 13 to 20% by weight, preferably 15-20%, have proved satisfactory. We have found that smaller amounts of polyalkylene glycol, such as 8% by weight, do not appreciably increase toughness, as shown (8 w%) in Table 5, hereafter. Use of a significant amount of DEG or TEG will generally affect the amount of polyalkylene glycol that is desirable. Since polyalkylene glycols, including PEG, are relatively expensive, as compared with 2G, DEG, or TEG, and cost is an important consideration, it will generally be preferred to avoid using more polyalkylene glycol than required, and to use DEG (or TEG), if desirable. Amounts up to 75 % by weight of polyalkylene glycol may be used, however, bearing in mind the increased cost.

The polyesters provide useful materials having applications in end uses where containment of body fluids is necessary and disposability is desirable in a degradable film or a fabric or paper 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 or coated paper should have a reduced tendency to rattle and rustle when flexed during body movements. Such a film, fabric or paper 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 (with MW 250 and 3500) are also satisfactorily digested by organisms typical of those found in waste disposal systems; typically, as the molecular weight increases, degradation generally becomes slower. Sodium dimethyl 5-sulfoisophthalate has shown slower degradation in these tests, and constitutes only a very small proportion of the copolymers. 4-sulfo-phthalic 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 the 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, up to about 40 mole % may be DEG and/or TEG (i.e., polyethylene ether radicals  $\text{-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-}$  and  $\text{-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-O-(CH}_2\text{)}_2\text{-}$ , respectively), as well as the PAG and 2G, 3G and/or 4G radicals.

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  $\text{[C(O)-R-C(O)-OGO-]}$ . 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 %.

5           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, T<sub>g</sub>.

10           Thus advantageously the T<sub>g</sub> 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 T<sub>g</sub> 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 T<sub>g</sub> of  
15           about 80 C. Even a 2GT polyester containing 2.5 mole % of 5SI has a T<sub>g</sub> 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 T<sub>g</sub> values. For example, the replacement of up to 5 mole % of  
20           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  
25           contemplated by the term "consisting essentially" used to describe the polyesters and other products of the invention.

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

30           The polyesters may be prepared by conventional polycondensation techniques using, for example, as the glycol component, a combination of about 15 to 20 % by weight (of the glycol/diacid polyester) of the polyalkylene glycol,

up to about 40 mole % of the diethylene glycol, with a complementary 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 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 also contains the polyethylene ether radical, such as DEG or TEG, to 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.

The acid component preferably includes about 1.5 to 2 mole % 5SI. 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 5SI contributes significantly to the degradability characteristics of the resultant fibers and films. Alternatively, as indicated, other sulfo group-containing units may be included, as taught in U. S. Patent No. 3,018,272. As indicated in some of the aforementioned copending cases, 4-sulfo-phthalic 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.

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 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 be below the decomposition temperature of the subsequently added hydroxy acid, oligomer or polymer;  
5 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.

The copolyesters of the invention are very hydrolytically sensitive,  
10 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 leakage points, and to transfer polymer in warm condition (e.g., above about 50 C) from the dryer to  
15 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 difficult to dry these polymers without fusing the flake into a solid mass when they are rapidly  
20 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  
25 polymerization of low molecular weight flake. This procedure may desirably be carried out after or in combination with the crystallization 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  
30 as Cab-o-sil grade MS-75D, and other finely divided inert solids, like TiO<sub>2</sub>, talc, carbon black and clay.

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 procedure is more fully described in commonly assigned U.S. application Serial No. 07/497,069 filed  
5 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 which in fiber or film form has a Tg of 70 C or less, preferably of about 65 C or less.

10 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 molded articles wherever polyesters with such properties are desired.

15 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.

20 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.

25 The polymer compositions of the invention can be formed into nonwoven fabrics via a number of processes. These may be roughly divided 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 simultaneously into webs of continuous  
30 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 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  
5 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 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  
10 thermoplastic polymers (British Patent 914,489 and 1,548,865 to Smith and Nephew Research Ltd.).

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,  
15 England, pp 74-76, 1971). During web preparation, bales of staple fiber are opened and formed into a web having either a random 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  
20 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  
25 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 powder-bonded nonwoven.  
30 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 patterned and/or flat heated rollers which  
35 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.

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

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

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

20 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.

25 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.

30 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  
5 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).

10 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  
15 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),  
20 hydrochlorofluorocarbons (e.g. HCFC-22, 123, 141b, 142b, 124), and hydrocarbons (e.g. isobutane, pentane). In addition to these 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  
25 such as fumed silica are usually added to encourage the formation of small uniform cells.

