

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 September 2010 (10.09.2010)

PCT

(10) International Publication Number
WO 2010/101562 A1

(51) International Patent Classification:
C08L 67/02 (2006.01) *C08L 69/00* (2006.01)

(21) International Application Number:
PCT/US2009/035704

(22) International Filing Date:
2 March 2009 (02.03.2009)

(25) Filing Language: English

(26) Publication Language: English

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ,
EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO,
NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG,
SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ,
TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE,
ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR),
OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML,
MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: MOLDED ARTICLES MADE FROM BLENDS OF POLYESTERS AND BISPHENOL A POLYCARBONATES

(57) Abstract: Molded articles are disclosed that comprise polymer blends prepared by blending polyesters prepared from terephthalic acid, 40 to 5 mole percent 2,2,4,4-tetramethy-1,3-cyclobutanediol, and 60 to 95 mole percent 1,4- cyclohexanedimethanol, with bisphenol A polycarbonate. The composition of the blend includes up to about 95 weight percent bisphenol A polycarbonate. These blends have a combination of clarity, toughness and heat resistance making the materials particularly useful in engineering molding plastics and packaging.



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MOLDED ARTICLES MADE FROM BLENDS OF POLYESTERS AND BISPHENOL A POLYCARBONATES

FIELD OF THE INVENTION

[0001] The present invention relates generally to molded articles made from polymer blends, and more specifically, blends of polyesters containing terephthalic acid (TPA), 1,4-cyclohexanedimethanol (CHDM), and 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD), blended with up to about 95 wt. percent of a polycarbonate comprised of bisphenol A. The blends may be used to provide molded articles having clarity, toughness, and heat resistance, making them especially useful in engineering molding plastics and in packaging.

BACKGROUND OF THE INVENTION

[0002] Polycarbonate comprised of bisphenol A, also known as 4,4'-isopropylidenediphenol or 2,2-bis-(4-hydroxyphenyl)propane), is a well known engineering molding plastic. Bisphenol A polycarbonate is a clear high-performance plastic having good physical properties such as dimensional stability, high heat resistance, and good impact strength. However, its relatively high melt viscosity leads to poor melt processing and the polycarbonate exhibits poor chemical resistance. It is also difficult to thermoform.

[0003] Polymers containing 2,2,4,4-tetramethyl-1,3-cyclobutanediol have also been generally described in the art. Generally, however, these polymers exhibit high melt viscosities and/or high Tgs (glass transition temperatures), such that the equipment used in industry can be insufficient to manufacture or post polymerization process these materials.

[0004] It would be desirable to combine the properties of these two types of polymers, especially those polycarbonates comprised predominantly of bisphenol A and those polyesters comprising substantial amounts of 2,2,4,4-tetramethyl-1,3-cyclobutanediol, while obtaining a clear polymer. However,

clear, miscible blends of any two polymers are difficult to obtain. The term "miscible" refers to blends that are a mixture on a molecular level wherein intimate polymer-polymer interaction is achieved. Miscible blends are clear, not translucent or opaque. In addition, differential scanning calorimetry testing detects only a single glass transition temperature (T_g) for miscible blends composed of two or more components. Conventional blends of two polymers are thus typically not clear, and show two glass transition temperatures. Clear blends of polyesters containing 2,2,4,4-tetramethyl-1,3-cyclobutanediol with bisphenol A polycarbonates have nonetheless been previously disclosed.

[0005] U.S. Pat. No. 6,005,059 discloses clear blends of polycarbonates and polyesters. The polycarbonates are comprised of dihydroxydiphenyl cycloalkanes, optionally with bisphenol A, and the polyesters are made from terephthalic acid, neopentyl glycol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol. The inventive blends are clear and exhibit a single glass transition temperature, indicating the existence of a single solid phase. Although the patent suggests that the polycarbonates may optionally contain bisphenol A, the comparative examples in which the polycarbonate was a bisphenol A homopolymer were opaque.

[0006] U.S. Pat. Nos. 6,011,124 and 6,037,424 disclose blends of polycarbonates with polyesters containing aromatic dicarboxylic acids, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and ethylene glycol. These blends were clear and exhibited a single glass transition temperature indicating the existence of a single solid phase.

[0007] U.S. Pat. No. 5,942,585 discloses blends of polycarbonates with polyesters containing aliphatic dicarboxylic acids, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and 1,4-cyclohexanedimethanol. These blends were clear and exhibited a single glass transition temperature indicating the existence of a single solid phase.

[0008] U.S. Pat. No. 6,043,322 discloses blends of polycarbonates with polyesters containing aromatic dicarboxylic acids, 2,2,4,4-tetramethyl-1,3-

cyclobutanediol, and 1,4-cyclohexanedimethanol. These blends were clear and exhibited a single glass transition temperature indicating the existence of a single solid phase. However the blends with the polycarbonate of pure bisphenol A were not miscible. Inclusion of a dihydroxydiphenyl cycloalkane as a second diol in the polycarbonate was required for miscibility.

[0009] U.S. Pat. Publ. Nos. 2007/0010650 and 2006/0287479 disclose polyesters prepared from terephthalic acid, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and 1,4-cyclohexanedimethanol. The addition of a second polymeric component including polycarbonates is disclosed in these applications. However the surprisingly clarity that can be obtained in blends of these polyesters with polycarbonates is not disclosed.

