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Palmer et al.(10) **Pub. No.: US 2010/0029837 A1**(43) **Pub. Date: Feb. 4, 2010**(54) **COPOLYETHERESTER COMPOSITIONS
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30, 2008.**Publication Classification**(51) **Int. Cl.****C08L 67/02** (2006.01)**C08L 67/00** (2006.01)(52) **U.S. Cl. 524/539; 525/419; 525/447**

(57)

ABSTRACT

Copolyetherester compositions comprising a melt-mixed blend of one or more copolyetherester(s) comprising a multiplicity of recurring long chain ester units and short chain ester units joined head-to-tail through ester linkages, and (b) about 0.25 to about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups; wherein all weight percentages are based on the total weight of the copolyetherester composition. Molded or extruded thermoplastic articles formed from the copolyetherester compositions, wherein 2 mm test bars prepared from said copolyetherester composition, and exposed at a test temperature of 150° C. for a test period of about 120 hours, in an atmosphere of air, and tested according to according to ISO 527-2/5A method have, on average, a retention of tensile strain at break of at least 50 percent as compared with an unexposed control having identical composition and shape.

COPOLYETHERESTER COMPOSITIONS AND ARTICLES MADE FROM THESE

REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority under 35 U.S.C. 119(e) to U.S. Provisional Application No. 61/137,345, filed Jul. 30, 2008 and currently pending.

FIELD OF INVENTION

[0002] The present invention relates to copolyetherester compositions having improved high temperature aging properties, and articles made from them.

BACKGROUND OF INVENTION

[0003] It is desirable to have high temperature resistant structures made of thermoplastic materials in applications such as components for motorized vehicles and electrical/electronic devices. High temperatures may be routinely reached in the under-hood areas of vehicles and inside laptops, cell phones, etc. Such high temperature resistant structures have reduced heat aging, a phenomenon that occurs to plastic parts when exposed to high temperatures for prolonged periods and is a decrease in the mechanical properties of the constituent polymers because of thermo-oxidation.

[0004] To lessen heat aging, the conventional practice has been to add heat stabilizers, also referred to as antioxidants, to thermoplastic polymer compositions. Such heat stabilizers include, for example, hindered phenol antioxidants, amine antioxidants and phosphorus-based antioxidants.

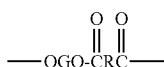
[0005] EP 1041109 discloses a polyamide composition comprising a polyamide resin, a polyhydric alcohol having a melting point of 150 to 280° C., that has good fluidity and mechanical strength and is useful in injection welding techniques. U.S. Pat. No. 4,205,158 discloses the formation of a copolyetherester including a polyhydric alcohol branching agent.

[0006] Despite existing technologies, copolyetherester compositions do not perform well when exposed to high temperatures. There remains a need for lower-cost, more effective heat resistant copolyetherester elastomer compositions for making molded or extruded thermoplastic articles exposed to high temperatures long-term, such as achieved under vehicle hoods and in electrical/electronics devices.

SUMMARY OF INVENTION

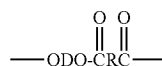
[0007] Described herein are copolyetherester compositions comprising a melt-mixed blend of

[0008] (a) one or more copolyetherester(s) comprising a multiplicity of recurring long chain ester units and short chain ester units, joined head-to-tail through ester linkages, said long chain ester units being represented by formula (I):



(I)

and said short chain ester units being represented by formula (II)



(II)

where G is a divalent radical remaining after the removal of terminal hydroxy groups from a poly(alkylene oxide) glycol that has a number average molecular weight of about 400 to about 6000;

[0009] R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid that has a molecular weight of less than about 300; and

[0010] D is a divalent radical remaining after removal of hydroxyl groups from a diol that has a molecular weight of less than about 250; wherein said copolyetherester(s), preferably contain from about 15 to about 99 weight percent short-chain ester units and about 1 to about 85 weight percent long-chain ester units; and

[0011] (b) about 0.25 to about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups; wherein all weight percentages are based on the total weight of the copolyetherester composition.

[0012] Also described herein are thermoplastic articles comprising a melt-mixed blend of the copolyetherester composition(s) described herein, wherein 2 mm test bars

[0013] made of the copolyetherester composition,

[0014] exposed in an atmosphere of air and at a temperature of 150° C. for a test period of about 120 hours, and

[0015] tested according to according to ISO 527-2/5A method

have, on average, a retention of tensile strain at break of at least 50 percent as compared with that of an unexposed control having identical composition and shape, whereby the article has high heat stability.

DETAILED DESCRIPTION OF INVENTION

Definitions

[0016] The following definitions should be used to interpret the compositions and articles described in the specification and defined by the claims.

[0017] As used herein, the term “high-temperature” refers to a temperature at or about 150° C.

[0018] As used herein, the term “melt-mixed blend” is a known term of art and refers to a result whereby all polymeric components of the compositions described herein are well-dispersed within each other and all of the non-polymeric ingredients are homogeneously dispersed in the polymer matrix.

[0019] As used herein, the term “high heat stability”, as applied to a copolyetherester composition described herein or to an article made from the composition, refers to the retention of strain at break of 2 mm molded test bars that comprise the composition and that have been exposed to air oven aging (AOA) conditions in an oven at a test temperature of 150° C. for a test period of 120 hours, in an atmosphere of air, and then tested according to ISO 527-2/5A method.