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

30 It is apparent that the fiber, film, foam, and sheet products made from compositions described herein have a great number of 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 following is a nonexclusive list of such end

5 uses:

- Agricultural mulch
- Agricultural mats containing seeds
- Nutrients
- Adhesive tape substrate
- 10 Baby pants
- Bags
- Bag closures
- Bed sheets
- Bottles
- 15 Cartons
- Disposable diapers
- Dust bags
- Fabric softener sheets
- Garment bags
- 20 Garbage and lawn waste bags
- Industrial bags
- Labels, tags
- Monofilaments
- Packaging materials and structures
- 25 Pillow cases
- Protective clothing
- Surgical drapes
- Surgical gowns
- Surgical sheets
- 30 Surgical sponges
- Tampon applicators
- Temporary enclosures
- Temporary siding
- Toys
- 35 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 toughness adequate for use in personal absorbent products, such as disposable diapers.

5           The fibers, films, coatings, 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 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  
10 et al.), the disclosures of which are incorporated herein by reference. Items which can be made of the compostable compositions of this invention include:-

(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  
15 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  
20 of a composition of the invention or a nonwoven fabric of the 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,

25 (3) the fastening tapes which may optionally be made from films or 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  
30 invention; the frontal landing strip is typically printed with a decorative design and coated with a pressure sensitive adhesive,

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

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

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

10 (8) additives to the absorbent cellulose pulp core, which may be short fibers, fibrils, synthetic pulp prepared by flash spinning, or some other 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,

15

(9) other minor components of the diaper which require the combination of compostability and thermoplastic fabrication and/or processing, and

20 (10) diaper packaging, which may comprise a bag made of film of compositions of this invention, or paper or cardboard coated with film and/or reinforced with fibers 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  
25 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  
30 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 Tg is determined from the second cycle scan  
5 done at 20 C/min. using the internal software to determine the inflection point of the baseline shift.

**Polymer melting point**, m.p., is determined on the first heating cycle as described in Tg determination. The temperature at which the highest endothermic peak occurs is reported as the polymer melting point.

10 **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  
15 (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 software provided by the instrument supplier.

20 **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.

25 **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.

30 **Relative viscosity** is the ratio of the viscosity of a solution of 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.

**Tensile Properties** of fibers and yarns are coded as T/E/M/To for tenacity, elongation, initial modulus, and toughness and are reported in their conventional units of grams per denier, percent, grams per denier, and grams per denier. These are measured on donconditioned samples (3 inch guage length) in a commercial testing machine at the rate of extension of 50% per minute (unless otherwise indicated). Toughness (To) is measured as the integrated area under the stress-strain curve. The counterpart properties of fabrics are similarly coded as T/E/M/To and are reported in units of lb./in./oz./sq.yd., percent, lb./in./oz./sq.yd., and lb./in./oz./sq.yd., respectfully. Fabric samples are 1 inch X 8 inches (with 5 inches guage length), are conditioned prior to testing, and are extended in a commercial testing machine at a rate of 100% per minute.

**Crimp index** is measured by straightening a crimped tow by application of about 0.1 gpd load. Then 0.5 gm clips 66.6 cm apart are attached to the extended tow. The tow is then cut 11.2 cm beyond each clip to give a sample of 90 cm extended length. The sample is suspended vertically, hanging freely from one of the clips to allow retraction to crimped length. After about 30 secs., clip to clip distance is measured.

$$\text{Crimp Index} = \frac{(66.6 - L_c)}{66.6} \times 100$$

where  $L_c$  is the clip-to-clip distance in the free-hanging state.

**Crystallinity index** is measured by first obtaining a diffractogram as described by Blades (U.S. Patent No. 3,869,429, col. 12) with some modifications. The high intensity X-ray source is a Phillips XRG-3100 with a long fine focus copper tube. Diffraction is analyzed with a Phillips single axis goniometer equipped with a thetacomensating slit and a quartz monochromator set to exclude copper  $K_\beta$  radiation. Diffracted radiation is collected in step scanning mode in 0.025 steps with a 1.5 sec. per step count time. The digital data so collected are analyzed by a computer and smoothed by a running fit to second order polynomial. The computer is programmed to define a straight base line which joins the diffractogram tangentially at about 113 and 343. Crystallinity index is defined as

19

$$\frac{A}{A - B} \times 100$$

A - B

where A is the intensity of the 18 010 peak above this base line and B is the intensity of the 20 minimum above this base line. Crystallinity index has been  
5 related to percent crystallinity determined by density (see U.S. 4,704,329, col. 8,9). Weight percent crystallinity = 0.676 X Crystallinity index.

