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(57) Abstract

The invention provides a multi–layered structure comprising: a) a first layer comprising a polyester or copolyester of poly(ethylene terephthalate); and b) a barrier layer comprising a residue of phenylenedi(oxyacetic acid), wherein the barrier layer is adjacent to the first polyester or copolyester layer.

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MULTI-LAYERED POLYESTER ARTICLES CONTAINING A RESIDUE OF PHENYLENEDI(OXYACETIC ACID) AND HAVING GOOD BARRIER TO GAS PERMEATION

This application claims the benefit of U.S. Provisional Applications 60/089,221, filed June 15, 1998, 60/089,220, filed June 15, 1998, and 60/089,391, filed June 15, 1998.

Field of the Invention

The invention relates to multilayer structures. Specifically the invention relates to multilayer structures such as containers wherein the barrier layer comprises a polyester or a copolyester containing a pheneylenedi(oxyacetic acid) residue, or a blend comprising a polyester or copolyester of a phenylenedi(oxyacetic acid) residue.

Background of the Invention

US 5,688,572, 5,221,507, 5,049,345 and 4,923,723, disclose multi-layer constructions containing a barrier layer. One multi-layer construction involves ethylene-vinyl alcohol copolymers (also referred to as EVOH), and the other multi-layer construction involves a nylon called MXD-6, prepared from meta-xylylene diamine and adipic acid. In the multi-layered construction, as a minimum, bottles employing these barrier layers have at least an inner and an outer layer of poly(ethylene terephthalate) with an inner layer of the chosen barrier material. Both the EVOH and MXD-6 constructions, however, have serious potential drawbacks. For the EVOH construction, the barrier is a steep function of the relative humidity of the storage environment with a very hot, humid environment degrading the barrier performance by more than an order of magnitude. In addition, only a very small amount of EVOH contamination in the poly(ethylene

terephthalate) recycle stream can have very adverse effects. The two polymers are totally incompatible and form a two phased mixture even in the presence of less than 1 wt% of EVOH. This causes haze if the material is used for containers such as bottles and causes tremendous spinning problems if the recovered poly(ethylene terephthalate) is used for fiber spinning. It is very difficult to eliminate the EVOH to the required level from the poly(ethylene terephthalate) recycle stream.

The MXD-6 nylon has similar problems although not to the same degree as EVOH. However, MXD-6 imparts an undesirable yellow color to polyesters at very low concentrations. In methanolysis recycling processes the MXD-6 nylon contaminates the raw materials exiting the process with a small amount of the diamine, rendering the recycled materials unsuitable for packaging applications.

While the above-named patents and those referenced therein disclose various technologies for the production of multi-layered structures having a barrier layer, they do not contemplate the use of multi-layered structures having a barrier layer comprised of a polyester or copolyester containing a phenylenedi(oxyacetic acid) residue, or a blend comprising a polyester or copolyester of a pheneylenedi(oxyacetic acid) residue, which exhibits a longer shelf life, design freedom, improved barrier properties and is recyclable.

Summary of the Invention

The present invention provides for multi-layered structures containing at least one barrier layer comprising a residue of phenylenedi(oxyacetic acid).

In one embodiment, the invention provides a multi-layered structure comprising:

(a) a first layer comprising a polyester or copolyester of poly(ethylene terephthalate); and

(b) a barrier layer comprising a residue of phenylenedi(oxyacetic acid), wherein the barrier layer is adjacent to the first polyester or copolyester layer.

In another embodiment, the invention provides a multi-layered structure comprising:

(a) a first layer comprising a polyester or copolyester of poly(ethylene terephthalate);

(b) a first barrier layer comprising a residue of phenylenedi(oxyacetic acid); and

(c) a second layer comprising a polyester or copolyester of poly(ethylene terephthalate),

wherein the first barrier layer is disposed intermediate the first polyester or copolyester layer and the second polyester or copolyester layer.

