

PATENT SPECIFICATION

(11) 1 585 403

1 585 403

- (21) Application No. 21826/77 (22) Filed 24 May 1977
(31) Convention Application No. 690 482
(32) Filed 27 May 1976 in
(33) United States of America (US)
(44) Complete Specification published 4 March 1981
(51) INT CL³ C08G 63/68
(52) Index at acceptance
C3R 3D13 3D2D 3D2E 3D6 3N1 5M
C3Y B200 B262 B284 F224 G320 H260



(54) LINEAR COPOLYESTERS

(71) We, OWENS-ILLINOIS INC., a Corporation organised under the laws of the State of Ohio, United States of America, of Toledo, Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present application is directed to linear copolyesters formed from saturated dicarboxylic acids and saturated glycols; the invention is also directed to packaging methods, and containers and packages formed from these copolyesters.

At present there is a strong interest in protecting comestibles by enveloping these comestibles, for example foodstuffs, e.g. carbonated beverages and medicines, in packages, for example molded containers and, especially, biaxially oriented molded containers, which packages are formed from materials which comprise poly(ethylene terephthalate). Such molded containers, whether they be biaxially oriented or unoriented possess many desirable characteristics for certain products but there is a need to provide for a polyester which will have a glass transition temperature higher than that of poly(ethylene terephthalate) whereby containers made of such a polyester may be subjected to environments, for example higher temperatures, to which poly(ethylene terephthalate) may not be subjected. Additionally in order to achieve wider versatility in the types of products which are packaged therein, for example, comestibles, there is also a need to provide polyesters which have an oxygen permeability which is lower than that of poly(ethylene terephthalate). Additionally, many products, for example carbonated beverages, need to be packaged in containers having low carbon dioxide permeability and accordingly there is also a need to provide containers having carbon dioxide permeabilities which are lower than that of poly(ethylene terephthalate).

U. S. Patent No. 2593,411 suggests that polyesters may be formed from dicarboxylic acids and from bis(4-beta-hydroxyalkoxyphenyl) sulfones and that mixed polyesters can likewise be obtained by employing such sulfones in combination with other dihydric and polyhydric alcohols. British Patent Specification 678,264 suggests linear polyesters formed from an aromatic dicarboxylic acid and a glycol, e.g. bis(4-beta-hydroxyethoxyphenyl) sulfone. Also in this regard, reference may be had to British Patent Specification 1,196,911 which discloses the reaction of ethylene glycol with for example bis(4-chlorophenyl) sulfone and indicates that such type materials may be employed in forming polyesters. Vol. 83 of *Chemical Abstracts*, No. 206808s (1975) discloses polyesters being formed from 4,4'-biphenyl-dicarboxylic acid and aliphatic glycols and bis(4-beta-hydroxyethoxyphenyl) sulfone. Similarly Vol. 83 *Chemical Abstracts* Nos. 165136a and 165644q (1975) disclose the use of such sulfones with naphthalene dicarboxylic acids. None of the foregoing are directed to forming polyesters having oxygen permeabilities and CO₂ permeabilities which are lower than that of poly(ethylene terephthalate) and which have glass transition temperatures higher than that of poly(ethylene terephthalate).

Japanese unexamined (Kokai) Patent Publication No. Showa 50-51595 (Patent Application No. Showa 48-101837) discloses transparent, dimensionally stable, linear polyesters having high glass transition points but has no recognition, or teachings, with regard to oxygen permeability and carbon dioxide permeability. It is taught therein to employ for example bis(4-beta-hydroxyethoxyphenyl) sulfone,

alone or with minor amounts of a glycol, and a dicarboxylic acid which is primarily terephthalic acid. In order to obtain polyesters suitable for the purposes of this patent application it is taught that, of the dicarboxylic acid, at least 70 mole percent, and preferably 80%, should be terephthalic acid and, based on the acid employed, at least 60%, and preferably 65—95%, should be the described sulfone. A wide variety of optional dicarboxylic acids which may be used in minor amounts are set forth from which it is possible to select isophthalic acid and sulfonyl dibenzoic acid. Similarly a wide variety of diols are disclosed, including ethylene glycol.