The "Hydrolysis" results are generally after boiling in water at 100 C, for 24 hours, except as indicated, e.g., in Example 4 to show any reductions in molecular weight (Mn), as a percentage.

10 This invention will be further illustrated by the following Examples. Parts and percentages are by weight unless otherwise indicated. The polymer compositions give the amount of PEG as a percentage by weight of the total [-C(O)-R-C(O)-OGO-] units, whereas the other components are indicated as mole %, as discussed earlier.

#### 15 EXAMPLE 1

This Example shows the laboratory preparation of a hydrolytically degradable copolyester, its use in extrusion coating of a thermally bonded non-woven fabric made from hydrolytically degradable fibers prepared according to Tietz, U.S. Patent No. 5,053,482, and the physical degradation of the copolyester  
20 by hydrolysis and composting.

#### COPOLYESTER RESIN

The copolyester resin for coating is made to have the following composition:

25 PEG (MW 600) 14 % by weight (about 5.7 mole %)  
5 mole % DEG  
89 mole % 2G  
2 mole % 55I  
98 mole % T.

30 Some deviation in composition may result from generation of DEG as a byproduct during polymerization and its incorporation in the copolymer in minor amounts.

In a 35 gallon reactor containing a stirrer, a nitrogen inlet and a distillation column are placed:

- 39372 grams dimethyl terephthalate (DMT)
- 24358 grams ethylene glycol (2G)
- 5 1134 grams diethylene glycol (DEG)
- 7031 grams (MW 600) PEG
- 1229 grams 55I dimethyl ester
- 9.1 grams Na(OAc).3H<sub>2</sub>O
- 41 grams Sb<sub>2</sub>O<sub>3</sub>
- 10 29 grams Mn(OAc)<sub>2</sub>.4H<sub>2</sub>O

The temperature of the reactor is slowly increased. Distillate (methanol) is collected in the amount of 11600 ml between 160 and 213 C. A second distillate (ethylene glycol) in the amount of 6300 ml is collected between 224-240 C. The resultant oligomer is transferred to a second vessel containing an agitator and vacuum capabilities. Then 20 g of 85% phosphoric acid is added to the transferred material, the temperature raised to 273 C and the maximum vacuum (0.5 mm Hg) is established over 90 minutes. After 2.5 hours at these conditions, the contents of the reactor are discharged through a ribbon die into a water quench. The yield of polymer is 91 lb. with an inherent viscosity of 0.84 (HFIP @ 30 C). The ribbon is cut to flake and dried at 60 C overnight in a vacuum tray dryer with a vacuum between 1 and 2 mm Hg and a nitrogen purge.

The coating resin has melting points of 105 C and 215 C by DSC. Its recrystallization and drying was achieved by placing 85 pounds of the resin in a Patterson Kelley double cone vacuum dryer model 124, establishing about 2 mm Hg absolute vacuum, rotating the dryer at 6 rpm and slowly heating the system to 150 C oil temperature. The temperature of the oil is raised in steps with sufficient time at each step for the polymer temperature to reach equilibrium with the oil. A sequence of temperature increases that has been found useful is 60, 75, 100, 135 and 150 C, with sufficient time at each temperature to permit the resin to reach thermal equilibrium with the heat transfer oil. The resulting resin has melting points by DSC of 160 C and 215 C.

### FABRIC FOR COATING

The nonwoven fabric for coating is prepared from 1.5 dpf, 1.5 inches long staple fibers with a composition of 2G/DEG(80/20)-T/5SI(98/2) prepared by extruding polymer at a rate of 475 cc/min through 900 orifices of about 0.38 mm diameter at 275 C into 21 C quench air to form filaments which are taken up at a speed of about 1625 yards/min. About 0.2% spin finish is applied (3.5% water emulsion of a mixture of an anionic surfactant "Zelec" NK from E. I. du Pont de Nemours and Company and a nonionic lubricant "Nopco" 2152P from Henkel Co.) to the yarn bundle. Bundles of filaments are collected to form a tow of about 490,000 filaments which are drawn at a draw ratio of 2.83X at 36 C in water. The fibers are crimped in a stuffer box crimper and heat treated at 133 C for about 10 minutes. The fibers have a tensile strength of 2.6 gpd (extension rate was 40% per minute), a 160 C dry heat shrinkage of 8%, and a crimp level of 12 crimps/in. The melting point of the fiber is 207 C.