[0020] As used herein and in relation to a stated measurement of temperature or duration, the term “about” refers to an approximation of the stated measurement such that one of

skill in the art would recognize that the approximation was close enough to the stated measurement as to be equivalent to the stated measurement.

[0021] As used herein, “high heat stability” means that the molded 2 mm test bars on average, meet or exceed a retention of tensile strain at break of 50% when exposed to the AOA conditions disclosed above. Compositions described herein which exhibit a higher retention of strain at break for a given exposure temperature and time period have better heat stability.

[0022] As used herein, the term “long-term” refers to an aging period equal to or about 120 hours.

[0023] As used herein, the term “aging”, “aged”, “heat aging” refers to a set of conditions for testing the retention of tensile strain at break and specifically refers to exposing and testing 2 mm test bars comprising the compositions described herein. Exposure is at a temperature of 150° C. for about 120 hours in an atmosphere of air. The testing method is ISO 527-2/5A.

[0024] As used herein, the term “retention of tensile strain at break” corresponds to the percentage of the strain at break after heat aging, relative to the tensile strain at break value of unexposed control bars, which is considered to be 100%.

[0025] As used herein, the term “(meth)acrylate” also includes acrylate esters and methacrylate esters.

[0026] As used herein, the terms “blend” and “mixture” are known terms of art and refer to a combining of entities to produce a result that contains the blended/mixed entities.

General

[0027] The copolyetheresters useful in the compositions described herein are one or more copolyetherester(s) that have a multiplicity of recurring long-chain ester units and short-chain ester units joined head-to-tail through ester linkages, said long-chain ester units being represented by formula (I):



and said short-chain ester units being represented by formula (II):



where

[0028] G is a divalent radical remaining after the removal of terminal hydroxyl groups from a poly(alkylene oxide)glycol, the poly(alkylene oxide)glycol having a number average molecular weight of between about 400 and about 6000, or preferably between about 400 and about 3000;

[0029] R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid, the dicarboxylic acid having a molecular weight of less than about 300;

[0030] D is a divalent radical remaining after removal of hydroxyl groups from a diol, the diol having a molecular weight less than about 250;

wherein said copolyetherester(s) preferably contain from about 15 to about 99 weight percent short-chain ester units and about 1 to about 85 weight percent long-chain ester units, or

wherein the copolyetherester(s) more preferably contain from about 25 to about 90 weight percent short-chain ester units and about 10 to about 75 weight percent long-chain ester units.

[0031] As used herein, the term “long-chain ester units” as applied to units in a polymer chain refers to the product of a reaction of a long-chain glycol with a dicarboxylic acid. Suitable long-chain glycols are poly(alkylene oxide)glycols having terminal (or as nearly terminal as possible) hydroxy groups and having a number average molecular weight of from about 400 to about 6000, and preferably from about 600 to about 3000. Preferred poly(alkylene oxide)glycols include poly(tetramethylene oxide)glycol, poly(trimethylene oxide)glycol, poly(propylene oxide)glycol, poly(ethylene oxide)glycol, copolymer glycols of these alkylene oxides, and block copolymers such as ethylene oxide-capped poly(propylene oxide)glycol. Mixtures of two or more of these glycols can be used.

[0032] As used herein, the term “short-chain ester units” as applied to units in a polymer chain of the copolyetheresters described herein refers to low molecular weight compounds, or polymer chain units, that have molecular weights less than about 550 and which are made by reacting a low molecular weight diol or a mixture of diols (molecular weight below about 250) with a dicarboxylic acid to form ester units represented by Formula (II) above.

[0033] The low molecular weight diols that react to form short-chain ester units suitable for use for preparing copolyetheresters are acyclic, alicyclic and aromatic dihydroxy compounds. Preferred compounds are diols with about 2-15 carbon atoms such as ethylene, propylene, isobutylene, tetramethylene, 1,4-pentamethylene, 2,2-dimethyltrimethylene, hexamethylene and decamethylene glycols, dihydroxycyclohexane, cyclohexane dimethanol, resorcinol, hydroquinone, 1,5-dihydroxynaphthalene, etc. Especially preferred diols are aliphatic diols containing 2-8 carbon atoms, and a more preferred diol is 1,4-butanediol. Included among the bisphenols which can be used are bis(p-hydroxy) diphenyl, bis(p-hydroxyphenyl)methane, and bis(p-hydroxyphenyl)propane. Equivalent ester-forming derivatives of diols are also useful. For example, ethylene oxide or ethylene carbonate can be used in place of ethylene glycol or resorcinol diacetate can be used in place of resorcinol). Although the term diol as used herein includes equivalent ester-forming derivatives, molecular weight requirements pertain to the corresponding diols and not to their derivatives.