[0010] U.S. Pat. Appl. Publ. Nos. 2006/0270773 and 2006/0270806 disclose the use of a miscible polymer blend in the production of films useful in various display applications. Blends of polyesters prepared from terephthalic acid, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and 1,4-cyclohexanedimethanol with bisphenol A polycarbonate are disclosed. However, the preferred range of less than 40 mole percent 2,2,4,4-tetramethyl-1,3-cyclobutanediol in the polyester required for miscibility with polycarbonate is not specifically disclosed.

[0011] Thus, there remains a need in the art for polymer blends that are miscible and that retain the benefits of each of the polymers from which they are comprised.

SUMMARY OF THE INVENTION

[0012] In one aspect, the invention relates to molded articles made from miscible blends that include at least one polyester which comprises:

- (a) a dicarboxylic acid component comprising 70 to 100 mole percent of terephthalic acid (TPA) and/or isophthalic acid (IPA) residues; and
- (b) a glycol component comprising:
 - i) 5 to 40 mole percent of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) residues; and

- ii) 60 to 95 mole percent of 1,4-cyclohexanedimethanol (CHDM) residues,

wherein the total mole percent of the dicarboxylic acid component is 100 mole percent, and the total mole percent of the glycol component is 100 mole percent. The miscible blends of the invention further comprise a polycarbonate made from bisphenol A. The molded articles of the invention are clear, tough, and heat resistant, making them especially useful in engineering molding plastics and in packaging.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention may be understood more readily by reference to the following detailed description of certain embodiments of the invention and the working examples.

[0014] In one aspect, the invention relates to molded articles made from clear, miscible blends of an aliphatic-aromatic copolyester of terephthalic acid (TPA) and/or isophthalic acid (IPA), 2,2,4,4, tetramethyl-1,3 cyclobutanediol (TMCD), and 1,4 cyclohexanedimethanol (CHDM), blended with a bisphenol A polycarbonate. Conventional blends of two polymers are not clear and typically show two glass transition temperatures. The compatible blends of this invention, on the other hand, have excellent clarity indicating miscibility and exhibit one glass transition temperature and have excellent heat resistance.

[0015] According to the present invention, there are provided molded articles made from a clear polymer blend comprising:

[0016] (1) 5-95 wt. percent of a copolyester having repeat units from TPA and/or IPA, TMCD (trans or cis or mixtures thereof), and CHDM (trans or cis or mixtures thereof) wherein the CHDM content is from 60 to 95 mole percent of the total glycol component, and the TMCD content is from 5 to 40 mole percent; and

[0017] (2) 5-95 wt. percent of a polycarbonate of bisphenol A.

[0018] The blends of the present invention are about 5 to 95 weight percent polyester portion and about 5 to 95 weight percent polycarbonate portion, with the total weight percent of the polycarbonate portion and polyester portion preferably being equal to 100 weight percent. The preferred blend of the present invention is about 20 to 95 weight percent polyester and about 5 to 80 weight percent polycarbonate, or from about 40 to 90 weight percent polyester and about 10 to 60 weight percent polycarbonate, or from 50 to 80 weight percent polyester and about 20 to 50 weight percent polycarbonate.

[0019] Greater concentrations of the polycarbonate of the blend nearer 95 weight percent produce blends having greater impact strength, heat resistance, and dimensional stability, while blends nearer 95 weight percent polyester have better chemical resistance and melt processing. The most useful blends will be those clear blends having a combination of physical properties best suited for a particular end use, as will be determined on a case by case basis.

[0020] The term "polyester", as used herein, refers to any unit-type of polyester falling within the scope of the polyester portion of the present blend, including but not limited to copolyesters and terpolyesters. The polyester portion of the blends of the present invention comprises a dicarboxylic acid component of typically about 70 to 100 mole percent TPA and/or isophthalic acid (IPA) units, and 0 to about 20 mole percent modifying dicarboxylic acid units, and a glycol component of about 5 to 40 mole percent TMCD units, and from 60 mole percent to 95 mole percent CHDM (trans or cis or mixtures thereof), with minor amounts of modifying glycol units, wherein the total dicarboxylic acid units is equal to 100 mole percent, the total glycol units is equal to 100 mole percent, with a total polyester units equal to 200 mole percent.

[0021] Terephthalic acid (TPA) and isophthalic acid (IPA) have been found to be the preferred primary dicarboxylic acids for providing a polyester that when blended with bisphenol A polycarbonate is clear. A higher concentration of TPA in the polyester than IPA is preferred because TPA produces a

polyester that provides greater impact strength to the blend. Therefore, it is preferred that the dicarboxylic acid component of the polyester portion be 50 to 100 mole percent TPA and 0 to 50 mole percent IPA, more preferably 70 to 100 mole percent TPA and 0 to 30 mole percent IPA, with at least 90 mole percent, up to 100 mole percent terephthalic acid, being preferred.