The fiber is converted to thermally bonded fabric on a conventional card non-woven line. First it is carded into three 9-10 g/yd<sup>2</sup> webs which are combined and drafted to a 25 g/yd<sup>2</sup> web which is passed at 200 m/min through the nip of a calendar having two male rolls, heated to 345 F to bond the fibers and give a 25 g/yd<sup>2</sup> basis wt. fabric with an average cross direction tensile of 230-250 g/linear inch and a machine direction strip tensile of 1000 g/linear inch.

### COATING THE FABRIC

The recrystallized coating resin is placed in a hopper above the inlet of a 1 inch extruder (Echlin Mfg. Company, Serial #0717) with an 18 inch wide film die with a 0.007 inch gap. The width of the die was reduced with plugs to 17 inches to accommodate the width of the fabric being coated, 16 inches.

The fabric for coating is led continuously at different speeds, varying from 47- 106 ft/min through an extrusion coating machine made by Bertek, Inc. of St. Albans, VT (their own design). The fabric is led through a corona treatment (made by Intercon) through an S-wrap between two 4 inch diameter rolls heated to 150-260 F on to a polytetrafluoroethylene-coated, matte-finished chill roll at 100-200 F, around 300 degrees of the circumference

of this 12 inch diameter roll, while the coating resin is extruded through the 17 inch wide die at a delivery rate of 83 cc/min (20 rpm when run at 49.6 ft/min.) at a position between the chill and nip rolls as close as possible to the chill roll (about 0.25-0.5 inch). The temperature of the extruder and die can range from  
5 430-460 F. A film with 0.5 mil thickness was applied to the fabric. The extrusion-coated fabric has a basis wt. of 1.1 oz/yd<sup>2</sup>, a machine direction strength of 3.9 lb/in/oz/yd<sup>2</sup>, a toughness of 0.72 lb/in/oz/yd<sup>2</sup> and a breaking elongation of 22%. The fabric exhibited a desirable softness and the substantial absence of a rustling sound when flexed. When the barrier (film-coated) side of  
10 this fabric is coated with a water or isopropyl alcohol solution of red dye, no penetration is noted.

When a sample of this fabric is boiled in water for 24 hours, it disintegrates into loose short brittle fibers, white particles and powder.

When samples of this fabric are placed in a 30 gallon reactor filled  
15 with municipal solid waste seeded with sewage sludge taken from a municipal waste composting facility, it decreases an average of 69% in tensile strength after 6.5 days exposure, during which time a temperature of at least 65 C is maintained. The final moisture content is 47.3%.

In place of the resin recrystallization described above, an alternate  
20 procedure for preparing a suitable coating resin is to subject a lower molecular weight resin to solid state polymerization to obtain a higher molecular weight resin. For example, a 75 g. sample of an unrecrystallized resin of the same composition as the coating resin used above, and having an inherent viscosity of 0.80 (in HFIP), is placed in a "BUCHI" Rotovapor model RE120 rotary  
25 evaporator fitted with a 500 ml round flask modified to encourage agitation of flake. Vacuum is established at or below 1 mm Hg absolute, rotation is carried out at 10 rpm and the contents of the flask are slowly heated from room temperature to 195 C for 3 hours. The solid phase polymerized resin has an inherent viscosity of 0.94 and a single DSC melt point of 228 C.

30 A similar extrusion-coated fabric (same fiber composition as above) was made using a resin with the composition 2G/PEG(94/14w)-T/5SI(98/2) with an inherent viscosity of 0.87 (30 C in HFIP). The coated fabric, with a basis weight of 1.3 oz/yd<sup>2</sup>, had T/E/M properties of 2.8/3/125 in



the machine direction and 1.4/2/73 in the cross direction (T and M being lb/in/oz/yd<sup>2</sup>). The fabric, with a 0.5 mil thick coating, showed relatively low noise generation (rustling) and enough toughness and adhesion to prevent bursting and delamination when pulled by hand at low tension in the cross  
 5 machine direction. When boiled in water for 24 hours, the fabric was reduced to small particles, powder and loose fibers.

### EXAMPLE 2

This Example shows degradable extrusion-coated spunlaced non-woven fabrics and a process for their preparation.