[0034] Dicarboxylic acids that may be reacted with long-chain glycols and low molecular weight diols to produce the copolyetheresters include aliphatic, cycloaliphatic or aromatic dicarboxylic acids of a low molecular weight, i.e., having a molecular weight of less than about 300. As used herein, the term dicarboxylic acids includes functional equivalents of dicarboxylic acids and includes those that have two carboxyl functional groups and that react similarly as dicarboxylic acids with glycols and diols to form copolyetherester polymers. Such functional equivalents include esters and ester-forming derivatives, such as acid halides and anhydrides. The molecular weight requirement pertains to the acid and not to its equivalent ester or ester-forming derivative. Thus, the term dicarboxylic acids as used herein includes

esters of dicarboxylic acids that have a molecular weight greater than 300 as well as functional equivalents of dicarboxylic acids that have a molecular weight greater than 300 so long as the corresponding acid has a molecular weight below about 300. The dicarboxylic acids may contain substituent groups or combinations of them that do not functionally interfere with either the formation of copolyetherester polymers or their use in the compositions described herein.

[0035] As used herein, the term "aliphatic dicarboxylic acids" refers to carboxylic acids having two carboxyl groups, with each group attached to a saturated carbon atom. If the carbon atom to which the carboxyl group is attached is saturated and in a ring, the acid is cycloaliphatic. Aliphatic or cycloaliphatic acids having conjugated unsaturation often cannot be used because of homopolymerization. However, some unsaturated acids, such as maleic acid, may be used.

[0036] As used herein, aromatic dicarboxylic acids are dicarboxylic acids having two carboxyl groups each attached to a carbon atom in a carbocyclic aromatic ring structure. It is not necessary that both functional carboxyl groups be attached to the same aromatic ring. When more than one ring is present, the functional carboxyl groups can be joined by aliphatic or aromatic divalent radicals or divalent radicals such as —O— or $\text{—SO}_2\text{—}$.

[0037] Useful aliphatic and cycloaliphatic acids include, but are not limited to, sebacic acid; 1,3-cyclohexane dicarboxylic acid; 1,4-cyclohexane dicarboxylic acid; adipic acid; glutaric acid; 4-cyclohexane-1,2-dicarboxylic acid; 2-ethyl-suberic acid; cyclopentanedicarboxylic acid decahydro-1,5-naphthylene dicarboxylic acid; 4,4'-bicyclohexyl dicarboxylic acid; decahydro-2,6-naphthylene dicarboxylic acid; 4,4'-methylenebis(cyclohexyl)carboxylic acid; and 3,4-furan dicarboxylic acid. Preferred acids are cyclohexane-dicarboxylic acids and adipic acid.

[0038] Aromatic dicarboxylic acids include, but are not limited to, phthalic, terephthalic and isophthalic acids; bibenzoic acid; substituted dicarboxy compounds with two benzene nuclei such as bis(p-carboxyphenyl)methane; p-oxy-1,5-naphthalene dicarboxylic acid; 2,6-naphthalene dicarboxylic acid; 2,7-naphthalene dicarboxylic acid; 4,4'-sulfonyl dibenzoic acid and $\text{C}_1\text{—C}_{12}$ alkyl and ring substitution derivatives of these, such as halo, alkoxy, and aryl derivatives. Only when an aromatic dicarboxylic acid is used may hydroxyl acids such as p-(beta-hydroxyethoxy)benzoic acid also be used.

[0039] Aromatic dicarboxylic acids are preferred for the copolyetherester compositions described herein, particularly those with 8-16 carbon atoms and more particularly, terephthalic acid either alone or with a mixture of phthalic and/or isophthalic acids.

[0040] The copolyetherester compositions described herein preferably comprise about 15 to about 99 weight percent short-chain ester units corresponding to Formula (II) above, the remaining weight percent comprising long-chain ester units corresponding to Formula (I) above. These copolyetherester compositions more preferably comprise about 20 to about 95 weight percent, and even more preferably about 25 to about 60 weight percent short-chain ester units, with the remaining weight percent comprising long-chain ester units. Preferably, at least 50 mole percent, and more preferably at least 70 mole percent, are diradicals represented by R in Formulae (I) and (II) above are 1,4-phenylene radicals. Preferably at least about 70% mole percent, 80 mole percent, and most preferably, 90 to 100 mole percent of the groups repre-

sented by D in Formula (II) are 1,4-butylene radicals. Preferably the sum of the percentages of R groups that are not 1,4-phenylene radicals and D groups that are not 1,4-butylene radicals does not exceed 30%. If a second dicarboxylic acid is used to make the copolyetherester, isophthalic acid is preferred.

[0041] A mixture of more than one copolyetherester may be used in these compositions. In such a mixture, the weight percent of the short-chain units and the weight percent of the long-chain units of each copolyetherester need not be the values disclosed above. For example, in a mixture that contains equal amounts of two different copolyetheresters, one copolyetherester may contain 60 weight percent short-chain ester units and the other copolyetherester may contain 30 weight percent short-chain ester units. Together, the composition has a weighted average of 45 weight percent short-chain ester units for both copolyetheresters, which does fall within the values disclosed above for these compositions. Thus, any mixture of copolyether esters must conform to the weight percent values disclosed above on a weighted average basis.

[0042] Preferably, the copolyetherester compositions described herein are prepared from esters or mixtures of esters of terephthalic acid and isophthalic acid, 1,4-butanediol and poly(alkylene oxide)glycols selected from the group consisting of poly(tetramethylene oxide)glycol, poly(trimethylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and mixtures of these. More preferably, the copolyetherester elastomers are prepared from esters of terephthalic acid, e.g. dimethylterephthalate, 1,4-butanediol and poly(tetramethylene ether)glycol.