In another embodiment, the invention provides a multi-layered structure comprising:

(a) a first layer comprising a polyester or copolyester of poly(ethylene terephthalate);

(b) a first barrier layer comprising a residue of phenylenedi(oxyacetic acid);

(c) a second layer comprising a polyester or copolyester of poly(ethylene terephthalate);

(d) a second barrier layer comprising a residue of phenylenedi(oxyacetic acid); and

(e) a third layer comprising a polyester or copolyester of poly(ethylene terephthalate),

wherein the first barrier layer is disposed intermediate the first polyester or copolyester layer and the second polyester or copolyester layer, and

the second barrier layer is disposed intermediate the second polyester or copolyester layer and the third polyester or copolyester layer.

Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary only and are not restrictive of the invention as claimed.

Detailed Description of the Invention

The present invention may be understood more readily by reference to the following detailed description of preferred embodiments of the invention and the examples therein.

It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include the plural referents unless the context clearly dictates otherwise.

Ranges are often expressed herein as from "about " one particular value, and/or to "about" another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment.

A weight percent of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

With respect to the polyester, mole % are based on 100 mole % diacid and 100 mole % diol, for a total of 200 mole %.

"Optional" or "optionally" means that the subsequently described event or circumstances may or may not occur, and that the description includes instances where said event or circumstances occurs and instances where it does not. For example, the phrase "optionally substituted lower alkyl" means that the alkyl group may or may not be substituted and that the description includes both unsubstituted lower alkyl and lower alkyl where there is substitution.

The term "adjacent" means that the layers in the multi-layered structure are in close proximity to one another, and may or may not imply that the layers are in direct contact with one another.

The term "contact" means that the layers in the multi-layered structure are touching one another, and are not separated by an intermediate layer(s).

The multi-layered structures in this invention contain a first layer, which is a polyester or copolyester of poly(ethylene terephthalate) ("PET"), preferably a copolyester of poly(ethylene terephthalate) comprising residues of ethylene glycol and terephthalic acid and further comprising residues of cyclohexanedimethanol and/or isophthalic acid. The first polyester or copolyester layer is typically in direct contact with the contents of the container and may also be referred to as the inner layer or the innermost layer.

The multi-layered structures in this invention also contain a barrier layer, which comprises a residue of a phenylenedi(oxyacetic acid), preferably a polyester or copolyester containing a phenylenedi(oxyacetic acid) residue, or a blend comprising a phenylenedi(oxyacetic acid) polyester or copolyester. The barrier layer is adjacent to, preferably in contact with, the first layer and may also be referred to as the internal or intermediate layer.

The multi-layered structures in this invention may also contain additional layers of a polyester or a copolyester of poly(ethylene

terephthalate). The additional layer of poly(ethylene terephthalate may be referred to as the second , third, fourth, etc. layers.

The multi-layered structures of this invention may also contain additional barrier layers containing a residue of a phenylenedi(oxyacetic acid). The additional barrier layer may be referred to as the second, third, fourth, etc. barrier layers.

In a multi-layered structure having at least three layers, the first barrier layer is disposed intermediate the first polyester or copolyester layer and the second polyester or copolyester layer. Preferably, the first barrier layer is in contact with both the first polyester or copolyester layer and the second polyester or copolyester layer.

In a multi-layered structure having at least five layers, an additional barrier layer having the same composition as the first barrier layer, and a third layer comprising a polyester or copolyester of poly(ethylene terephthalate) is added to the three-layer structure, wherein the second barrier layer is disposed intermediate the second polyester or copolyester layer and the third polyester or copolyester layer. Preferably, the first barrier layer is in contact with the first polyester or copolyester layer and the second polyester or copolyester layer, and the second barrier layer is in contact with both the second polyester or copolyester layer and the third polyester or copolyester layer.

A layer of the polyesters or copolyesters of PET in the multi-layered structure may be the layer furthest from the inner layer, which is also referred to as the outer or outermost layer, which is formed from a polyester or copolyester of poly(ethylene terephthalate), or a blend comprising a polyester or copolyester of phenylenedi(oxyacetic acid), preferably a polyester of poly(ethylene terephthalate).

When the outermost layer is a polyester or copolyester of poly(ethylene terphthalate), either a virgin poly(ethylene terephthalate) or

recycled poly(ethylene terephthalate) may be utilized, preferably virigin poly(ethylene terephthalate).