10 The spunlaced non-woven fabrics are made by the teachings of U.S. Patent No.3,485,706, using the degradable fibers described in Example 2 of Tietz U.S. Patent No. 5,053,482.. Fabric A consists of 100% degradable staple fiber which has a dpf of 2.6, 12 crimps/in. and is cut to a length of 2.2 cm. It had tenacity/elongation of 1.3 gpd/67%. It is carded into a 1.3 oz/yd<sup>2</sup> web by an air-  
 15 laydown process of the type described in U.S. Patent No. 3,797,074. Then in a continuous operation, the web is carried by a screen and forwarded at a speed of 50m/min past a series of banks of water jets under the conditions shown in Table A, around a drum screen where a second series of banks of water jets treats the back side of the web. This fabric A has a basis weight of 1.3 oz/yd<sup>2</sup>  
 20 with grab tensile and elongations in the machine direction (MD) of 10.3 lb/oz/yd<sup>2</sup> and 73.5% and in the cross direction (CD) of 8.1 lb/oz/yd<sup>2</sup> and 138% (ASTM method D1682).

TABLE A

25	Jet Bank	Orifice	# Jets/ in.(cm)	Pressure	
	No.	dia.in(mm)		psi	kPa
	1	0.004(0.102)	40(15.7)	528	3640
	2	0.005(0.127)	40(15.7)	740	5110
	3	0.005(0.127)	40(15.7)	1057	7290
30	4	0.007(0.178)	20(7.9)	1242	8570
	5	0.007(0.178)	20(7.9)	1490	10280

Jet Bank No.	Orifice dia.in(mm)	<sup>24</sup> # Jets/	Pressure	
		in.(cm)	psi	kPa
<u>Drum Screen Jets</u>				
1	0.005(0.127)	40(15.7)	586	4040
5 2	0.005(0.127)	40(15.7)	586	4040
3	0.005(0.127)	40(15.7)	845	5830
4	0.005(0.127)	40(15.7)	0	0
5	0.005(0.127)	40(15.7)	1535	10590
6	0.005(0.127)	60(23.6)	1385	9560

10 Fabric B consists of 50 wt% degradable fiber and 50% wood pulp. It is made by forming a 0.9 oz/yd<sup>2</sup> air laid web as described for Fabric A; then, in a continuous operation, carrying this web on the same type of screen as in A, at a speed of 60 m/min together with a continuous sheet of Harmac paper under banks of jets operating at the conditions in Table B. No jet treatment of the back of the sheet was carried out. Fabric B has a basis weight of 2.2 oz/yd<sup>2</sup>, with grab tensiles and elongations in the MD of 16.2 lb/oz/yd<sup>2</sup> and 27% and in the CD of 14.2 lb/oz/yd<sup>2</sup> and 79% (ASTM method D 1682). It is asymmetrical with a high wood pulp side and a high degradable polyester side.

20

TABLE B

Jet Bank No.	Orifice dia.in(mm)	# Jets/ in.(cm)	Pressure	
			psi	kPa
	10.005(0.127)	40(15.7)	89	610
25	20.005(0.127)	40(15.7)	157	1080
	30.005(0.127)	40(15.7)	704	4860
	40.007(0.178)	20(7.9)	1157	7980
	50.005(0.127)	40(15.7)	00	
	60.005(0.127)	40(15.7)	1096	7560

30

The fabrics are coated using the resin with composition 2G/PEG(94/14w)-T/5SI(98/2) described in Example 1 with the same machine as described in Example 1. The 1 mil coatings are made at an extrusion speed of 230 cc/min and a windup speed of 65 ft/min. The 0.5 mil thick coatings are made at 166 cc/min and 94 ft/min. The properties of the coated fabrics are in

35

TABLE 1.

TABLE 1

	Fabric	Thick. (mil)	Basis Wt. oz/yd--	T/E/M/To MD/XD
5	A	0.75	1.5	3.8/60/75/1.8 1.8/130/32/1.5
	B	0.5	1.6	2.3/60/88/0.99 1.1/141/47/0.79
10	B*	1.0	3.5	3.7/7/148/0.18 2.3/61/88/1.3
	B*	0.75	2.9	3.6/12/143/0.36 2.1/61/60/1.1
	B*	0.5	2.8	3.6/16/129/0.50 2.0/60/46/0.91
15	B**	1.0	3.6	3.6/3/228/0.07 2.0/92/107/1.64
	B**	0.75	2.9	2.7/19/154/0.44 1.7/72/62/0.92
20	B**	0.5	2.7	3.2/13/204/0.37 2.0/85/71/1.30

\* High polyester side

\*\* High Wood Pulp side

25 When Fabric B was boiled in water for 24 hours, the Mn of the polyester film and coating was reduced by more than 80%.