The art is generally aware of the use of 4,4'-sulfonyldibenzoic acid, or its ester, or its halides, for use as a dicarboxylic acid in the formation of linear polyesters.

In accordance with the present invention applicant has satisfied a need in the art by providing a linear copolyester which is the polymeric reaction product of reactants consisting essentially of (A) isophthalic acid and 4,4'-sulfonyldibenzoic acid, and (B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol. While these polyesters have numerous uses, by adjusting the amounts of the (A) reactants and the (B) reactants linear copolyesters can be formed having oxygen permeabilities, carbon dioxide permeabilities, and glass transition temperatures which will allow for their use in a wide variety of applications in the packaging industry. Generally on a mole basis the combined amounts of the (B) reactants above will be 110 mole percent to 300 mole percent of the combined amount of the (A) reactants.

For many applications in the packaging industry a copolyester having quite advantageous properties will be formed wherein the (A) reactants comprise 15 mole percent to 60 mole percent of 4,4'-sulfonyldibenzoic acid and 85 mole percent to 40 mole percent of isophthalic acid; the amount of bis(4-beta-hydroxyethoxyphenyl) sulfone being between 15 mole % and 90 mole % of the combined amounts of the (A) reactants, with the amounts of the (A) and (B) reactants being sufficient to provide an oxygen permeability of less than that of poly(ethylene terephthalate) and a glass transition temperature in excess of that of poly(ethylene terephthalate). The percentages are based on reactant feed. Preferably, the bis(4-beta-hydroxyethoxyphenyl) sulfone will be at least 50 mole % relative to the combined amounts of the (A) reactants.

In passing it should be mentioned that when reference is made to oxygen and carbon dioxide permeability of poly(ethylene terephthalate) it is generally considered that the homopolymer has an oxygen permeability of about 8—9 cc-mil/100 in²-day-atm. and a carbon dioxide permeability of about 62 cc-mil/100 in²-day-atm. when measured on pressed films. Generally the glass transition temperature of unoriented poly(ethylene terephthalate) is considered to be about 72°C.

A quite desirable linear copolyester suitable for use in a wide variety of applications in the packaging industry is a copolyester formed as the polymeric reaction product in which the (A) reactants, on a mole basis, comprise 45 to 80% of isophthalic acid and 20% to 55% of 4,4'-sulfonyldibenzoic acid, the amount of the bis(4-beta-hydroxyethoxyphenyl) sulfone being 60 mole percent to 85 mole percent of the combined amounts of the (A) reactants; such copolyesters will have an oxygen permeability of less than about 7.4 cc-mil/100 in²-day-atm. (at about 50% relative humidity and about 73°F.) and a carbon dioxide permeability of less than about 65.6 cc-mil/100 in²-day-atm. (at about 50% relative humidity and about 73°F.) and glass transition temperatures of at least about 121°C.

Quite outstanding copolyesters are formed as the reaction product when the (A) reactants comprise, on a mole basis, 60% to 80% of isophthalic acid and 20% to 40% of 4,4'-sulfonyldibenzoic acid, the amount of bis(4-beta-hydroxyethoxyphenyl) sulfone being between 60% and 85% of the combined amount of the (A) reactants; such polymers will have a carbon dioxide permeability of less than about 50.3 and an oxygen permeability of less than about 7.0 and a glass transition temperature in excess of about 121°C. These polymers will be of outstanding utility for the packaging of carbonated beverages, e.g. pop, and exhibit excellent heat stability.

As indicated the present invention also contemplates molded containers which are formed from materials which comprise linear copolyesters with the copolyesters consisting essentially of the polymeric reaction product of the (A) and (B) reactants indicated hereinbefore. Biaxially oriented molded containers formed from the polyesters contemplated herein are of especially outstanding characteristics. Packages which comprise comestibles, for example carbonated beverages or medicines, enveloped in a molded container formed from materials which

comprise a linear copolyester with the copolyester consisting essentially of the reaction product of the reactants indicated above will find utilization, and a flexibility of use, not possessed by that of poly(ethylene terephthalate). The present application likewise contemplates improvements in methods for protecting comestibles wherein the comestibles are enveloped in packages which are formed from the copolyesters contemplated herein.