[0022] In addition to TPA and IPA, the dicarboxylic acid component of the polyester can be substituted with up to 20 mole percent, but preferably less than 10 mole percent of other modifying dicarboxylic acids having 2 to 20 carbon atoms. Suitable examples of modifying aromatic dicarboxylic acids include 4,4'-biphenyldicarboxylic acid, 1,4-, 1,5-, 2,6-, 2,7-naphthalenedicarboxylic acid, 4,4'-oxybenzoic, trans-4,4'-stilbenedicarboxylic acid, or mixtures thereof. Suitable examples of modifying aliphatic dicarboxylic acids are those containing 2 to 12 carbon atoms, such as oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, and sebacic acids, or mixtures thereof.

[0023] It is important to note that the dicarboxylic acid component of the polyester portion of the present blend may be prepared from dicarboxylic acids, their corresponding esters, or mixtures thereof. Examples of esters of the dicarboxylic acids useful in the present invention include the dimethyl, dipropyl, diisopropyl, dibutyl, and diphenyl esters, and the like.

[0024] In one embodiment, terephthalic acid may be used as the starting material to prepare the polyesters of the blends of the invention. In another embodiment, dimethyl terephthalate may be used as the starting material. In yet another embodiment, mixtures of terephthalic acid and dimethyl terephthalate may be used as the starting material and/or as an intermediate material.

[0025] The aliphatic-aromatic copolyester portion of this invention thus comprises TPA and/or IPA units, 40 to 5 mole percent TMCD units (trans or cis or mixtures thereof), and 60 to 95 mole percent CHDM units (trans or cis or mixtures thereof). The preferred range of the compositions of the copolyester comprises 100 mole percent TPA units, 15 to 35 mole percent TMCD (trans

or cis or mixtures thereof), and 65 to 85 mole percent cyclohexanedimethanol units (trans or cis or mixtures thereof).

[0026] The glycol component of the polyester portion of the present blend is thus formed from 5 to 40 mole percent of TMCD units, or from 10 to 35 mole percent TMCD units, or from 15 to 25 mole percent TMCD units. The glycol component of the polyester portion of the present blend further comprises from 60 mole percent to 95 mole percent CHDM units, or from 65 to 90 mole percent CHDM units, or from 75 to 85 mole percent CHDM units.

[0027] The 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCD) can be cis, trans, or a mixture thereof, preferably 45-55 mole percent trans, where the total of cis and trans isomer content is equal to 100 mole percent, or alternatively, about a 50/50 trans/cis ratio.

[0028] In other aspects of the invention, the glycol component for the polyesters useful in the invention include but are not limited to at least one of the following combinations of ranges: 5 to 40 mole percent 2,2,4,4-tetramethyl-1,3-cyclobutanediol and 60 to 95 mole percent 1,4-cyclohexanedimethanol; 10 to 35 mole percent 2,2,4,4-tetramethyl-1,3-cyclobutanediol and 65 to 90 mole percent 1,4-cyclohexanedimethanol; or 15 to 30 mole percent 2,2,4,4-tetramethyl-1,3-cyclobutanediol and 70 to 85 mole percent 1,4-cyclohexanedimethanol.

[0029] The 1,4-cyclohexanedimethanol may be cis, trans, or a mixture thereof, for example, a cis/trans ratio of 60:40 to 40:60. In another embodiment, the trans-1,4-cyclohexanedimethanol can be present in an amount of 60 to 80 mole percent.

[0030] Modifying glycols useful in the polyesters useful in the invention refer to diols other than 2,2,4,4-tetramethyl-1,3-cyclobutanediol and 1,4-cyclohexanedimethanol and can contain 2 to 16 carbon atoms. Examples of suitable modifying glycols include, but are not limited to, ethylene glycol, 1,2-propanediol, 1,3-propanediol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, p-xylene glycol, or mixtures thereof. In one embodiment, the modifying glycol is ethylene glycol. In another embodiment,

the modifying glycols include, but are not limited to, 1,3-propanediol and 1,4-butanediol. In another embodiment, ethylene glycol is excluded as a modifying diol. In another embodiment, 1,3-propanediol and 1,4-butanediol are excluded as modifying diols. In another embodiment, 2, 2-dimethyl-1,3-propanediol is excluded as a modifying diol.

[0031] The glycol component can also be modified with 0 to about 10 mole percent polyethylene glycol or polytetramethylene glycol to enhance elastomeric behavior.

[0032] The polyesters and/or the polycarbonates useful in the polyesters compositions of the invention can comprise from 0 to 10 mole percent, for example, from 0.01 to 5 mole percent, from 0.01 to 1 mole percent, from 0.05 to 5 mole percent, from 0.05 to 1 mole percent, or from 0.1 to 0.7 mole percent, based on the total mole percent ages of either the diol or diacid residues, respectively, of one or more residues of a branching monomer, also referred to herein as a branching agent, having 3 or more carboxyl substituents, hydroxyl substituents, or a combination thereof. In certain embodiments, the branching monomer or agent may be added prior to and/or during and/or after the polymerization of the polyester. The polyester(s) useful in the invention can thus be linear or branched. The polycarbonate can also be linear or branched. In certain embodiments, the branching monomer or agent may be added prior to and/or during and/or after the polymerization of the polycarbonate.