[0043] The copolyetherester compositions described herein may be prepared from esters of terephthalic acid, e.g. dimethylterephthalate, 1,4-butanediol and poly(trimethylene oxide)glycol or from ethylene oxide-capped poly(propylene oxide)glycol.

Making the Compositions Described Herein

[0044] The copolyetherester compositions described herein may be made by polymerization methods known to those skilled in the art, such as, using a conventional ester interchange reaction. A preferred method involves heating the ester of an aromatic acid, e.g., dimethyl ester of terephthalic acid, with the poly(alkylene oxide)glycol and a molar excess of the low molecular weight diol, 1,4-butanediol, in the presence of a catalyst, followed by distilling off methanol formed by the interchange reaction. Heating is continued until methanol evolution is complete. Depending on temperature, catalyst and glycol excess, the polymerization is complete within a few minutes to a few hours. This method results in the preparation of a low molecular weight prepolymer which can be further processed to a high molecular weight copolyetherester by the methods below.

[0045] Such prepolymers may also be prepared by a number of alternate esterification or ester interchange methods. For example, the long-chain glycol can be reacted with a high or low molecular weight short-chain ester homopolymer or copolymer in the presence of catalyst until randomization occurs. The short-chain ester homopolymer or copolymer can be prepared by ester interchange from either the dimethyl esters and low molecular weight diols as disclosed above, or from the free acids with the diol acetates. Alternatively, the short-chain ester copolymer can be prepared by direct esterification from appropriate acids, anhydrides or acid chlorides,

for example, with diols or by other processes such as reaction of the acids with cyclic ethers or carbonates. As known in the art, the prepolymer may also be prepared by carrying out these methods in the presence of the long-chain glycol.

[0046] The resulting prepolymer is then further processed to high molecular weight by distillation of the excess of short-chain diol by a method known as "polycondensation". Additional ester interchange occurs during this distillation to increase the molecular weight and to randomize the arrangement of the copolyetherester units. Best results are usually obtained if this final distillation, i.e., polycondensation, is carried out at less than 1 mm pressure and 240-260° C. for less than 2 hours in the presence of antioxidants such as 1,6-bis-[3,5-di-tert-butyl-4-hydroxyphenyl]propionamido]-hexane or 1,3,5-trimethyl-2,4,6-tris[3,5-di-tert-butyl-4-hydroxybenzyl]benzene. Most practical polymerization techniques rely upon ester interchange to complete the polymerization reaction.

[0047] To avoid excessive hold time at high temperatures with possible irreversible thermal degradation, a catalyst for ester interchange reactions may be used. While a wide variety of catalysts are suitable, organic titanates, such as tetrabutyl titanate, either alone or in combination with magnesium or calcium acetates are preferred. Complex titanates, such as derived from alkali or alkaline earth metal alkoxides and titanate esters may also be effective. Inorganic titanates, such as lanthanum titanate, calcium acetate/antimony trioxide mixtures, and lithium and magnesium alkoxides, may also be used. Also preferred are stannous catalysts.

[0048] Both batch and continuous methods can be used for any stage of copolyetherester polymer preparation. Polycondensation of prepolymer may also be accomplished in the solid phase by heating divided solid prepolymer in a vacuum or in a stream of inert gas to remove liberated low molecular weight diol. This method can reduce thermal degradation because it must be used at temperatures below the softening point of the prepolymer.

[0049] U.S. Pat. Nos. 3,023,192; 3,651,014; 3,763,109; and 3,766,146 provide detailed description of suitable copolyetheresters that can be used in the compositions described herein and methods for their preparation. Typical copolyetheresters are, for example, those made and marketed by Du Pont (Wilmington, Del.) under the name Hytrel® polyester elastomers.

[0050] The copolyetherester may be present in the copolyetherester compositions described herein at about 50 to about 99.75 weight percent, and preferably 60, 70 and 80 to 99.75 weight percent, based upon the total weight of the composition. In addition, the copolyetherester compositions described herein comprise from at or about 0.25 to at or about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups, preferably from at or about 0.5 to at or about 10 weight percent; more preferably, at or about 0.5 to at or about 7 weight percent; and still most preferably from 0.5 weight percent to at or about 5 weight percent, wherein the weight percentages are based on the total weight of the composition.

[0051] Polyhydric alcohols may be selected from aliphatic hydroxylic compounds containing more than two hydroxyl groups, aliphatic-cycloaliphatic compounds containing more than two hydroxyl groups, cycloaliphatic compounds containing more than two hydroxyl groups, aromatic and saccharides.

[0052] An aliphatic chain in the polyhydric alcohol can include not only carbon atoms but also one or more hetero atoms selected, for example, from nitrogen, oxygen and sulfur atoms. A cycloaliphatic ring present in the polyhydric alcohol can be monocyclic or part of a bicyclic or polycyclic ring system and may be carbocyclic or heterocyclic. A heterocyclic ring present in the polyhydric alcohol can be monocyclic or part of a bicyclic or polycyclic ring system and may include one or more hetero atoms which may be selected, for example, from nitrogen, oxygen and sulfur atoms. The one or more polyhydric alcohols may contain one or more substituents, such as ether, carboxylic acid, carboxylic acid amide or carboxylic acid ester groups.