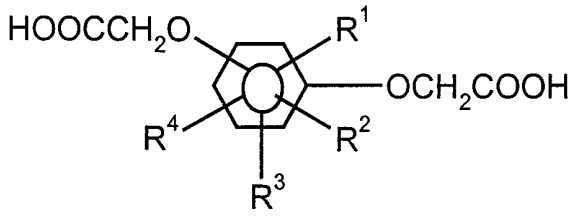
When the outermost layer is formed from a blend comprising a polyester or copolyester of phenylenedi(oxyacetic acid), a protective layer may be provided on the outside of the outermost layer for the purpose of protecting the surface. The protective layer is adjacent to and in contact with the outermost layer of the multi-layered structure.

Typical phenylenedi(oxyacetic) compositions are disclosed in US 4,440,922 and US 4,552,948, the disclosure of which is incorporated by this reference in their entireties. Blends comprising a phenylenedi(oxyacetic acid) polyester or copolyester are also useful as a barrier layer and are disclosed in U.S. Serial No._____(05015.0227), entitled "High Barrier Polyester Phenylenedi(Oxyacetic Acid) Blends," filed on _____ and U.S. Serial No. _____(05015.0229), entitled "Polyester Phenylenedi(Oxyacetic Acid) Copolyester Blends Having Improved Gas Barrier Properties," filed on _____, the disclosures of which are also incorporated by reference.

U.S. Serial No. _____(05015.0227) discloses polyester blend compositions comprising:

I. from about 5 to about 85 weight % of a polyester which is the reaction product of:

(A) a repeat unit of phenylenedi(oxyacetic acid) represented by the formula (I);



(I)

wherein R^1,R^2,R^3 and R^4 each independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, a phenyl group, a chlorine atom, a bromine atom, or a fluorine atom or an ester derivative of phenylenedi(oxyacetic acid) of the formula I;

(B) a repeat unit of a diol containing up to 24 carbon atoms; and

II. from about 95 to about 15 weight % a thermoplastic polyester of poly(ethylene terephthalate), a copolyester of poly(ethylene terephthalate) modified with from greater than 0 to about 70 mole % of a glycol comprising diethylene glycol, propanediol, butanediol, hexanediol or 1,4-cyclohexanedimethanol, and/or a dicarboxylic acid comprising isophthalic acid or naphthalenedicarboxylic acid, or a mixture of a poly(ethylene terephthalate) copolyester with poly(ethylene terephthalate);

from about 95 to about 15% of a polyester of poly(ethylene naphthalate), a copolyester of poly(ethylene naphthalate) modified from greater than 0 to 30 mole % of a glycol comprising diethylene glycol, propone diol, butanediol, hexanediol or 1,4-cyclohexanedimethanol, and/ or a dicarboxylic acid comprising isophthalic acid or terephthalic acid, or a mixture of the poly(ethylene naphthalate) copolyester with poly(ethylene naphthalate);

from about 95 to about 15% of poly(butylene terephthalate);

from about 95 to about 15% of poly(trimethylene terephthalate); or

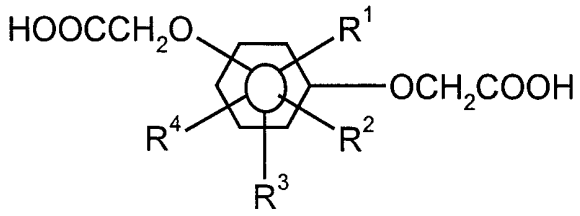
from about 95 to about 15% of poly(butylene naphthalate).

U.S. Serial No. _____(05015.0229) discloses polyester blend compositions comprising:

I. from about 5 to about 85 weight % of a copolyester which is the reaction product of components comprising:

(A) a repeat unit of a dicarboxylic acid component comprising

(i) from about 5 to 99 mole % of a phenylenedi(oxyacetic acid) represented by the formula (I):



(I)

wherein R^1,R^2,R^3 and R^4 each independently represents a hydrogen atom, an alkyl group having from 1 to 6 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, a phenyl group, a chlorine atom, a bromine atom, or a fluorine atom, or an ester derivative of phenylenedi(oxyacetic acid) of formula I;

