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(54) Title: POLYESTERS HAVING IMPROVED GAS BARRIER PROPERTIES AND CONTAINERS MADE THEREFROM

(57) Abstract

Containers having improved resistance to gas permeability. The containers are formed from a polyester resin which comprises the reaction product of a diol containing up to about 8 carbon atoms and a diacid component which comprises about 5 to 100 mole percent of a first diacid selected from 1,4-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, 1,2-phenylenedioxy diacetic acid, and mixtures thereof, and 0 to about 95 mole percent of terephthalic acid. The polyester resin has an inherent viscosity of about 0.5 to 1.5. The containers which are provided by the present invention may be in the form of sheet, film, molded articles, such as bottles, and other such structures.

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POLYESTER HAVING IMPROVED GAS BARRIER PROPERTIES AND CONTAINERS MADE THEREFROM

The present invention relates to polyesters suited for packages for protecting edible materials. More specifically, it relates to films and molded containers which are formed from such polyesters.

Presently there is a strong interest in the packaging industry for protecting edible materials, such as foodstuffs, medicines, and especially carbonated beverages, by enveloping the substances in packages which are formed from various polymers. One polymer in which there is an especially strong interest is polyethylene terephthalate. Containers formed from this material, which may be biaxially oriented, possess many desirable characteristics. Molded biaxially oriented containers which are formed from polyethylene terephthalate and certain copolyesters are disclosed in U.S. Patent No. 3,733,309. Molded containers formed from polyethylene terephthalate have, as indicated, many desirable characteristics which make them ideally suited for packaging uses. On the other hand, packages made from polyethylene terephthalate still suffer from having gas permeabilities which are lower than the level normally required for certain uses such as for packaging edible materials. Solving this problem would contribute to provide improved containers much more versatile in their utilization and to allow the containers to be used to package substances for which the polyethylene terephthalate containers may not be suitable.

The present invention provides a novel polyester which is suitable for use in forming packages for protecting edible materials. The present invention also provides improved containers made of the polyester which exhibit a desirable balance of physical properties, including improved gas barrier properties, i.e., improved resistance to gas permeability which render them advantageous for use in the packaging of edible materials.

U.S. Patent No. 3,522,328 discloses copoly(ester-amides) wherein the amide moieties may comprise *p*-phenylenedioxydiacetic acid. The patent neither discloses nor suggests the use of *p*-phenylenedioxy diacetic acid in the preparation of polyesters nor the use of such polyesters as containers having improved gas barrier properties.

In one aspect of the present invention, there is provided a novel polyester which comprises the reaction product of

A) a diol containing up to 8 carbon atoms and
B) a diacid component.

The diacid component comprises

I) 5 to 100 mole percent of a first diacid selected from 1,4-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, 1,2-phenylenedioxy diacetic acid, and mixtures thereof, and

II) 0 to 95 mole percent of terephthalic acid.

In another aspect, the present invention provides containers having improved resistance to gas permeability. The containers are formed from the novel polyester of the present invention.

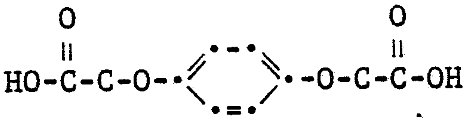
As used herein, the term "container" is intended to mean shaped articles formed from the specified polyester which are suitable for use in packaging edible materials. Such shaped articles include sheets and films which are extruded from the polyester and which may be used as such or as barrier layers, container liners, as components of laminates or other composites, etc. Such shaped articles also include molded containers, such as bottles.