[0053] Examples of polyhydric alcohol containing more than two hydroxyl groups include, without limitation, triols, such as glycerol, trimethylolpropane, 2,3-di-(2'-hydroxyethyl)-cyclohexan-1-ol, hexane-1,2,6-triol, 1,1,1-tris-(hydroxymethyl)ethane, 3-(2'-hydroxyethoxy)-propane-1,2-diol, 3-(2'-hydroxypropoxy)-propane-1,2-diol, 2-(2'-hydroxyethoxy)-hexane-1,2-diol, 6-(2'-hydroxypropoxy)-hexane-1,2-diol, 1,1,1-tris-[(2'-hydroxyethoxy)-methyl]-ethane, 1,1,1-tris-[(2'-hydroxypropoxy)-methyl]-propane, 1,1,1-tris-(4'-hydroxyphenyl)-ethane, 1,1,1-tris-(hydroxyphenyl)-propane, 1,1,3-tris-(dihydroxy-3-methylphenyl)-propane, 1,1,4-tris-(dihydroxyphenyl)-butane, 1,1,5-tris-(hydroxyphenyl)-3-methylpentane, di-trimethylolpropane, trimethylolpropane ethoxylates, or trimethylolpropane propoxylates; polyols such as pentaerythritol, dipentaerythritol, and tripentaerythritol; and saccharides, such as cyclodextrin, D-mannose, glucose, galactose, sucrose, fructose, xylose, arabinose, D-mannitol, D-sorbitol, D- or L-arabitol, xylitol, iditol, talitol, allitol, altritol, guilitol, erythritol, threitol, and D-gulonic-γ-lactone; and the like.

[0054] Alternative polyhydric alcohols include polyhydric polymers selected from the group consisting of ethylene/vinyl alcohol copolymer and poly(vinyl alcohol) having a weight average molecular weight of (M_w) of at least 2000; and preferably 5000 to 50,000; as measured by gel permeation chromatography (GPC). Preferably the ethylene/vinyl alcohol copolymer has a vinyl alcohol content of 10 to 90 mol % and preferably 30 to 80 mol %, 40 to 75 mol %, 50 to 75 mol %, and 50 to 60 mol %, wherein the remainder mol % is ethylene. The vinyl alcohol polymer has a degree of hydrolysis preferably greater than 85%, and preferably greater than 89%.

[0055] Preferred polyhydric alcohols include those having a pair of hydroxyl groups which are attached to respective carbon atoms which are separated one from another by at least one atom. Especially preferred polyhydric alcohols are those in which a pair of hydroxyl groups is attached to respective carbon atoms which are separated one from another by a single carbon atom.

[0056] Preferably, the polyhydric alcohol is selected from the group consisting of pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylolpropane, D-mannitol, D-sorbitol and xylitol. More preferably, the polyhydric alcohol used in the compositions described herein is dipentaerythritol and/or pentaerythritol.

Additives

[0057] The copolyetherester compositions described herein may further comprise about 0.1 to 30 weight percent of one or more additives selected from the group consisting of colorants, carbon black, nucleating agents, mold release

agents, lubricants, viscosity modifiers, impact modifiers, filler and reinforcing agents, polyester polymers, flame retardant and combinations of these.

[0058] Additional additives may be preferably present in about 0.1 to about 30 weight percent, based on the total weight of the composition. A preferred additive is carbon black, which may be preferably present in about 0.1 to about 4 weight percent, or more preferably in about 0.25 to about 3.5 weight percent, or yet more preferably in about 0.5 to about 3 weight percent, based on the total weight of the composition. When fillers other than carbon black are used, they are present in about 0.1 to 10 weight percent, and preferably 0.1 to 5 weight percent.

[0059] Another preferred group of additives includes viscosity modifiers selected from the group consisting of ionomer resins, ethylene copolymers comprising glycidyl esters and polyesters. As used herein, the term "ionomer resins" refers to a polymer that comprises ionic groups that are alkali metal ion carboxylates, for example, sodium carboxylates. Such polymers are generally produced by partially or fully neutralizing the carboxylic acid groups of precursor acid copolymers, as discussed above, for example, by reaction with a base. An example of an alkali metal ionomer is a sodium ionomer (or sodium neutralized ionomer), for example a copolymer of ethylene and methacrylic acid wherein all or a portion of the carboxylic acid groups of the copolymerized methacrylic acid units are in the form of sodium carboxylates.

[0060] The ionomer resin comprises a polymer that is an ionic, neutralized, or partially neutralized, derivative of a precursor acid copolymer. The precursor acid copolymer comprises copolymerized units of an α -olefin having 2 to 10 carbons and about 5 to about 30 wt %, about 5 to 25 wt %, or about 10 to about 25 wt %, of copolymerized units of an α,β -ethylenically unsaturated carboxylic acid having 3 to 8 carbons, based on the total weight of the precursor acid copolymer.