(ii) 1 to 95 mole % of a repeat unit of a second diacid selected from the group comprising terephthalic acid, isophththalic acid, naphthalenedicarboxylic acid, or cyclohexanedicarboxylic acid, or ester thereof, or mixture thereof;

(B) a repeat unit of a diol containing up to 24 carbon atoms; and

II. from about 95 to about 15 weight % of a thermoplastic polyester of poly(ethylene terephthalate), a copolyester of poly(ethylene terephthalate) modified with from greater than 0 to about 70 mole % of a glycol comprising diethylene glycol, propanediol, butanediol, hexanediol or 1,4-cyclohexanedimethanol, and/or a dicarboxylic acid comprising isophthalic acid or naphthalenedicarboxylic acid, or a mixture of the poly(ethylene terephthalate) copolyester with poly(ethylene terephthalate);

from about 95 to about 15% of a polyester of poly(ethylene naphthalate), a copolyester of poly(ethylene naphthalate) modified from greater than 0 to 30 mole % of a glycol comprising diethylene glycol, propone diol, butanediol, hexanediol or 1,4-cyclohexanedimethanol, and/ or a dicarboxylic acid comprising isophthalic acid or terephthalic acid, or a mixture of the poly(ethylene naphthalate) copolyester with poly(ethylene naphthalate);

from about 95 to about 15% of poly(butylene terephthalate);

from about 95 to about 15% of poly(trimethylene terephthalate); or from about 95 to 15% of poly(butylene naphthalate).

Preferred phenylenedi(oxyacetic acids) of formula (I) include 1,2-phenylenedi(oxyacetic acid), 1, 3-phenylenedi(oxyacetic acid), 1, 4-phenylenedi(oxyacetic acid), 2-methyl-1, 3-phenylenedi(oxyacetic acid), 5-methyl-1,3-phenylenedi(oxyacetic acid), 4-methyl-1,3-phenylenedi(oxyacetic acid), 5-ethyl-1,3-phenylenedi(oxyacetic acid), 4-ethyl-1, 3 phenylenedi(oxyacetic acid), 5-methoxy-1,3 phenylenedi(oxyacetic acid), 4-methoxy- 1,3 phenylenedi(oxyacetic acid), 4-chloro-1,2-phenylenedi(oxyacetic acid), or 4-chloro-1,3-phenylenedi(oxyacetic acid) or an ester thereof.

An even more preferred phenylenedi(oxyacetic acid) of formula (I) includes derivatives of 1,2-phenylenedi(oxyacetic acid), 1,3-phenylenedi(oxyacetic acid), 1,4-phenylenedi(oxyacetic acid), or an ester thereof.

Phenylenedi(oxyacetic acids) as the dicarboxylic acid component (IA) in the present invention may be used as a raw material of a polyester of the present invention either in the form of an acid itself or in the form of an ester forming derivative such as an acid halide and an ester, in particular, an ester forming derivative such as a C1-4 alkyl ester. Alternatively, an oligomer obtained by reacting a phenylenedi(oxyacetic acid) with a glycol may be used for polymerization.

The polyester or copolyester component I is present in the range of from about 5 to about 85 weight % of the blend composition, more preferably from about 5 to about 60 weight % of the blend composition, and most preferably from about 5 to about 40 weight % of the blend composition.

As the diol component (IB) for the polyester of the present invention, typical diols include ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, pentamethylene glycol, hexamethylene glycol, neopentyl glycol, cyclohexanedimethanol, 1,3 bis (2-hydroxyethoxy)benzene, diethylene glycol, and a derivative of an aromatic dihydroxy compound. A preferable

diol component is ethylene glycol, and typical aromatic dihydroxy derivatives include resorcinol, hydroquinone, Bisphenol A, or Bisphenol S.

The polyester component II is present in the range of from about 95 to about 15 weight % of the blend composition, more preferably from about 95 to about 40 weight % of the blend composition, and most preferably from about 95 to about 60 weight % of the blend composition.

The preparation of phenylenedi(oxyacetic acid) monomers is disclosed in US 4, 935,540, the teachings of which are incorporated herein by reference.