When reference is made herein to bis(4-beta-hydroxyethoxyphenyl) sulfone and to ethylene glycol, it is contemplated that this likewise includes esters thereof as being employed for the reactants. Similarly when reference is made to isophthalic acid and to 4,4'-sulfonyldibenzoic acid that terminology likewise contemplates not only the acid but also the esters and acid halides thereof for use as reactants. Preferably in practicing the invention the ethylene glycol and bis(4-beta-hydroxyethoxyphenyl) sulfone will be used as the diol per se, whereas the diesters of isophthalic acid and the 4,4'-sulfonyldibenzoic acid will be used as the (A) reactants. These esters may be the aliphatic esters or aromatic esters with the preferred esters being the alkyl esters having from 1—4 carbon atoms, with methyl being especially highly preferred. The phenyl esters are the preferred aromatic esters.

The copolyesters as contemplated herein are synthesized by methods generally known in the art for producing polyesters. The reactants may all be reacted in a single operation by first charging them to an appropriate reactor or a sequential operation may be employed by first reacting isophthalic and ethylene glycol to form bis(beta-hydroxyethyl) isophthalate and then in turn reacting the latter with the remaining ingredients. Since, as indicated, in the preferred practice the diesters of isophthalic acid and 4,4'-sulfonyldibenzoic acid will be employed, conventional transesterification followed by polycondensation is contemplated as the preferred approach. Temperatures employed which will be quite suitable for forming the copolyesters will generally range between 200 or 210°C. and 295°C. with the preferred range being between 225°C. and 285°C. Of course the reaction will be done under an inert atmosphere.

Conventional catalysts are likewise employed. For example transesterification is effected in the presence of effective catalytic amounts of transition metal compounds, alkaline earth metal compounds, or alkali metal compounds, for example the acetates, oxides, phenoxides, and alkoxides. Specific suitable catalysts will be, for example, zinc acetate, manganese acetate, magnesium acetate, calcium acetate, and titanium alkoxides, like titanium tetrabutoxides as well as mixed metal salts for example potassium titanium oxalate. Suitable polycondensation catalysts include, for example, antimony acetate, antimony trioxide, titanium alkoxide, and organotin oxides, for example stannous alkoxides. Usually the catalysts will be present in an amount of about 10^{-5} to about 10^{-3} moles of catalysts per mole of total acid employed.

Of course suitable adjuvants, such as antioxidants and stabilizers may be employed and they may be added directly to the reaction mass or added to the final polymer.

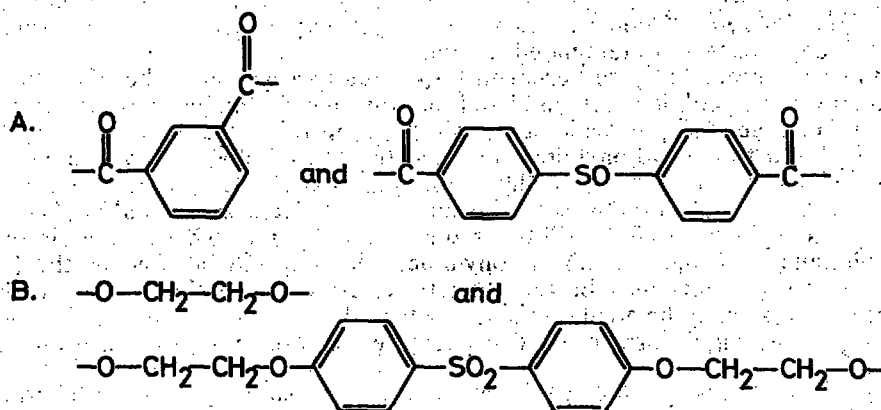
The linear copolyesters contemplated herein may be formed into clear packages, for example molded containers, and preferably biaxially molded containers, using conventional plastic forming techniques such as, for example, that disclosed in U.S. Patent No. 3,733,309. These packages are ideally suited for protecting foodstuffs, for example, carbonated soft drinks and beer, or medicines, or other related substances, by simply enveloping those substances in these packages.

The following Examples are given for the purpose of illustrating the invention.