[0033] Examples of branching monomers include, but are not limited to, multifunctional acids or multifunctional alcohols such as trimellitic acid, trimellitic anhydride, pyromellitic dianhydride, trimethylolpropane, glycerol, pentaerythritol, citric acid, tartaric acid, 3-hydroxyglutaric acid and the like. In one embodiment, the branching monomer residues can comprise 0.1 to 0.7 mole percent of one or more residues chosen from at least one of the following: trimellitic anhydride, pyromellitic dianhydride, glycerol, sorbitol, 1,2,6-hexanetriol, pentaerythritol, trimethylolethane, and/or trimesic acid. The branching monomer may be added to the polyester reaction mixture or

blended with the polyester in the form of a concentrate as described, for example, in U.S. Patent Nos. 5,654,347 and 5,696,176, whose disclosure regarding branching monomers is incorporated herein by reference.

[0034] The polyesters of the invention can comprise at least one chain extender.

Suitable chain extenders include, but are not limited to, multifunctional (including, but not limited to, bifunctional) isocyanates, multifunctional epoxides, including for example, epoxylated novolacs, and phenoxy resins. In certain embodiments, chain extenders may be added at the end of the polymerization process or after the polymerization process. If added after the polymerization process, chain extenders can be incorporated by compounding or by addition during conversion processes such as injection molding or extrusion. The amount of chain extender used can vary depending on the specific monomer composition used and the physical properties desired but is generally about 0.1 percent by weight to about 10 percent by weight, such as about 0.1 to about 5 percent by weight, based on the total weight of the polyester.

[0035] Thermal stabilizers are compounds that stabilize polyesters during polyester manufacture and/or post polymerization, including but not limited to phosphorous compounds including but not limited to phosphoric acid, phosphorous acid, phosphonic acid, phosphinic acid, phosphonous acid, and various esters and salts thereof. These can be present in the polyester compositions useful in the invention. The esters can be alkyl, branched alkyl, substituted alkyl, difunctional alkyl, alkyl ethers, aryl, and substituted aryl. In one embodiment, the number of ester groups present in the particular phosphorous compound can vary from zero up to the maximum allowable based on the number of hydroxyl groups present on the thermal stabilizer used. The term "thermal stabilizer" is intended to include the reaction product(s) thereof. The term "reaction product" as used in connection with the thermal stabilizers of the invention refers to any product of a polycondensation or esterification reaction between the thermal stabilizer and any of the

monomers used in making the polyester as well as the product of a polycondensation or esterification reaction between the catalyst and any other type of additive.

[0036] In some embodiments, use of the polyester compositions useful in the invention minimizes and/or eliminates the drying step prior to melt processing and/or thermoforming.

[0037] The polyester portion of the polyester compositions useful in the invention can be made by processes known from the literature such as, for example, by processes in homogenous solution, by transesterification processes in the melt, and by two phase interfacial processes. Suitable methods include, but are not limited to, the steps of reacting one or more dicarboxylic acids with one or more glycols at a temperature of 100°C to 315°C at a pressure of 0.1 to 760 mm Hg for a time sufficient to form a polyester. See U.S. Patent No. 3,772,405 for methods of producing polyesters, the disclosure regarding such methods is hereby incorporated herein by reference.

[0038] In another aspect, the invention relates to molded articles comprising a polyester produced by a process comprising:

(I) heating a mixture comprising the monomers useful in any of the polyesters useful in the invention in the presence of a catalyst at a temperature of 150 to 240°C for a time sufficient to produce an initial polyester;

(II) heating the initial polyester of step (I) at a temperature of 240 to 320°C for 1 to 4 hours; and

(III) removing any unreacted glycols.

[0039] Suitable catalysts for use in this process include, but are not limited to, organo-zinc or tin compounds. The use of this type of catalyst is well known in the art. Examples of catalysts useful in the present invention include, but are not limited to, zinc acetate, butyltin tris-2-ethylhexanoate, dibutyltin diacetate, and dibutyltin oxide. Other catalysts may include, but are not limited to, those based on titanium, zinc, manganese, lithium, germanium,

and cobalt. Catalyst amounts can range from 10 ppm to 20,000 ppm or 10 to 10,000 ppm, or 10 to 5000 ppm or 10 to 1000 ppm or 10 to 500 ppm, or 10 to 300 ppm or 10 to 250 based on the catalyst metal and based on the weight of the final polymer. The process can be carried out in either a batch or continuous process.

[0040] Typically, step (I) can be carried out until 50 percent by weight or more of the 2,2,4,4-tetramethyl-1,3-cyclobutanediol has been reacted. Step (I) may be carried out under pressure, ranging from atmospheric pressure to 100 psig. The term "reaction product" as used in connection with any of the catalysts useful in the invention refers to any product of a polycondensation or esterification reaction with the catalyst and any of the monomers used in making the polyester as well as the product of a polycondensation or esterification reaction between the catalyst and any other type of additive.

[0041] Typically, Step (II) and Step (III) can be conducted at the same time. These steps can be carried out by methods known in the art such as by placing the reaction mixture under a pressure ranging, from 0.002 psig to below atmospheric pressure, or by blowing hot nitrogen gas over the mixture.

[0042] The term "polycarbonate" is herein defined as the condensation product of a carbonate source and a diol source, having a carbonate component containing 100 mole percent carbonate units and a diol component containing 100 mole percent diol units, for a total of 200 mole percent monomeric units. The term "diol" as used herein, includes both aliphatic and aromatic compounds having two hydroxyl groups.