The polyesters (I or II) of the present invention can be produced by any polymerization method that is conventionally known for a polymerization method for poly(ethylene terephthalate). For example, a polycondensation method may be adopted, which the method comprises the steps of directly esterifying terephthalic acid and a phenylenedi (oxyacetic acid) represented by the formula [I] such as 1,3-phenylenedi (oxyacetic acid) and ethylene glycol under a pressure and thereafter gradually reducing the pressure while raising the temperature to polycondense the reaction product. It is also possible to produce a copolyester of the present invention by subjecting an ester derivative of terephthalic acid such as dimethyl terephthalate, an ester derivative of a phenylenedi(oxyacetic acid) represented by the general formula [I] such as dimethyl 1,3-phenylenedi(oxyacetate) and ethylene glycol to an ester exchange reaction, and further polycondensing the reaction product.

In the production of such a polymer (I or II), it is preferable to use an esterifying catalyst, ester exchanging catalyst, polycondensing catalyst, stabilizer, etc.

As the ester exchanging catalyst, at least one known compound selected from calcium, manganese, zinc, sodium and lithium compounds is usable. From the point of view of transparency, a manganese compound if more preferable. As the polycondensing catalyst, at least one known

compound selected from antimony, germanium, titanium and cobalt compounds is usable. Antimony, germanium and titanium compounds are preferably used.

When a polyester blend comprising a phenylenedi(oxyacetic acid) of the present invention forms the barrier layer, the blend may contain a polyfunctional compound such as trimethylolpropane, pentacrythritol, glycerin, trimellitic acid, trimesic acid and pyromellitic acid, or a monofunctional compound such as o-benzoylbenzoic acid in the range which does not impair the effect of the present invention.

The polyfunctional or monofunctional compound may be added to the resultant blend comprising the polyester or copolyester of phenylenedi(oxyacetic acid), or the polyfunctional or monofuctional compound may be employed as an additional monomeric component to form the copolyester of pheneylenedi(oxyacetic acid). Such a polyfunctional or monofunctional compound is preferably used in the range of not more than 20 mol % of the diol component (IB).

The polyester or copolyester containing a phenylenedi(oxyacetic acid) residue, or blends comprising a polyester or copolyester of phenylenedi(oxyacetic acid) disclosed as the barrier layer in the present invention do not display the drawbacks associated with EVOH or MXD-6 barrier layer constructions. In addition, use of catechol as the base diphenol to prepare the oxydiacetic acid derivative also leads to high barrier polymers like those described in US 4,440,922 and US 4,552,948 which can also be used to make polyester and polyester/copolyester blends, such as disclosed in U.S Serial No. _____(05015.0227) and U.S. Serial No. _____(05015.0229). In addition to these copolymers, one can also employ a phenoxy resin as described in U.S. 4,267,301 and US 4,383,101. These resins are particularly well tolerated in the recycle stream while giving improved barrier to gas permeation. In

addition, polyglycolic acid or copolymers thereof can function in this multi-layer technology as well.

The barrier layer in this invention exhibits very high barrier to gas transmission, in particular to carbon dioxide. This is particularly useful in the case of carbonated beverage bottles, including soft drinks, mineral water, beer and the like, as it allows the product stored in such a bottle to retain carbonation over a longer period of time than is observed with bottles made solely of poly(ethylene terephthalate), which are now being used. This allows a longer "shelf life" for the beverage in such a bottle. Shelf life is defined as the time it takes the bottle to lose 15% of its carbon dioxide pressure. A longer shelf life is advantageous to the bottling company. For the current soft drink bottles made of poly(ethylene terephthalate), for example, the smaller sizes such as 20 and 24 oz. need to be kept cold in order to increase the shelf life of the container to an acceptable level so that the consumer does not open the bottle only to find that the soft drink contained therein is "flat", i.e. has lost too much carbon dioxide. Thus, bottles of the present invention allow an inherently longer shelf life which has a distinct advantage in that the distribution system does not have to depend on keeping the bottles cold to enhance the shelf life of the product as is now commonly done. This is an advantage to the bottler and retailer as costs of storage of the bottles are greatly reduced without the need for refrigeration of the same. There is also an advantage to the consumer in that the costs of this special distribution system (so-called cold channel distribution) will not be passed on in the form of higher prices for the soft drink.