60

Example 1

A linear copolyester was prepared having the following units in its backbone:



The specific reactant materials employed in the feed stock was about 0.1 mole of an admixture of dimethyl isophthalate (DMI) and dimethyl 4,4'-sulfonyldibenzoic acid (DMS) with the former being present in an amount of about .08 mole and the latter in an amount of about .02 mole. About 0.2 mole of ethylene glycol (EG) and about .085 mole of bis(4-beta-hydroxyethoxyphenyl) sulfone (BSE) were employed as the glycol. Additionally about 6.5×10^{-6} mole of Sb_2O_3 and about 5×10^{-6} mole of $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ were employed for catalytic purposes.

The mixture of the reactants along with the catalysts were weighed into a 300 ml three-necked round bottom flask equipped with a stirrer, nitrogen inlet tube, and a condenser. The contents of the flask were heated to and held at about 225°C. for about 3 hrs. with nitrogen flowing into the reaction flask to provide a nitrogen blanket and with methanol being removed. The reactant system was then heated to about 265°C. and held there for about 45 minutes during which time additional methanol was removed. A vacuum of 0.2 to 0.45 mm Hg was then applied and the reactants heated to between 275°C. and 285°C. with ethylene glycol being removed. The system was held at that latter temperature under that vacuum for approximately 6 hours after which time the polymer was removed. Table A sets forth the glass transition temperature of the polymer and as well as the carbon dioxide and oxygen permeability of films which were pressed from that polymer. The carbon dioxide permeability and the oxygen permeability were measured on pressed films employing ASTM D-1434-66 at a temperature of about 73°F. and 50% relative humidity and is in the units cc. mil/100 in² day atm. The glass transition temperature was measured with a Differential Scanning Calorimeter. In Table A the percentages are based on feed stock.

Examples 2-4

The procedure of Example 1 was substantially repeated using a total molar charge of the (A) reactants of about 0.1 mole with the mole percentage of the respective (A) constituents being varied as indicated in Table A. Additionally, in Example 3 instead of employing .085 moles of BSE there was employed about .060 moles of BSE and about 0.19 moles of ethylene glycol.

TABLE A.

Example	% DMI	% DMS	% BSE	Mole Ratio EG/BSE	O ₂	CO ₂	T _g
1	80	20	85	70/30	5.5	35.4	121°C.
2	60	40	85	70/30	7.0	50.3	129°C.
3	60	40	60	76/24	5.1	46	124°C.
4	45	55	85	70/30	7.4	65.6	135°C.

Following the known forming procedures of the prior art, for example U. S. Patent No. 3,733,309, a biaxially oriented molded container (i.e., a container having a bottom wall and circumferential sidewall merging with and proceeding upwardly from the bottom wall, the sidewall at its upper margin tapering inwardly and merging with a neck portion defining a mouth opening) is formed from the above copolyesters of Examples 1—4. The containers are clear and upon being filled with comestibles, for example foodstuffs, like apple sauce, or medicines, so as to envelope these substances, show outstanding characteristics for the packaging of such products. The polyesters of Examples 1—3 show particularly outstanding characteristics for the packaging of carbonated beverages.

WHAT WE CLAIM IS:—

1. A linear copolyester which is the polymeric reaction product of reactants consisting essentially of

(A) isophthalic acid and 4,4'-sulfonyldibenzoic acid, and

(B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol.

2. The copolyester of claim 1 wherein the combined amount of said (B) reactants is from 110 mole percent to 300 mole percent of the combined amount of said (A) reactants.

3. The copolyester of claim 2 wherein the molar amounts of said (A) reactants are 45% to 80% of isophthalic acid and 20% to 55% of 4,4'-sulfonyldibenzoic acid and the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is 60% to 85% of the combined amount of said (A) reactants, said copolyester having an O₂ permeability of less than about 7.4, a CO₂ permeability of less than about 65.6 and a glass transition temperature of at least about 121°C.

4. The copolyester of claim 3, said copolyester having a CO₂ permeability of less than about 50.3 and an O₂ permeability of less than about 7.0, said (A) reactants comprising 60% to 80% isophthalic acid and 20% to 40% 4,4'-sulfonyldibenzoic acid, on a mole basis.