### EXAMPLE 3

30 This Example shows the preparation of two copolyesters of the invention in film form and their hydrolytic degradation. The polymers are made by the general procedure described below. Some deviation in DEG content may result from distillation during polymerization.

In a 500 cc, 4 necked resin kettle fitted with a mechanical stirrer, condenser, distillation head with receiver flask, and a capillary N2 inlet tube are placed:

26

81.8 g ethylene glycol

63.0 g polyethylene glycol (MW 600)

8.5 g diethylene glycol

0.138 g Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (150 ppm)5 0.074 g Sb<sub>2</sub>O<sub>3</sub>.

This is warmed to 160 C to bring the contents of the flask into solution and

142.8 g Dimethyl terephthalate

3.51 g sodium salt of dimethyl-5-sulfoisophthalate

10 are added and the temperature gradually raised to 230 C while methanol distillate is collected. Then 0.5 ml of a H<sub>3</sub>P0<sub>4</sub> solution (4.79 g of 85% H<sub>3</sub>P0<sub>4</sub> diluted to 50 ml with ethylene glycol) is added. The resultant molten monomer is poured into a polymer tube to fill it about 2/3, a capillary inlet tube drawn to a fine point is inserted to reach the bottom of the tube and a filter flask attached

15 to the sidearm of the tube to act as a receiver. Polymerization is continued by heating the tube in a dimethyl phthalate vapor bath (284 C) first under laboratory vacuum for about 1 hour and then down to 0.35 mm Hg over 1.5 hours, then about 2 hours at 0.35 mm. The capillary is removed from the molten polymer and, after cooling, the polymer is recovered from the tube and ground

20 into small particles in a Thomas mill. This flake is dried at 100-130 C under laboratory vacuum. It is pressed into the films evaluated below by pressing between polytetrafluoroethylene films at a temperature 5-10 C above the highest melting point determined by DSC. Hydrolysis was carried out by placing a piece of film 1-2 mils thick, about 1 g, in 250 ml deionized water and boiling for 24

25 hours.

TABLE 2

30	Composition	Press	Hydrolysis	
	DEG/PEG/5SI	T C	Initial M <sub>n</sub>	% loss M <sub>n</sub>
	1) 10/29w/1.6	170	20260	47
	2) 10/15w/1.6	180	26660	59

EXAMPLE 4

This Example describes the preparation and rapid hydrolysis of soft films of this invention by blow molding of three polymer compositions. The first was similar to what was used above, 2G/PEG(94/14w)-T/5SI(98/2).

5 There were also prepared films from 4G-T (instead of 2G-T) that include substantial proportions of polypropylene glycol capped with ethylene oxide (called "Thanol" E2103, MW=2100, from Texaco). These were hydrolyzed in water at 60 C for 8 weeks in contrast to the 24 hour hydrolysis at 100 C for item 1. Item 2 was made by the general procedure in Example 1, using  
 10 14 weight % (1.7 mole %) of the ethylene oxide capped polypropylene glycol (P03), 2000 ppm tetrabutyl titanate ("Tyzor" TBT) as a catalyst, 0.1 mole % trimethyltrimellitate (TMTM) branching agent and a polymerization temperature of 250 C for 45 min. at a vacuum of 0.8 mm Hg. Item 3 was made  
 15 similarly, but 33 weight % (5 mole %) of the ethylene oxide capped polypropylene glycol and 0.2 mole % TMTM were used.

The apparatus used for blow molding the films consists of a 3/4 inch Brabender extruder feeding a 1 inch diameter die with a 0.08 inch gap. The die is supplied in the center with an air feed which is maintained at a pressure which expands the extruded tube to a diameter of about 2.7 inch. The feed rate  
 20 was about 40 cc/min for 1 mil thick film and about 80 cc/min for the 2 mil thick films. The blown film was wound up at about 25 ft/min.

TABLE 4

Composition	Blow Molding T 3	<u>Hydrolysis</u>		
		Mn	Init. Final Mn	% Mn Loss
1) 2G/PEG-T/5SI (94/14w)-(98/2)	235	47680	6005	87
30 2) 4G/P03-T/5SI (98.3/14w)-(98/2)	230	29145	6260	79*
3) 4G/P03-T/5SI (95/33w)-(98/2)	215	25530	7910	69*

Notes:

\* Items 2 and 3 were hydrolyzed under different conditions from Item 1, as mentioned.