[0043] The polycarbonate portion of the blend of the present invention is based upon the polycarbonate of 4,4'-isopropylidenediphenol, commonly known as bisphenol A. Suitable examples of commercially available bisphenol A polycarbonate include LEXAN, from General Electric, and MAKROLON, from Bayer, Inc.

[0044] The polycarbonate portion of the present blend has a diol component containing about 90 to 100 mole percent bisphenol A units, wherein the total mole percent of diol units is 100 mole percent. Alternatively,

the amount of bisphenol A may be at least 95 mole percent, or at least 98 mole percent, bisphenol A, again, wherein the total mole percent of diol units is 100 mole percent. 0 to about 10 mole percent of the diol component of the polycarbonate portion can be substituted with units of other modifying aliphatic or aromatic diols, besides bisphenol A, having from 2 to 16 carbons. It is preferable to have at least 95 mole percent of diol units in the polycarbonate being bisphenol A, more preferably 100 mole percent. Suitable examples of modifying aromatic diols include those disclosed in U.S. Pat. Nos. 3,030,335 and 3,317,466.

[0045] The inherent viscosity of the polycarbonate portion of the blends according to the present invention is preferably at least about 0.3 dL/g, more preferably at least 0.5 dL/g, determined at 25°C in 60/40 wt/wt phenol/tetrachloroethane.

[0046] The polycarbonate of this invention thus consists of the polycarbonate of 4,4'-isopropylidenediphenol (bisphenol A). The polycarbonate portion of the blend is prepared in the melt, in solution, or by interfacial polymerization techniques well known in the art. Commercially available polycarbonates are normally made by reacting bisphenol A with phosgene, dibutyl carbonate, diphenyl carbonate, etc. Small amounts of other modifying glycols or aromatic diols may also be included in the polycarbonate.

[0047] The polycarbonates may be prepared according to known procedures by reacting the dihydroxyaromatic compound with a carbonate precursor such as phosgene, a haloformate or a carbonate ester, a molecular weight regulator, an acid acceptor and a catalyst. Methods for preparing polycarbonates are known in the art and are described, for example, in U.S. Patent 4,452,933, which is hereby incorporated by reference herein.

[0048] Examples of suitable carbonate precursors include carbonyl bromide, carbonyl chloride, and mixtures thereof; diphenyl carbonate; a di(halophenyl)-carbonate, e.g., di(trichlorophenyl) carbonate, di(tribromophenyl) carbonate, and the like; di(alkylphenyl)carbonate, e.g.,

di(tolyl)carbonate; di(naphthyl)carbonate; di(chloronaphthyl)carbonate, or mixtures thereof; and bis-haloformates of dihydric phenols.

[0049] Examples of suitable molecular weight regulators include phenol, cyclohexanol, methanol, alkylated phenols, such as octylphenol, para-tertiary-butyl-phenol, and the like. The preferred molecular weight regulator is phenol or an alkylated phenol.

[0050] The acid acceptor may be either an organic or an inorganic acid acceptor. A suitable organic acid acceptor is a tertiary amine and includes such materials as pyridine, triethylamine, dimethylaniline, tributylamine, and the like. The inorganic acid acceptor can be either a hydroxide, a carbonate, a bicarbonate, or a phosphate of an alkali or alkaline earth metal.

[0051] The catalysts that can be used are those that typically aid the polymerization of the monomer with phosgene. Suitable catalysts include tertiary amines such as triethylamine, tripropylamine, N,N-dimethylaniline, quaternary ammonium compounds such as, for example, tetraethylammonium bromide, cetyl triethyl ammonium bromide, tetra-n-heptylammonium iodide, tetra-n-propyl ammonium bromide, tetramethyl ammonium chloride, tetramethyl ammonium hydroxide, tetra-n-butyl ammonium iodide, benzyltrimethyl ammonium chloride and quaternary phosphonium compounds such as, for example, n-butyltriphenyl phosphonium bromide and methyltriphenyl phosphonium bromide.

[0052] The blend compositions of the present invention are clear. The term "clear" is defined herein as an absence of cloudiness, haziness, and muddiness, when inspected visually. The blends of the present invention also exhibit a single glass transition temperature (T_g), as determined by differential scanning calorimetry (DSC).

[0053] The polyester/polycarbonate blends of the present invention can be made by methods which include the steps of blending the polycarbonate and polyester portions of the present invention at a temperature of about 25°C to 350°C for a time sufficient to form a clear blend composition. Suitable conventional blending techniques include the melt method and the solution-

prepared method. Other suitable blending techniques include dry blending and/or extrusion.

[0054] The melt blending method includes blending the polymers at a temperature sufficient to melt the polycarbonate and polyester portions, and thereafter cooling the blend to a temperature sufficient to produce a clear blend. The term "melt" as used herein includes, but is not limited to, merely softening the polymers. For melt mixing methods generally known in the polymers art, see *Mixing and Compounding of Polymers* (I. Manas-Zloczower & Z. Tadmor eds., Carl Hanser Verlag publisher, N.Y. 1994).

[0055] The solution-prepared method includes dissolving the appropriate weight/weight ratio of polyester and polycarbonate in a suitable organic solvent such as methylene chloride or a 70/30 mixture of methylene chloride and hexafluoroisopropanol, mixing the solution, and separating the blend composition from solution by precipitation of the blend or by evaporation of the solvent. Solution-prepared blending methods are generally known in the polymers art.