[0061] Suitable α -olefin comonomers include, but are not limited to, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3 methyl-1-butene, 4-methyl-1-pentene, and the like and mixtures of two or more of these α -olefins. Preferably, the α -olefin is ethylene.

[0062] Suitable α,β -ethylenically unsaturated carboxylic acid comonomers include, but are not limited to, acrylic acids, methacrylic acids, itaconic acids, maleic acids, maleic anhydrides, fumaric acids, monomethyl maleic acids, and mixtures of two or more of these acid comonomers. Preferably, the α,β -ethylenically unsaturated carboxylic acid is selected from acrylic acids, methacrylic acids, and mixtures of two or more acrylic acids or methacrylic acids.

[0063] To obtain the ionomers useful in the compositions described herein, the precursor acid copolymers are neutralized with a base so that their carboxylic acid groups react to form carboxylate groups. Preferably, the precursor acid copolymers are neutralized to a level of about 40% to about 90%, or about 40% to about 70%, or about 43% to about 60%, based on the total carboxylic acid content of the precursor acid copolymers as calculated for the non-neutralized precursor acid copolymers.

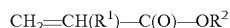
[0064] The precursor acid copolymers may be neutralized by any conventional method, such as those disclosed in U.S. Pat. Nos. 3,404,134 and 6,518,365. Ionomer resins particularly useful are available from E.I. du Pont de Nemours and Co., Wilmington, Del., under the Surllyn® resin brand.

[0065] The compositions described herein may comprise one or more ionomer resins that comprise an ethylene/methacrylic acid copolymer having about 5 to 25 wt % methacrylic acid repeat units based on the weight of the ethylene/methacrylic acid copolymer; and more particularly, the ethylene/methacrylic acid copolymer has a neutralization ratio of 0.40 to about 0.70.

[0066] The ethylene copolymer comprises glycidyl esters and has the formula E/X/Y where

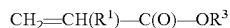
[0067] E comprises 40-89.5 weight percent of the ethylene copolymer and is the radical formed from ethylene;

[0068] X comprises 10-40 weight percent of the ethylene copolymer and is one or more radicals formed from



[0069] wherein R^1 is H, CH_3 or C_2H_5 , (preferably H or CH_3 , and most preferably H) R^2 is an alkyl group having 1-8 carbon atoms; vinyl acetate; or a mixture of these; and

[0070] Y comprises 0.5-20 weight percent and preferably about 5 to 20 weight percent of the ethylene copolymer and is a radical formed from monomers selected from the group consisting of



wherein R^3 is glycidyl, and R^1 is H, CH_3 or C_2H_5 .

[0071] Commercial examples of ethylene copolymers comprising glycidyl esters are Evaloy® EP1001 resin from E.I. du Pont de Nemours and Company, Wilmington, Del., and Bondfast E® copolymer available from Sumitomo Chemical Co. Ltd.

[0072] Suitable polyester modifiers include poly(butylene terephthalate)s.

Articles Made from the Compositions Described Herein and their Uses

[0073] Also described herein are thermoplastic articles having high heat stability over about 120 hours at 150° C. These comprise a melt-mixed blend of the copolyetherester compositions described herein, wherein 2 mm test bars prepared from said copolyetherester composition according to ISO 527-2/5A (2 mm test bars according to type 5A) method, and exposed in an atmosphere of air at a test temperature of 150° C. for a test period of about 120 hours, and tested according to ISO 527-1 have a retention of tensile strain at break of at least 50 percent, and preferably at least 60, 70, and 80 percent, as compared with that of an unexposed control having identical composition and shape. The retention of tensile strain at break is an appropriate measure of the thermal stability of molded thermoplastic articles of polymer elastomer compositions having no reinforcing agent and little or no filler present in the composition.

[0074] The thermoplastic article comprising the melt-mixed blend of the copolyetherester composition has a retention of tensile strain at break of at least 60, 70, 80 and, most preferably, 90 percent as compared with that of an unexposed control.

[0075] Inasmuch as the compositions described herein are melt-mixed blends—wherein the blend forms a unified whole—any melt-mixing method may be used to combine the polymeric components and non-polymeric components. This means that the polymeric components and non-polymeric ingredients may be added to a melt mixer, such as, a single or twin-screw extruder; a blender; a kneader; or a Banbury mixer, either all at once through a single step addition or in a stepwise fashion, and then melt-mixed. When blended in a

stepwise fashion, a portion of the polymeric components and/or a portion of the non-polymeric components are added together and melt-mixed, followed by subsequent additions and melt mixing of the remaining components together until all components are mixed.

[0076] The compositions described herein may be formed into articles using methods known to those skilled in the art, such as, for example, injection molding, blow molding, extrusion, thermoforming, melt casting, rotational molding, and slush molding. These compositions may be over molded onto an article made from a different material, extruded into the form of films, sheets, tubing and other geometric shapes, or formed into monofilaments.

[0077] Articles comprising the compositions described herein may be used in, or to form part of, air bag doors; automotive dashboard components; components of a motorized engine; other automotive parts; tubing; components for furniture; footwear components; roof liners; outdoor apparel; water management system components; and cable and wire jacketing.