The use of resins comprising phenylenedi(oxyacetic acid) in a multi-layer structure, such as a bottle as opposed to a monolayered system has several very great advantages. Because obtaining an FDA regulation is a long and arduous process, the most important advantage is that the approval process for multilayered bottles is relatively simple and quick.

Poly(ethylene terephthalate) has food contact approval but copolymers containing phenylenedi(oxyacetic acid) do not. Use of a multilayered construction, however, allows immediate use of the phenylenedi(oxyacetic acid) resins as long as the inner layer of the container is poly(ethylene terephthalate). This is true because the poly(ethylene terephthalate) acts as a functional barrier against the migration of any components of the subject copolyesters into the food contained. This satisfies the law in regard to food contact items.

Another advantage of the multilayer structures, and preferably bottles of the present invention, concerns processing of the resin to form the desired structure, such as a container. The usual process for manufacture involves injection molding of a preform followed by reheating of the preform and blowing it into a suitable mold to obtain the final bottle. In the process, the polymer in the bottle itself becomes oriented and crystallized thereby imparting much higher strength and rigidity to the bottle. This is a necessary step in preparation of suitable containers to hold the pressure of carbonation that is attained in a soft drink bottle.

By using a multilayered preform of the present invention, one can maintain a current parison design and have a lower permeation rate for the container and thus a longer shelf life.

A multi-layered polyester hollow container according to the present invention is produced by forming a preform of a multi-layered hollow container wherein at least one layer comprises a polyester or copolyester containing a phenylenedi(oxyacetic acid) residue, or a blend comprising a polyester or copolyester of phenylenedi(oxyacetic acid), and stretching the thus obtained preform at a temperature above the glass transition point (Tg) of the polyester at least in the biaxial direction. The multilayer may be composed of either two layers or not less than three layers. A multilayer of three to five layers is preferable. In this case, it is preferable that the inner

layer of the hollow container is a layer of a polyester or copolyester of poly(ethylene terephthalate).

The outermost layer of the hollow container may be a polyester or copolyester of poly(ethylene terephthalate), or a blend comprising a polyester or copolyester of phenylenedi(oxyacetic acid), however, a polyester of poly(ethylene terephthalate) is preferable as the outermost layer in terms of surface strength. When the outermost layer is composed of a copolyester or polyester blends containing a phenylenedi(oxyacetic acid), a protective layer may be provided on the outside of the outermost layer for the purpose of protecting the surface. The protective layer may be formed at a stage for forming the preform of the hollow container. Alternatively, the protective layer may be formed after the preform is stretched so as to produce the hollow container by labeling or the like. The protective layer may be formed from a polymer, an organic coating, or an inorganic coating, preferably polypropylene, an epoxy coating, or a silica or aluminum based coating, or the like.

Generally, the total thickness of a container body is 200 to 700 μ, preferably 250 to 600 μ. The thickness of the phenylenedi(oxyacetic acid) containing polyester layer varies depending upon the desired barrier property, but it is generally 5 to 300 μ, preferably 10 to 200 μ.

Suitable containers of the present invention may also be produced by extrusion blow molding or biaxial orientation blow molding which is conventionally known. In the case of using biaxial orientation blow molding, the preform of the hollow container is formed, and after the preform is heated to the stretching temperature, it is stretched within a blow mold.

Suitable preforms may be produced by forming a bottomed preform by injection molding, or a multi-layered pipe, and forming one end thereof into a bottom. When a multilayer preform is produced, the layers may be formed sequentially from the inner layer by an ordinary injection molding machine or a molding machine having a plurality of melt injection

apparatuses, or the respective layers may be extruded from a plurality of injecting apparatuses into a single mold one by one, so that the poly(ethylene terephthalate) injected first may constitute the inner layer and the outermost layer, and the blend comprising the polyester or copolyester of phenylenedi(oxyacetic acid) injected later constitutes a barrier layer. By selecting the injection timing, it is possible to design the preform so as to have three layers, five layers or more.