The polyester of the present invention comprises the reaction product of a diol component and a diacid component. The diol component comprises one or more diols containing up to about 8 carbon atoms. Examples of such diols include ethylene glycol; 1,4-butanediol; 1,4-cyclohexanedimethanol; propylene glycol; diethylene glycol; 2,2,4-trimethyl-1,3-pentanediol; 2,2-dimethyl-1,3-propanediol; 2,2-diethyl-1,3-propanediol; 2-methyl-2-propyl-1,3-propanediol; 1,3-butanediol; 1,5-pentanediol; 1,6-hexanediol; 1,2-cyclohexanedimethanol; 1,3-cyclohexanedimethanol; 2,2,4,4-tetramethyl-1,3-cyclobutanediol; *o*-, *m*-, and *p*-xylylene diols; etc. The diol component is preferably selected from ethylene glycol, 1,4-butanediol, and 1,4-cyclohexanedimethanol, and is more preferably selected from ethylene glycol and 1,4-butanediol. Most preferably, the diol component comprises ethylene glycol. In addition to the diol containing up to 8 carbon atoms and to the terephthalate acid, minor amounts (i.e., less than 50 mole percent, and, preferably, less than 10 mole percent, based on the total amount of diol present in the polyester) of other known polyester-forming glycols may also be employed. Such diols may include, for example, 2,4-dimethyl-2-ethylhexane-1,3-diol; 2-ethyl-2-butyl-1,3-propanediol; 2-ethyl-2-isobutyl-1,3-propanediol; 2,2,4-trimethyl-1,6-hexanediol; 4,4'-sulfonyldiphenol; 4,4'-oxydiphenol; 4,4'-isopropylidenediphenol; 2,5-naphthalenediol; and other well known polyester-forming diols.

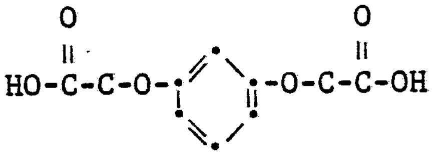
The polyester resin further comprises a diacid component. The diacid component comprises a first diacid selected from 1,4-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, 1,2-phenylenedioxy diacetic acid, and mixtures thereof. The diacid component may further comprise terephthalic acid. Other well known polyester-forming diacids may be employed in minor amounts. Such diacids may include, for example, isophthalic acid, 1,4-cyclohexanedicarboxylic acid, linear lower alkyl dicarboxylic acids, etc.

The first diacid, which is selected from 1,4-phenylenedioxy diacetic acid (Formula I), 1,3-phenylenedioxy diacetic acid (Formula II), 1,2-phenylenedioxy diacetic acid (Formula III), and mixtures thereof, is present in the polyester in a concentration of 5 to 100 mole percent, based upon the total amount of diacid present in the polyester.

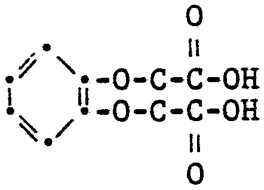
I.



II.



III.



In preferred embodiments of the present invention, 1,3-phenylenedioxy diacetic acid is employed as the first diacid. The diacid component further comprises 0 to 95 mole percent of terephthalic acid.

When the polyester is to be formed into a sheet or film, the first diacid is preferably present in an amount of at least 15 mole percent and, more preferably, in an amount of at least 30 mole percent (i.e., 50 to 100 mole percent). When a molded container, such as a bottle, is desired, the first diacid is preferably present in an amount of 5 to 20 mole percent and, more preferably, is present in an amount of 10 to 20 mole percent.

The polyester which is employed in the present invention exhibits an I.V. of 0.5 to 1.5. The I.V. is measured at 25°C in a 60/40 by weight mixture of phenol/tetrachloroethane at a concentration of 0.5 g/100 mL. Polymers having an I.V. within the range specified above are of sufficiently high molecular weight to be used in the formation of containers.

The polyesters of the present invention are synthesized by methods generally known in the art for producing polyesters. The reactants may all be reacted in a single operation or, alternatively, sequential operation may be employed. Temperatures which are suitable for forming the polyesters generally range between 180°C and 295°C, with the preferred range being 200 to 285°C. The reaction may be conducted under an inert atmosphere, such as nitrogen. Preferably, the latter stage of the reaction is conducted under a vacuum.