Materials

[0078] Hytrel® 5556 is a copolyetherester elastomer, available from DuPont. It has a nominal hardness of 55 Shore D and comprises hard segments of poly(butylene terephthalate) [PBT] with soft segments of poly(tetramethylene oxide) terephthalate.

[0079] DPE refers to dipentaerythritol that was from Perstorp Speciality Chemicals AB, Perstorp, Sweden as Di-Penta 93.

Methods

[0080] The Hytrel® 5556 was melt compounded in a 30 mm twin screw extruder with various levels of additives as listed in Table 1. The control resin was Hytrel® 5556 put through the same compounding process but without the addition of additives. The extruder was operating with a barrel temperature setting of about 230° C. using a screw speed of about 250 rpm, and a throughput of 20 kg/hour.

[0081] Physical Properties Measurement

[0082] Mechanical tensile properties, i.e. tensile strength and strain at break (i.e., elongation at break) were measured according to ISO 527-2/5A on an injection molded tensile bar.

[0083] Prior to injection molding, the granules of the thermoplastic molding composition were dried so as to have a moisture level below 0.08%. Mold temperature for the test specimens was 40° C.; Melt temperature was 230° C. and a hold pressure of 70 MPa.

[0084] The thickness of the test specimens was 2 mm according to ISO 527-2/5A at a testing speed of 50 mm/min (tensile strength and elongation).

[0085] Air Oven Ageing (AOA)

[0086] The test specimens were heat aged in a re-circulating air ovens (Heraeus type UT6060) according to the procedure detailed in ISO 2578. At various heat aging times, the test specimens were removed from the oven, allowed to cool to room temperature (23° C.). The tensile mechanical properties were then measured according to ISO 527 using a Zwick tensile instrument. The average values obtained from 5 specimens are given in the Table.

[0087] Retention of tensile strain at break corresponds to the percentage of the strain at break after heat aging for the

various times listed in comparison with the value of unexposed control considered as being 100%.

EXAMPLES 1-3 AND COMPARATIVE

EXAMPLE C-1

[0088] Compositions of Examples 1-3 and Comparative Examples C-1 are listed in Table 1. Tensile properties after AOA at 150° C. at various test times, and retention of tensile strain at break are listed in Table 1. Higher values of tensile strength (TS) mean better mechanical properties. Higher percentage of retention of tensile strain at break indicates a higher degree of thermal stability.

[0089] The Examples indicate that DPE provides surprising and unexpected improvement in the retention of tensile strain at break as compared to Comparative Example C-1 having no DPE.

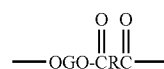
TABLE 1

	Example			
	C-1	1	2	3
Hytrel ® 5556	100	99.25	98.5	97.0
DPE	0	0.75	1.5	3.0
AOA - 0 hrs				
Tensile strength (MPa)	28.1	29.3	31.7	32.3
Strain at break (%)	362	413	472	577
AOA - 150° C., 120 hrs				
Tensile strength (MPa)	14.6	24.0	25.6	19
Strain at break (%)	22	392	470	302
% Retention of tensile strain at break	6	95	100	52
AOA - 150° C., 144 hrs				
Tensile strength (MPa)	0	20.8	22.1	16.8
Strain at break (%)	0	298	316	57
% Retention of tensile strain at break	0	72	67	10
AOA - 150° C., 168 hrs				
Tensile strength (MPa)	0	6.9	19.2	9.1
Strain at break (%)	0	8.2	262	4.4
% Retention of tensile strain at break	0	2	56	1

We claim:

1. A copolyetherester composition comprising a melt-mixed blend of

- (a) one or more copolyetherester(s) comprising a multiplicity of recurring long chain ester units and short chain ester units joined head-to-tail through ester linkages, said long chain ester units being represented by formula (I):



(I)

and said short chain ester units being represented by formula (II):



where

G is a divalent radical remaining after the removal of terminal hydroxy groups from a poly(alkylene oxide) glycol that has a number average molecular weight of about 400 to about 6000;

R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid that has a molecular weight of less than about 300; and

D is a divalent radical remaining after removal of hydroxyl groups from a diol that has a molecular weight of less than about 250;

wherein said copolyetherester(s) preferably contain from about 15 to about 99 weight percent short-chain ester units and about 1 to about 85 weight percent long-chain ester units; and

(b) about 0.25 to about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups;

wherein all weight percentages are based on the total weight of the copolyetherester composition.

2. The copolyetherester composition of claim 1, wherein the polyhydric alcohol is selected from the group consisting of pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylpropane, D-mannitol, D-sorbitol and xylitol.

3. The copolyetherester composition of claim 1, wherein at least 50 mole percent diradicals represented by R in Formula (I) and (II) are 1,4-phenylene radicals.

4. The copolyetherester composition of claim 1, wherein at least about 70% mole percent of the groups represented by D in Formula (II) are 1,4-butylene radicals.

5. The copolyetherester composition of claim 1, wherein the copolyetheresters are prepared from esters or mixtures of esters of terephthalic acid and isophthalic acid, 1,4-butanediol and poly(alkylene oxide)glycols selected from the group consisting of poly(tetramethylene oxide)glycol, poly(trimethylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and mixtures of these.

6. The copolyetherester composition of claim 5, wherein said poly(alkylene oxide)glycol comprises poly(tetramethylene oxide)glycol.