#### EXAMPLES 5-9

5 These Examples show compositions which will give tough degradable materials such as films and coatings.

10 These polyesters are prepared by the procedure in Example 1 or by a procedure similar to that in Example 3. The MW of the PEG was again 600. The properties are evaluated by extruding the polymers at temperatures from the melting point to 10 C above the melting point through a 0.009 inch diameter spinneret at a pump rate of 0.07 cc/min while the extrudate is wound up about 6 inches below the spinneret at wind up speeds from 7.5 to 38 m/min.

15 The properties are listed in Table 5 for fibers having a denier close to 30. Hydrolyses were carried out on some fibers (as indicated) wound up at 38 m/min, by boiling in water for 24 hours. Mn is determined by gpc. The compositions of Examples 5-9 of the invention show suitable toughness for use as extruded coatings and films. Each shows high toughness ( $T_0$ , integrated area under stress strain curve in gpd) of at least 0.4 gpd. The test rate is 50% elongation/min.

20 In contrast, Comparisons C-H (made similarly, but with less PEG or without any PEG), did not show adequate toughness, usually much less than 0.01 gpd. Indeed, although Comparisons C, D and H had similar PEG (MW 600) in lower amounts than the Examples, their toughness was only comparable or even less than for Comparison F, without any PEG at all. This shows the importance of a threshold minimum amount of PEG, if a tough coating is  
25 desired.

TABLE 5

Sample	Composition			T / E / M / To				Mn		
	DEG/PEG /5SI			gpd/	% /	gpd /	gpd	Init.	24Hr	%
	<u>Inv</u>									
5	5	14w	2	0.66	682	9	1.9			
	6	15w	1.6	0.42	507	24	1.44	36325	8235	77
	7	10# 14w	1.6	0.22	701	5.4	0.75	48470	11650	76
	8	10 29w	1.6	Fused filaments				63420	17430	73
	9	6.5 17w 2	0.45	684	--	0.45	49325	8415	83	
10	<u>Comp</u>									
	C	0 8w	1.6	0.13	1.6	15.7	.0014			
	D	15 8w	1.6	0.25	3.7	10.8	.0059	36725	8675	76
	E	15 4w	1.6	0.08	1	9	.0002	27860	5870	79
	F	24 0	3	0.36	2.8	18.3	.0064			
15	G	10 4w	1.6	0.29	2.6	14.2	.0048			
	H	10 8w	1.6	0.30	2.1	15	.0039	25270	7375	71

Notes: # - TEG was used in Example 7. The last column shows the % loss of Mn over 24 hours.

20

EXAMPLE 10

This example shows the incorporation of polycaprolactone (6E) to give a copolymer 6E//2G/PEG(600)(94/14w)-T/5SI(98/2)[14//86 wt%] which is tough and highly degradable by hydrolysis, essentially as described in application (QP-4710-A).

25

The 2G/PEG(600)(94/14w)-T/5SI(98/2) polymer was made essentially as described hereinbefore;

72.2 g ethylene glycol

21.6 g polyethylene glycol (MW = 600)

30

0.114 g Sb<sub>2</sub>O<sub>3</sub>

0.092 g Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O

114.0 g Dimethyl Terephthalate

3.79 g Sodium salt of dimethyl 5-sulfoisophthalate.

After removal of methanol at temperature up to 220 C

22.8 g of polycaprolactone

is added and stirring continued for 30 min. The molten product is transferred to  
5 a polymer tube as described in QP-4710, and polymerization is continued while  
the tube is heated with a glycol vapor bath (198 C) for 1 hour under laboratory  
vacuum and then for 20 hours under 0.3mm Hg pressure. The polymer is  
cooled, ground and dried as in QP-4710-A, then spun using a press spinning  
10 apparatus fitted with a 0.009 inch single hole spinneret at a temperature of 177  
C with a delivery rate of 0.7 cc/min and a windup speed of 38 m/min. These (38  
m/min) fibers are tacky and they adhere together so strongly that only  
consolidated multifilament yarns are collected. These are drawn at room  
temperature 4.2X. They relax to 2.4X. T/E/M of the consolidated yarn is 0.6  
gpd/156 %/2.3 gpd. Toughness is 0.48 gpd.

15 As indicated hereinbefore, copending application QP-4710-A  
describes more fully various aspects of polyesters analogous to those in Example  
10 herein, and details of preparation thereof.