Alternatively, the multilayer stucture may be formed by separately forming a preform from the polyester and a sleeve or sock from the barrier material. The sleeve or sock may be inserted over the preform at any time up to just prior to reheating the preform. Once the sleeve or sock and preform are in intimate contact the container is formed via conventional blow molding methods.

The preform of the hollow container obtained is generally heated in a heating zone having a heater such as a block heater and an infrared heater for the subsequent stretching process. The heating temperature for the preform for a polyester multi-layered hollow container of the present invention is determined by the glass transition temperature (hereunder referred to as Tg of the polyester layer of poly(ethylene terephthalate). The heating temperature is preferably in the range of Tg +5°C to Tg +80°C. If the heating temperature is too low, micro voids are produced due to a cold stretching and the container unfavorably presents the pearl or foggy appearance. On the other hand, if the heating temperature is too high, the preform becomes too soft to obtain a hollow container having a sufficient stretching effect.

When the preform of a polyester multi-layered hollow container is stretched to form the hollow container, the preform is preferably stretched by 1 to 4 times in the machine direction and by 2 to 6 times in the transverse direction (hoop direction of the container) by moving a rod in the machine direction and blowing pressurized air. In order to enhance the

heat resistance of the container, it is possible to heat set the container by further heating the stretched hollow container within the mold at a temperature the same as or higher than the stretching temperature for a short time.

The multilayer structures of the present invention are useful as packaging materials and can also be widely used as a container, sheet, film, etc.

A polyester hollow molded product of the present invention, which has a high mechanical strength as well as excellent transparency and gas barrier property, can be widely used for packaging beverages, flavoring material, oil, alcoholic beverages such as beer, wine and sake, and cosmetics. Particularly, the polyester hollow molded product of the present invention can be used as a small-sized container for carbonated drink, beer, wine or the like. The improved barrier of the multilayer structures of the present invention would insure that the contents would be preserved for extended periods of time.

Multi-layered containers of the present invention have excellent gas barrier properties, a high mechanical strength free from ply separation and an excellent transparency in the external appearance. Multi-layered hollow containers of the present invention can therefore be widely used for fresh beverage, flavoring material, oil, alcoholic drink such as beer, wine and sake, and cosmetics.

Methods of preparing the multi-layer structure and equipment for doing so are well known in the art. Thus, multi-layered structures of the invention can be prepared according to the methods disclosed in any one of US Patent nos. 5,688,572, 5,221,507, 5,040,963, 5,523,045, 4,751,035, 4,525,134, 4,710,118, 5,200,207, or 4,863,665. The multi-layer container forming equipment is available from Kortec, which is located in Gloucester, Massuchusetts.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

What is claimed is:

1. A multi-layered structure comprising:
   (a) a first layer comprising a polyester or copolyester of poly(ethylene terephthalate); and
   (b) a barrier layer comprising a residue of phenylenedi(oxyacetic acid), wherein the barrier layer is adjacent to the first polyester or copolyester layer.

2. The multi-layered structure of claim 1, wherein the barrier layer is in contact with the first polyester or copolyester layer.

3. The multi-layered structure of claim 1, wherein the first layer comprises a copolyester of poly(ethylene terephthalate) comprising residues of ethylene glycol and terephthalic acid and further comprising residues of cyclohexanedimethanol and/or isophthalic acid.

4. The multi-layered structure of claim 1, wherein the first polyester or copolyester layer is the inner layer.

5. The multi-layered structure of claim 1, wherein the barrier layer is a polyester or copolyester containing a phenylenedi(oxyacetic acid) residue, or a blend comprising a phenylenedi(oxyacetic acid) polyester or copolyester.

6. The multi-layered structure of claim 5, wherein the barrier layer is a polyester comprising a phenylenedi(oxyacetic acid) residue.

7. The multi-layered structure of claim 5, wherein the barrier layer is a copolyester comprising a phenylenedi(oxyacetic acid) residue.

8. The multi-layered structure of claim 5, wherein the barrier layer is a blend comprising a phenylenedi(oxyacetic acid) polyester.

9. The multi-layered structure of claim 5, wherein the barrier layer is a blend comprising a phenylenedi(oxyacetic acid) copolyester.