5. The copolyester of claim 2 wherein said (A) reactants are present, on a mole basis, in an amount of 15% to 60% 4,4'-sulfonyldibenzoic acid and 85% to 40% isophthalic acid and the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is 15% to 90% of the combined amounts of said (A) reactants, the amounts of said (A) and (B) reactants being sufficient to provide an O₂ permeability of less than that of poly(ethylene terephthalate) and a glass transition temperature in excess of poly(ethylene terephthalate).

6. A molded container formed from a material which comprises a linear copolyester as claimed in any of claims 1 to 5.

7. A molded container of claim 6 wherein said container is a biaxially oriented container.

8. A package comprising comestibles enveloped in a molded container, said molded container being as claimed in claim 6 or 7.

9. A method for protecting comestibles comprising enveloping said comestibles in packages formed from the copolyester of any of claims 1 to 5.

10. A linear copolyester as claimed in claim 1, substantially as hereinbefore described.

11. A molded container as claimed in claim 6, substantially as hereinbefore described.



1,585,403

TABLE A.

Example	% DMI	% DMS	% BSE	Mole Ratio EG/BSE	O ₂	CO ₂	T _g
1	80	20	85	70/30	5.5	35.4	121°C.
2	60	40	85	70/30	7.0	50.3	129°C.
3	60	40	60	76/24	5.1	46	124°C.
4	45	55	85	70/30	7.4	65.6	135°C.

Following the known forming procedures of the prior art, for example U. S. Patent No. 3,733,309, a biaxially oriented molded container (i.e., a container having a bottom wall and circumferential sidewall merging with and proceeding upwardly from the bottom wall, the sidewall at its upper margin tapering inwardly and merging with a neck portion defining a mouth opening) is formed from the above copolyesters of Examples 1—4. The containers are clear and upon being filled with comestibles, for example foodstuffs, like apple sauce, or medicines, so as to envelope these substances, show outstanding characteristics for the packaging of such products. The polyesters of Examples 1—3 show particularly outstanding characteristics for the packaging of carbonated beverages.

WHAT WE CLAIM IS:—

1. A linear copolyester which is the polymeric reaction product of reactants consisting essentially of

(A) isophthalic acid and 4,4'-sulfonyldibenzoic acid, and

(B) bis(4-beta-hydroxyethoxyphenyl) sulfone and ethylene glycol.

2. The copolyester of claim 1 wherein the combined amount of said (B) reactants is from 110 mole percent to 300 mole percent of the combined amount of said (A) reactants.

3. The copolyester of claim 2 wherein the molar amounts of said (A) reactants are 45% to 80% of isophthalic acid and 20% to 55% of 4,4'-sulfonyldibenzoic acid and the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is 60% to 85% of the combined amount of said (A) reactants, said copolyester having an O₂ permeability of less than about 7.4, a CO₂ permeability of less than about 65.6 and a glass transition temperature of at least about 121°C.

4. The copolyester of claim 3, said copolyester having a CO₂ permeability of less than about 50.3 and an O₂ permeability of less than about 7.0, said (A) reactants comprising 60% to 80% isophthalic acid and 20% to 40% 4,4'-sulfonyldibenzoic acid, on a mole basis.

5. The copolyester of claim 2 wherein said (A) reactants are present, on a mole basis, in an amount of 15% to 60% 4,4'-sulfonyldibenzoic acid and 85% to 40% isophthalic acid and the amount of said bis(4-beta-hydroxyethoxyphenyl) sulfone is 15% to 90% of the combined amounts of said (A) reactants, the amounts of said (A) and (B) reactants being sufficient to provide an O₂ permeability of less than that of poly(ethylene terephthalate) and a glass transition temperature in excess of poly(ethylene terephthalate).

6. A molded container formed from a material which comprises a linear copolyester as claimed in any of claims 1 to 5.

7. A molded container of claim 6 wherein said container is a biaxially oriented container.

8. A package comprising comestibles enveloped in a molded container, said molded container being as claimed in claim 6 or 7.

9. A method for protecting comestibles comprising enveloping said comestibles in packages formed from the copolyester of any of claims 1 to 5.

10. A linear copolyester as claimed in claim 1, substantially as hereinbefore described.

11. A molded container as claimed in claim 6, substantially as hereinbefore described.

(b)



1,585,403

For the Applicants,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43, Bloomsbury Square,
London WC1A 2RA.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1981.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.