In addition to the direct extrusion-coating of film onto a nonwoven  
substrate, preformed films of the polyesters of the invention have been  
20 laminated onto a nonwoven, using heat and pressure, with the film acting as its  
own adhesive, for instance casting 0.5, 0.75, and 1 mil films onto release paper,  
using similar extrusion temperatures and conditions, as described for coating,  
with line speed being adjusted to vary thickness. Such film on release paper may  
then be passed through a calendar (heated nips, one smooth and one patterned  
25 roll), with the film against the nonwoven fabric. Suitable temperatures used have  
been 116-121 C, and 121-127 C, depending on the particular materials,  
measured on the surface of the flat roll via thermal tapes, with a nip pressure of  
10 kN, and line speed of 10 yards/minute. A variety of configurations have been  
used for laminating, preferably with the paper/film next to the flat roll, and the  
30 nonwoven next to the patterned roll. Higher nip pressures (up to 40 kN), with a  
patterned roll on either side - paper/film or nonwoven - have caused  
piercing/melting of the film, and unacceptable flattened and melted nonwoven  
aesthetics. Two flat, heated rolls may also be used, for an all-over bond, as in



conventional extrusion coating.

Other means to combine film and nonwoven layers into a composite, waterproof structure include ultrasonic bonding (preferably with some discontinuous bonding pattern), and glueing (using compatible degradable  
5 hot melt adhesives), preferably, also, with a discontinuous bonding pattern, either printed into a regular pattern (as in an existing commercial backsheets), extruded in a regular pattern (e.g., series of parallel lines), or extruded in an irregular pattern (e.g., a spiral glue application system such as is commercially available, from Meltex or Nordson).

10 Another route is to use pressure alone to bond a nonwoven layer to a film layer (with precautions to avoid holes in the film layer of the composite), by running the layers to be bonded between the nip of 2 bonding rolls, as in a calendar, for instance, one roll being engraved with a pattern and the other flat.

15 Still further techniques may include using powdered degradable polymer adhesive composition to bind higher melting fibers together into a powder bonded nonwoven, to bond a degradable film to an existing degradable nonwoven; or to bond the fibers to each other and to a film, simultaneously, e.g., using a radiant or other heat source.

20 As will be understood by those skilled in these various arts, variations may be used to suit the materials particularly selected, such materials and commercial equipment as may be convenient and/or commercially available and/or desirable, and economic factors.

**What is claimed is:-**

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



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

wherein G consists essentially of the following radicals:

a radical of a polyalkylene ether glycol of molecular weight at least about 250, in amount at least about 13% by weight of the total of the  $[\text{C}(\text{O})\text{-R-C}(\text{O})\text{-OGO-}]$

10 units,

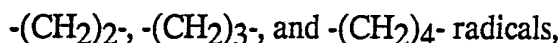
a polyethylene ether radical selected from the group consisting of



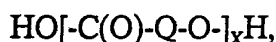
in amount up to about 40 mole % of G,

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

15 consisting of



wherein Q is derived from an hydroxy acid of formula



20 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  $\text{-(CH}_2\text{)}_n\text{-}$ , where n is an integer from

1 to 5,  $\text{-C(R')H-}$ , and  $\text{-C(R')HCH}_2\text{-}$ , wherein R' is selected from the group of

$\text{-CH}_3$  and  $\text{-CH}_2\text{CH}_3$ ,

25 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%,

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 mole % of R is p-phenylene.

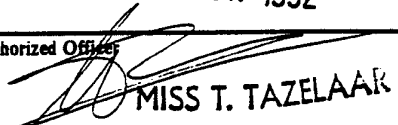
30 3. A fiber of the polyester of Claim 1 or 2.

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 92/00230**

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl.5 D 01 F 6/86	C 08 G 63/688 C 08 G 63/66	A 61 L 15/00
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl.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>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
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) ---	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 ---	1,2
A	EP,A,0311943 (AKZO N.V.) 19 April 1989, see abstract; claim 1 ---	1,2,9
A	US,A,4335220 (C.H. CONEY) 15 June 1982, see claim 1; column 2, line 62 - column 4, line 56 ---	1,2
A	US,A,4052368 (W.K. LARSON) 4 October 1977, see claim 1; examples 24,25 -----	1,2
<p><sup>10</sup> Special categories of cited documents:</p> <ul style="list-style-type: none"> <li>"A" document defining the general state of the art which is not considered to be of particular relevance</li> <li>"E" earlier document but published on or after the international filing date</li> <li>"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)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the priority date claimed</li> <li>"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</li> <li>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</li> <li>"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.</li> <li>"&amp;" document member of the same patent family</li> </ul>		
<b>IV. CERTIFICATION</b>		
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	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 MISS T. TAZELAAR	

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

US 9200230  
SA 56012

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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