[0056] The melt blending method is the preferred method for producing the blend compositions of the present invention. The melt method is more economical and safer than the solution-prepared method which requires the use of volatile solvents. The melt method is also much more effective in providing clear blends. Any of the clear blends of the present invention that can be prepared by solution blending can also be prepared by the melt method. However, some of the blends of the present invention can be prepared by the melt method, but not by the solution method. Any blending process which provides clear blends of the present invention is suitable. One of ordinary skill in the art will be able to determine appropriate blending methods for producing the clear blends of the present invention.

[0057] The compositions of this invention may thus be prepared by any conventional mixing methods. For example, a preferred method comprises mixing the aliphatic-aromatic polyester and polycarbonate in powder or

granular form in an extruder and extruding the mixture into strands, chopping the strands into pellets and molding the pellets into the desired article.

[0058] It should, of course be clear that other additives may be included in the present compositions. These additives include plasticizers, pigments flame retardant additives, reinforcing agents such as glass fibers, stabilizers, processing aids, impact modifiers, etc.

[0059] The term "container" as used herein is understood to mean a receptacle in which material is held or stored. "Containers" include but are not limited to bottles, bags, vials, tubes and jars. Applications in the industry for these types of containers include but are not limited to food, beverage, cosmetics and personal care applications.

[0060] The term "bottle" as used herein is understood to mean a receptacle containing plastic which is capable of storing or holding liquid.

[0061] The term "molded article" is intended to include any article made in a mold that takes on the shape of the mold in which it is formed, including without limitation a bottle, tray, or bottle preform, but is not intended to include films which are simply passed through a dye, for example.

[0062] In addition, the polyester compositions and the polymer blend compositions useful in the containers of this invention may also contain from 0.01 to 25 percent by weight of the overall composition common additives such as colorants, dyes, mold release agents, flame retardants, plasticizers, nucleating agents, stabilizers, including but not limited to, UV stabilizers, thermal stabilizers and/or reaction products thereof, fillers, and impact modifiers. Examples of typical commercially available impact modifiers well known in the art and useful in this invention include, but are not limited to, ethylene/propylene terpolymers, functionalized polyolefins such as those containing methyl acrylate and/or glycidyl methacrylate, styrene-based block copolymeric impact modifiers, and various acrylic core/shell type impact modifiers. Residues of such additives are also contemplated as part of the polyester composition

[0063] Reinforcing materials may be useful in the compositions of this invention. The reinforcing materials may include, but are not limited to, carbon filaments, silicates, mica, clay, talc, titanium dioxide, Wollastonite, glass flakes, glass beads and fibers, and polymeric fibers and combinations thereof. In one embodiment, the reinforcing materials include glass, such as, fibrous glass filaments, mixtures of glass and talc, glass and mica, and glass and polymeric fibers.

[0064] The invention further relates to containers described herein. The methods of forming the polymer blends into containers are well known in the art.

[0065] The invention further relates to bottles described herein. The methods of forming the polymer blends into bottles are well known in the art. Examples of bottles include but are not limited to bottles such as baby bottles; water bottles; juice bottles; large commercial water bottles having a weight from 200 to 800 grams; beverage bottles which include but are not limited to two liter bottles, 20 ounce bottles, 16.9 ounce bottles; medical bottles; personal care bottles, carbonated soft drink bottles; hot fill bottles; water bottles; alcoholic beverage bottles such as beer bottles and wine bottles; and bottles comprising at least one handle. These bottles include but are not limited to injection blow molded bottles, injection stretch blow molded bottles, extrusion blow molded bottles, and extrusion stretch blow molded bottles. Methods of making bottles include but are not limited to extrusion blow molding, extrusion stretch blow molding, injection blow molding, and injection stretch blow molding. In each case, the invention further relates to the preforms (or parisons) used to make each of said bottles.

[0066] These bottles include, but are not limited to, injection blow molded bottles, injection stretch blow molded bottles, extrusion blow molded bottles, and extrusion stretch blow molded bottles. Methods of making bottles include but are not limited to extrusion blow molding, extrusion stretch blow molding, thermoforming, injection blow molding, and injection stretch blow molding.

[0067] Other examples of containers include, but are not limited to, containers for cosmetics and personal care applications including bottles, jars, vials and tubes; sterilization containers; buffet steam pans; food pans or trays; frozen food trays; microwaveable food trays; hot fill containers; food storage containers; for example, boxes; tumblers, pitchers, cups, bowls, including but not limited to those used in restaurant smallware; beverage containers; retort food containers; centrifuge bowls; vacuum cleaner canisters, and collection and treatment canisters.

[0068] For the purposes of this invention, the term "wt" means "weight".

[0069] The following examples further illustrate how the molded articles of the invention can be made and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope thereof. Unless indicated otherwise, parts are parts by weight, temperature is in degrees C or is at room temperature, and pressure is at or near atmospheric.

EXAMPLES

Measurement Methods

[0070] The inherent viscosity of the polyesters and polycarbonates was determined in 60/40 (wt/wt) phenol/tetrachloroethane at a concentration of 0.5 g/100ml at 25 °C. The composition of the polyesters was determined by proton nuclear magnetic resonance spectroscopy (NMR). The glass transition temperatures were determined using a TA Instruments Differential Scanning Calorimeter (DSC) at a scan rate of 20°C/min. The polycarbonate used in all of the examples was Makrolon™ 2608 which is manufactured by Bayer Materials Science Inc. It had a measured inherent viscosity of 0.522.