10. The multi-layered structure of claim 1, wherein the structure further comprises at least one additional layer.

11. The multi-layered structure of claim 10, wherein the at least one additional layer comprises a polyester or copolyester of poly(ethylene terephthalate).

12. The multi-layered structure of claim 1, wherein the structure comprises at least five layers.

13. The multi-layered structure of claim 1, wherein the structure is a molded container.

14. The multi-layered structure of claim 13, wherein the molded container is a bottle.

15. The multi-layered structure of claim 1, wherein the structure is a packaging material.

16. The multi-layered structure of claim 1, wherein the structure is a sheet.

17. The multi-layered structure of claim 1, wherein the structure is a film.

18. A multi-layered structure comprising:

(a) a first layer comprising a polyester or copolyester or poly(ethylene terephthalate);

(b) a first barrier layer comprising a residue of phenylenedi(oxyacetic acid); and

(c) a second layer comprising a polyester or copolyester or poly(ethylene terephthalate),

wherein the first barrier layer is disposed intermediate the first polyester or copolyester layer and the second polyester or copolyester layer.

19. The multi-layered structure of claim 18, wherein the first barrier layer is in contact with both the first polyester or copolyester layer and the second polyester or copolyester layer.

20. The multi-layered structure of claim 18, further comprising a second barrier layer having the same composition as the first barrier layer, and a third layer comprising a polyester or copolyester of poly(ethylene terephthalate), wherein the second barrier layer is disposed intermediate the second polyester or copolyester layer and the third polyester or copolyester layer.

21. The multi-layered structure of claim 20, wherein the first barrier layer is in contact with the first polyester or copolyester layer and the second polyester or copolyester layer, and the second barrier layer is in contact with both the second polyester or copolyester layer and the third polyester or copolyester layer.

22. The multi-layered structure of claim 18, wherein the barrier layer is a polyester or copolyester comprising a phenylenedi(oxyacetic acid) residue or a blend containing a phenylenedi(oxyacetic acid) polyester or copolyester.

23. The multi-layered structure of claim 18, wherein the structure further comprises at least one additional layer.

24. The multi-layered structure of claim 23, wherein the structure comprises at least two additional layers.

25. The multi-layered structure of claim 18, wherein the stucture is a molded container.

26. The multi-layered structure of claim 25, wherein the molded container is a bottle.

27. The multi-layered structure of claim 18, wherein the structure is a packaging material.

28. The multi-layered structure of claim 18, wherein the structure is a sheet.

29. The multi-layered structure of claim 18, wherein the structure is a film.

30. A multi-layered structure comprising:

(a) a first layer comprising a polyester or copolyester of poly(ethylene terephthalate);

(b) a first barrier layer comprising a residue of phenylenedi(oxyacetic acid);

(c) a second layer comprising a polyester or copolyester of poly(ethylene terephthalate);

(d) a second barrier layer comprising a residue of phenylenedi(oxyacetic acid); and

(e) a third layer comprising a polyester or copolyester of poly(ethylene terephthalate),

wherein the first barrier layer is disposed intermediate the first polyester or copolyester layer and the second polyester or copolyester layer, and the second barrier layer is disposed intermediate the second polyester or copolyester layer and the third polyester or copolyester layer.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 99/13352

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/672 C08J5/18 C08G63/181

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G B32B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 335 594 A (MITSUBISHI CHEM IND) 4 October 1989 (1989-10-04) page 5, line 28 -page 9, line 35; claims 1,3,9,10,14; examples 37-42 page 9, line 17-27-50 -page 10, line 21-51 ---	30
X Y	EP 0 492 999 A (MITSUBISHI CHEM IND) 1 July 1992 (1992-07-01) page 2, line 13-15 -page 4, line 14-18-53; claims 1,4-6 ---	1-9, 13-17 1-30
X Y	US 4 663 426 A (WICKER JR THOMAS H ET AL) 5 May 1987 (1987-05-05) column 3, line 58 -column 4, line 28; claims 1-16 --- -/--	1-9, 13-17 10-12, 18-30

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 1999	28/10/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Interr nal Application No
PCT/US 99/13352

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 4 440 922 A (BARBEE ROBERT B ET AL) 3 April 1984 (1984-04-03) cited in the application claims 1-9	1-30

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