Conventional catalysts are employed in the preparation of the polyester. For example, polymerization can be effected in the presence of catalytic amounts of transition metal compounds, such as antimony acetate, antimony trioxide, titanium alkoxides, and organo tin compounds (for example, stannous alkoxides). Preferred catalysts are titanium alkoxides, such as titanium tetraisopropoxide, titanium tetrabutoxides, etc. Usually, the catalysts will be present in an amount of about 10^{-5} to 10^{-3} moles of catalyst per mole of total acid employed.

Of course, suitable additives, such as dyes, pigments, plasticizers, fillers, antioxidants, stabilizers, etc., may be employed in conventional amounts. Such additives may be added directly to the reaction or may be added to the final polymer.

The polyesters described above may be formed into the containers of the present invention by conventional plastic processing techniques. For example, sheets, films, and other like structures can be formed by well known extrusion techniques.

Film or sheet material made from the compositions of the present invention is strong, flexible, and clear. It may be formed into articles such as wrappers, bags, and the like.

The polyesters may also be used to form a laminating layer between two or more permeable layers of film. In like manner, a layer of the polyester of the present invention (preferably, a composition containing at least 50%, more preferably, 100%, of the first diacid), may be coextruded as a pipe or similar structure between two or more permeable layers. The polyesters may also be used for dip coating containers from a polymer solution in order to improve the barrier properties of a package. In each of these embodiments, the present invention offers the additional advantage of not requiring the use of a tie layer.

Molded containers can be made from the above-described polyester by compression molding, blow molding, and other such molding techniques, all of which are well known in the art. Preferred molded containers are biaxially oriented blow-molded containers.

The polyesters and the containers of the present invention concur to solve the problem of gas permeability encountered when polyesters of the prior art are used for protecting edible materials, such as foodstuffs (especially carbonated soft drinks), medicines, and like substances. The advantages of these containers are due to low oxygen and carbon dioxide permeability relative to polyethylene terephthalate. Because of the decreased gas transmission rates of these polyesters, they perform well in packaging applications where improved gas barrier properties are required. Typically, the containers of the present invention exhibit an oxygen permeability of less than about 8.5 (preferably, less than about 7.5) and a carbon dioxide permeability of less than about 50 (preferably, less than about 30), measured as cubic centimeters permeating a 1 mil (25.4 μm) thick sample, 100 inches square (1639 cm^2), for a 24 hour period under a partial pressure difference of 1 atmosphere (101.3 kPa) at 30°C.

This invention will be further illustrated by the following examples.

Example 1

This example illustrates the improved gas barrier properties of containers formed of polyethylene terephthalate which has been modified with 5 mole percent of 1,4-phenylenedioxy diacetic acid.

A reaction vessel was charged with dimethyl terephthalate, ethylene glycol, 5 mole percent of 1,4-phenylenedioxy diacetic acid, based upon the total diacid present, and 100 ppm of titanium from titanium tetraisopropoxide. The reaction mixture was heated and stirred under nitrogen at 200°C for 60 minutes. The temperature was then increased to 210°C for 120 minutes until all of the methanol and water had distilled out of the reaction mixture. The temperature was then raised to 275°C, the nitrogen was evacuated from the reaction system, and a vacuum was applied. The melt condensation was continued at 275°C for 90 minutes under 0.5 mm Hg (66.5 Pa) pressure. The heating was discontinued, the reaction mixture was brought to atmospheric pressure with nitrogen, and the polymer was collected.

The oxygen permeability of the polyester was determined in cubic centimeters permeating a 1 mil (2.4 μm) thick sample, 10 inches square (64.5 cm^2), for a 24-hour period under an oxygen partial pressure difference of one atmosphere at 30°C. The polyester was extruded into amorphous (i.e., unoriented) film using a Brabender extruder at 240-260°C. The film actually used to measure permeability was 3-8 mils (76.2 µm-203.2 µm) in thickness, but the permeability was converted to a one mil (25.4 µm) basis using conventional calculations. In like manner, the carbon dioxide permeability of the polyester was determined.