[0071] The following abbreviations apply throughout the working examples and figures:

TPA	Terephthalic acid
DMT	Dimethyl terephthalate
TMCD	2,2,4,4-tetramethyl-1,3-cyclobutanediol
CHDM	1,4-cyclohexanedimethanol
IV	Inherent viscosity

Example 1.

[0072] The aliphatic-aromatic copolyester used contained terephthalic acid, 24.8 mole percent 2,2,4,4, tetramethyl-1,3 cyclobutanediol (54.6 mole percent cis isomer), and 75.2 mole percent cyclohexanedimethanol. The inherent viscosity was measured to be 0.72.

[0073] The aliphatic-aromatic copolyester was dried at 90°C and the polycarbonate was dried at 100 °C. Blends were prepared in an 18mm Leistritz twin screw extruder. The polymers were premixed by tumble blending and fed into the extruder and the extruded strand was pelletized. The pellets were injection molded into parts on a Toyo 90 injection molding

machine. The extruder was run at 350 rpms at a feed rate to give a machine torque between 80-100 percent. Processing temperatures used were in the range of 260°C to 280°C. The compositions and properties of the blends are shown in Table 1.

[0074] Heat deflection temperature, at 264 psi, was determined according to ASTM D648. Flexural modulus and flexural strength were determined according to ASTM D790. Tensile properties were determined according to ASTM D638.

Table 1.		UNITS									
% Aliphatic-aromatic polyester		100	85	70	50	30	15	0			
% Polycarbonate		0	15	30	50	70	85	100			
Heat Deflection Temperature 264 Psi		83	90	93	106	115	121	127			
Tensile Strength		50	52	53	55	60	67	71			
Tensile Break Elongation		147	130	122	107	105	115	128			
Flexural Modulus		1524	1637	1727	1845	2010	2177	2259			
Flexural Strength		64	68	73	80	89	94	97			
DSC Tg (second cycle)		111	116	120	128	136	143	149			
Visual Clarity		clear	clear	clear	clear	clear	clear	clear			

Example 2.

[0075] The aliphatic-aromatic copolyester used contained terephthalic acid, 33.9 mole percent 2,2,4,4, tetramethyl-1,3 cyclobutanediol and, 66.1mole percent cyclohexanedimethanol. The inherent viscosity was measured to be 0.66.

[0076] The aliphatic-aromatic copolyester was dried at 90°C and the polycarbonate was dried at 100°C. Blends were prepared in a 30mm Werner-Pfleider twin screw extruder. The polyesters were premixed by tumble blending and fed into the extruder and the extruded strand was pelletized. The pellets were injection molded into parts on a Toyo 90 injection molding machine. The extruder was run at 350 rpms at a feed rate to give a machine torque between 80-100 percent. Processing temperatures used were in the range of 260°C to 280 °C. The compositions and properties of the blends are shown in Table 2.

Table 2.	UNITS						
% Aliphatic-aromatic polyester	%	100	85	70	60	50	25
% Polycarbonate	%	0	15	30	40	50	75
Heat Deflection Temperature 264 Psi	(deg C)	88	95	99	101	106	114
Tensile Strength	MPa	48	48	51	53	54	59
Tensile Break Elongation	%	117	96	81	74	73	79
Flexural Modulus	MPa	1689	1790	1929	2028	2080	2266
Flexural Strength	MPa	67	72	77	82	83	90
DSC Tg (second cycle)	°C	118	123	125	128	131	138
Visual Clarity		clear	clear	clear	clear	clear	clear

Comparative Example 1.

[0077] The aliphatic-aromatic copolyester used contained terephthalic acid, 46.6 mole percent 2,2,4,4, tetramethyl-1,3 cyclobutanediol (54.1 mole percent cis isomer), 53.7 mole percent cyclohexanedimethanol. The inherent viscosity was measured to be 0.59.

[0078] The aliphatic-aromatic copolyester was dried at 70°C and the polycarbonate was dried at 100 °C. Blends were prepared in a 18mm Leistritz twin screw extruder. The polymers were premixed by tumble blending and fed into the extruder and the extruded strand was pelletized. The pellets were injection molded into parts on a Toyo 90 injection molding machine. The extruder was run at 350 rpms at a feed rate to give a machine torque between 80-100 percent. Processing temperatures used were in the range of 260 °C to 280 °C. The compositions and properties of the blends are shown in Table 3.

[0079] For the blends containing 25 wt. percent of one of the polymers there appeared to be a second Tg in the DSC scan due to the minor component. However, the transition was too weak to accurately assign a Tg value.

Table 3.	UNITS					
% Aliphatic-aromatic polyester	%	100	75	50	25	0
% Polycarbonate	%	0	25	50	75	100
Heat Deflection Temperature 264 Psi	(deg C)	103	107	114	122	127
Tensile Strength	MPa	48	53	55	60	67
Tensile Break Elongation	%	100	99	92	101	105
Flexural Modulus	MPa	1499	1725	1861	2052	2245
Flexural Strength	MPa	72	78	83	91	97
DSC Tg (Second Cycle)	°C	128	130	131	weak	146
			weak	144	146	
Visual Clarity		clear	hazy	hazy	hazy	clear

Counter Example 2.

[0080] The aliphatic-aromatic copolyester used contained terephthalic acid, 95.7 mole percent 2,2,4,4, tetramethyl-1,3 cyclobutanediol, and 4.3 percent ethylene glycol. Its inherent viscosity was 0.457.

[0081] The aliphatic-aromatic copolyester was dried at 120°C and the polycarbonate was dried at 100 °C. Blends were prepared in an 18mm Leistritz twin screw extruder. The polymers were premixed by tumble blending and fed into the extruder and the extruded strand was pelletized. The pellets were injection molded into parts on a Toyo 90 injection molding machine. The extruder was run at 350 rpms at a feed rate to give a machine torque between 80-100 percent. Processing temperatures used were in the range of 270 °C to 290 °C. The composition and properties of the blend are shown in Table 4.

[0082] There appeared to be a second Tg in the DSC scan at higher temperatures. However the transition was too broad to accurately assign a Tg value.

Table 4.	UNITS	
% Aliphatic-aromatic polyester	%	50
% Polycarbonate	%	50
Heat Deflection Temperature 264 Psi	(deg C)	127
Tensile Strength	MPa	61
Tensile Break Elongation	%	10
Flexural Modulus	MPa	2106
Flexural Strength	MPa	92
DSC Tg (second cycle)	°C	148
		broad
Visual Clarity		hazy

[0083] The invention has been described in detail with reference to the embodiments disclosed herein, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

CLAIMS

We claim:

1. A molded article made from a miscible blend comprising:
a polyester which comprises: from 70 to 100 mole percent of terephthalic acid and/or isophthalic acid residues; 5 to 40 mole percent of 2,2,4,4-tetramethyl-1,3-cyclobutanediol residues; and 60 to 95 mole percent of 1,4-cyclohexanedimethanol residues, wherein the total mole percent of dicarboxylic acids in the polyester is 100 mole percent, and the total mole percent of diols in the polyester is 100 mole percent; and
a polycarbonate comprised of at least 90 mole percent bisphenol A, wherein the total mole percent of diols in the polycarbonate is 100 mole percent.
2. The molded article of claim 1, wherein the polyester comprises at least 70 mole percent terephthalic acid.
3. The molded article of claim 1, wherein the polyester comprises at least 90 mole percent terephthalic acid.
4. The molded article of claim 1, wherein the polyester is present in an amount from 5 wt. % to 95 wt. %, and the polycarbonate is present in an amount from 5 wt.% to 95 wt.%, with respect to the total weight of the blend.
5. The molded article of claim 1, wherein the polyester is present in an amount from 50 wt. % to 80 wt. %, and the polycarbonate is present in an amount from 20 wt.% to 50 wt.%, with respect to the total weight of the blend.
6. The molded article of claim 1, wherein the 2,2,4,4-tetramethyl-1,3-cyclobutanediol residues are present in the polyester in an amount from 15 to 35 mole percent, and the cyclohexanedimethanol residues are present in the polyester in an amount from 65 to 85 mole percent.

7. The molded article of claim 1, wherein the polyester consists essentially of terephthalic acid residues, 2,2,4,4-tetramethyl-1,3-cyclobutanediol residues, and cyclohexanedimethanol residues.
8. The molded article of claim 1, wherein the polycarbonate comprises at least 95 mole percent bisphenol A.
9. The molded article of claim 1, wherein the polycarbonate comprises at least 98 mole percent bisphenol A.
10. The molded article of claim 1, wherein the inherent viscosity of the polycarbonate is at least 0.5 dL/g, determined at 25°C in 60/40 wt/wt phenol/tetrachloroethane.
11. The molded article of claim 1, wherein the inherent viscosity of the polyester is at least 0.5 dL/g, determined at 25°C in 60/40 wt/wt phenol/tetrachloroethane.
12. The molded article of claim 1, wherein the miscible blend is clear.
13. The molded article of claim 1, wherein the miscible blend exhibits a single glass transition temperature (T_g), as determined by differential scanning calorimetry (DSC).
14. The molded article of claim 1, wherein the molded article is in the form of a bottle, tray, or bottle preform.
15. The molded article of claim 1, wherein the molded article is in the form of a bottle, a jar, a vial, a tube, a pan, a tray, a hot fill container, a food

storage container, a tumbler, a pitcher, a cup, a bowl, or a vacuum cleaner canister.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/035704

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L67/02 C08L69/00

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)

C08L

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)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 043 322 A (SCOTT CHRISTOPHER EDWARD [US] ET AL) 28 March 2000 (2000-03-28) example 2	1-5,7-11
Y	example 2 claims 23,24	6,12-15
X	WO 2006/137961 A (EASTMAN CHEM CO [US]) 28 December 2006 (2006-12-28) paragraph [0187] claims 1,13,21-26	1-3,6,7, 11,14,15
Y	claims 1,13,26	6,12-15
A	US 6 011 124 A (SCOTT CHRISTOPHER EDWARD [US] ET AL) 4 January 2000 (2000-01-04) column 2, line 3 - line 9 example 1	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

18 November 2009

Date of mailing of the international search report

25/11/2009

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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