The results are given in Table I.

Example 2

Example 1 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 1,3-phenylenedioxy diacetic acid. The oxygen permeability and carbon dioxide permeability of the polyester were determined as in Example 1, and the results are given in Table I.

Example 3

Example 1 was repeated except that 10 mole percent of 1,4-phenylenedioxy diacetic acid was employed. The oxygen permeability and carbon dioxide permeability and carbon dioxide permeability of the polyester were determined as in Example 1, and the results are given in Table I.

Example 4

Example 3 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 1,3-phenylenedioxy diacetic acid. The oxygen permeability and carbon dioxide permeability and carbon dioxide permeability of the polyester were determined as in Example 1, and the results are given in Table I.

Example 5

Example 3 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 1,2-phenylenedioxy diacetic acid. The oxygen permeability of the polyester were determined as in Example 1, and the results are given in Table I.

Example 6

Example 1 was repeated except that 20 mole percent of 1,4-phenylenedioxy diacetic acid was employed. The oxygen permeability and carbon dioxide permeability of the polyester were determined as in Example 1, and the results are given in Table I.

Example 7

Example 6 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 1,3-phenylenedioxy diacetic acid. The oxygen permeability and carbon dioxide permeability of the polyester were determined as in Example 1, and the results are given in Table I.

Example 8

Example 6 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 1,2-phenylenedioxy diacetic acid. The oxygen permeability of the polyester was determined as in Example 1, and the results are given in Table I.

Example 9

Example 1 was repeated except that 50 mole percent of 1,4-phenylenedioxy diacetic acid was employed. The oxygen permeability of the polyester was determined as in Example 1, and the results are given in Table I.

Example 10

Example 9 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 1,3-phenylenedioxy diacetic acid. The oxygen permeability of the polyester was determined as in Example 1 and the results are given in Table I.

Example 11

A reaction vessel was charged with 22.42 grams of 1,4-phenylenedioxy diacetic acid, 24.60 grams of ethylene glycol, and 100 ppm of titanium from titanium tetraisopropoxide. The reaction mixture was heated and stirred under nitrogen at

210°C for 60 minutes. The temperature was then increased to 220°C for 120 minutes until all of the water had distilled out of the reaction mixture. The temperature was then raised to 260°C, the nitrogen was evacuated from the reaction system, and a vacuum was applied. The melt condensation was continued at 260°C for 75 minutes under 0.5 mm Hg (66.5 Pa) pressure. The heating was discontinued, the reaction mixture was brought to atmospheric pressure with nitrogen, and the polymer was collected. The polymer had an inherent viscosity of 0.88. The oxygen permeability and carbon dioxide permeability of the polyester were determined as in Example 1. The results are given in Table I.

Example 12

Example 11 was repeated except that 1,3-phenylenedioxy diacetic acid was used in place of 1,4-phenylenedioxy diacetic acid. The resulting polymer had an I.V. of 0.56. The oxygen permeability and carbon dioxide permeability of the polyester were measured as in Example 1, and the results are given in Table I.

Comparative Example 1

A control sample of polyethylene terephthalate was prepared according to the procedure given in Example 1. The oxygen permeability and carbon dioxide permeability of the sample were determined as in Example 1, and the results are given in Table I.

Comparative Example 2

Example 3 was repeated except that 1,4-phenylenedioxy diacetic acid was replaced with 2,2'-[1,4-phenylenebis(oxy)]bisethanol. The oxygen permeability and carbon dioxide permeability of the polyester were determined as in Example 1, and the results are given in Table I.

TABLE I

Example	Oxygen Permeability	CO_2 Permeability
1	8.3	47
2	7.5	49
3	6.3	39
4	5.0	26
5	6.2	-
6	4.8	22
7	3.1	18
8	3.2	-
9	1.0	-
10	0.6	-
11	0.6	4.5
12	0.1	0.6
Comp. 1	10.0	59
Comp. 2	11.0	63

An analysis of the data of Table I indicates the superior properties exhibited by the polyesters of the present invention which make them extremely advantageous for use in the formation of containers. It will be noted that the compositions described in the examples, without exception, exhibit oxygen and, for those compositions tested, carbon dioxide permeabilities below those exhibited by polyethylene terephthalate as exemplified by Comparative Example 1. The data of Table I further indicate that, while all the compositions are useful for the formation of improved containers, those compositions employing the meta isomer are preferred due to their improved resistance to gas permeability.

The uniqueness of the polyesters of the present invention and of the properties exhibited by containers formed therefrom is indicated by a comparison of the Examples with Comparative Example 2, which employs a structurally similar second diacid.

However, the polyester of Comparative Example 2 exhibits poor resistance to gas permeability, whereas the compositions of the Examples of the present invention demonstrate a much improved resistance to gas permeability, as compared to polyethylene terephthalate.

TABLE II

Physical Data for Polymers

Example	I.V.	Tm (°C by DSC)	Tg (°C by DSC)	Break Strength 10^3 kg/cm^2	Break Elongation (%)	Film Density	Tangent Modulus (10^5 kg/cm^2)
1	0.88	241	67	.476	277	1.340	.203
2	0.73	239	71				
3	0.82	228	64				
4	0.70	229	65	.578	3	1.344	.21
5	0.66	227	69	.448	3	1.344	.21
6	0.85	209	58				
7	0.78	209	56	.553	3	1.345	.224
8	0.67	195	51	.476	3	1.347	.259
9	1.00	--	47				
10	0.96	--	49				
11	0.88	--	--				
12	0.56	--	--				
Comp. 1	0.72	250	78	.602	400	1.335	.162
Comp. 2	--	--	--				

DSC = differential scanning calorimetry

Claims

1. A polyester comprising the reaction product of

A) a diol containing up to 8 carbon atoms, and

B) a diacid component comprising

I) about 5 to 100 mole percent of a first diacid selected from 1,4-phenylenedioxy diacetic acid, 1,3-phenylenedioxy diacetic acid, 1,2-phenylenedioxy diacetic acid, and mixtures thereof, and,

II) 0 to about 95 mole percent of terephthalic acid.

2. The polyester of claim 1 wherein said diol comprises ethylene glycol, 1,4-butanediol, 1,4-cyclohexanedimethanol, or a mixture thereof.

3. The polyester of claim 1 wherein said diol comprises ethylene glycol.

4. The polyester of claim 1 wherein said first diacid comprises 1,3-phenylenedioxy diacetic acid.

5. The polyester of claim 1 wherein said first diacid is present in a concentration of about 5 to 20 mole percent.

6. The polyester of claim 1 wherein said first diacid is present in a concentration of 15 to 100 mole percent.

7. The polyester of claim 1 wherein said first diacid is present in a concentration of 50 to 100 mole percent.

8. A container formed from the polyester of any of claims 1-7.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 84/00545

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

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

IPC^3: C 08 G 63/66

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC^3	C 08 G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
	GB, A, 970969 (SHELL) 23 September 1964, siehe Patentansprüche 1-10; Seite 2, rechte Spalte, Zeilen 85-100	1-7
	--	
X	US, A, 2470651 (G.S. SCHAFFEL) 17 May 1949	1-7
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* Special categories of cited documents: [15]

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"P" document published prior to the international filing date but later than the priority date claimed

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"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 [2] 17th July 1984	Date of Mailing of this International Search Report [2] 16 AOUT 1984
International Searching Authority [1] EUROPEAN PATENT OFFICE	Signature of Authorized Officer [10] G.L.M. Kruydenberg

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 84/00545 (SA 7003)

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 09/08/84

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 970969		None	
US-A- 2470651		None	

For more details about this annex :
see Official Journal of the European Patent Office, No. 12/82