7. The copolyetherester composition of claim 1, further comprising

(c) about 0.1 to 30 weight percent of one or more additives selected from the group consisting of colorants, carbon black, nucleating agents, mold release agents, lubricants, viscosity modifiers, impact modifiers, fillers, reinforcing agents, polyester polymers, flame retardants, and combinations of these.

8. A copolyetherester composition comprising a melt-mixed blend of

(a) one or more copolyetherester(s) comprising a multiplicity of recurring long chain ester units and short chain ester units joined head-to-tail through ester linkages, said long chain ester units being represented by formula (I):



and said short chain ester units being represented by formula (II):



where

G is a divalent radical remaining after the removal of terminal hydroxy groups from a poly(alkylene oxide) glycol that has a number average molecular weight of about 400 to about 6000;

R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid that has a molecular weight of less than about 300; and

D is a divalent radical remaining after removal of hydroxyl groups from a diol that has a molecular weight of less than about 250;

wherein said copolyetherester(s) preferably contain from about 15 to about 99 weight percent short-chain ester units and about 1 to about 85 weight percent long-chain ester units; and

(b) about 0.25 to about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups;

wherein all weight percentages are based on the total weight of the copolyetherester composition,

wherein 2 mm test bars

made from said copolyetherester composition,

exposed in an atmosphere of air at a test temperature of 150° C. for a test period of about 120 hours, and

tested according to according to ISO 527-2/5A method have, on average, a retention of tensile strain at break of at least 50 percent as compared with that of an unexposed control having identical composition and shape.

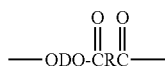
9. A thermoplastic article comprising a melt-mixed blend of a copolyetherester composition comprising

(a) about 85 to about 99.75 weight percent of at least one copolyetherester comprising a multiplicity of recurring long chain ester units and short chain ester units joined head-to-tail through ester linkages,

said long chain ester units being represented by formula (I):



and said short chain ester units being represented by formula (II)



where

G is a divalent radical remaining after the removal of terminal hydroxy groups from a poly(alkylene oxide) glycol having a number average molecular weight of about 400 to about 6000;

R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid having a molecular weight of less than about 300; and

D is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight of less than about 250;

wherein said short chain ester units comprise about 15 to about 99 weight percent of the copolyetherester and said long chain ester units comprise about 1 to about 85 weight percent of the copolyetherester; and

(b) about 0.25 to about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups,

wherein weight percentages are based on the total weight of the copolyetherester composition;

wherein the article has been molded or extruded, and

wherein 2 mm test bars

made from said copolyetherester composition,

exposed in an atmosphere of air at a test temperature of 150° C. for a test period of about 120 hours, and

tested according to according to ISO 527-2/5A method have, on average, a retention of tensile strain at break of at least 50 percent as compared with that of an unexposed control having identical composition and shape.

10. The thermoplastic article of claim 9, wherein the polyhydric alcohol is selected from the group consisting of pentaerythritol, dipentaerythritol, tripentaerythritol, di-trimethylpropane, D-mannitol, D-sorbitol and xylitol.

11. The thermoplastic article of claim 9, wherein at least 50 mole percent diradicals represented by R in Formula (I) and (II) are 1,4-phenylene radicals.

12. The thermoplastic article of claim 9, wherein at least about 70% mole percent of the groups represented by D in Formula (II) are 1,4-butylene radicals.

13. The thermoplastic article of claim 9, wherein the copolyetheresters are prepared from esters or mixtures of esters of terephthalic acid and isophthalic acid, 1,4-butanediol and poly(alkylene oxide) glycols selected from the group consisting of poly(tetramethylene oxide)glycol, poly(trimethylene oxide)glycol, ethylene oxide-capped poly(propylene oxide)glycol, and mixtures of these.

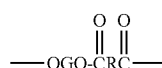
14. The thermoplastic article of claim 13, wherein the poly(alkylene oxide)glycol is poly(tetramethylene ether)glycol.

15. The thermoplastic article of claim 9, further comprising (c) about 0.1 to 30 weight percent of one or more additives selected from the group consisting of colorants, carbon black, nucleating agents, mold release agents, lubri-

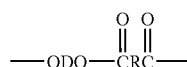
cants, viscosity modifiers, impact modifiers, fillers, reinforcing agents, polyester polymers, flame retardants and combinations of these.

16. A method of using the composition of claim 1, comprising:

- a) making a thermoplastic article comprising a melt-mixed blend of a copolyetherester composition comprising
 - (i) about 85 to about 99.75 weight percent of at least one copolyetherester comprising a multiplicity of recurring long chain ester units and short chain ester units joined head-to-tail through ester linkages, said long chain ester units being represented by formula (I):



and said short chain ester units being represented by formula (II)



where

G is a divalent radical remaining after the removal of terminal hydroxy groups from a poly(alkylene oxide) glycol having a number average molecular weight of about 400 to about 6000;

R is a divalent radical remaining after removal of carboxyl groups from a dicarboxylic acid having a molecular weight of less than about 300; and

D is a divalent radical remaining after removal of hydroxyl groups from a diol having a molecular weight of less than about 250; wherein said short chain ester units comprise about 15 to about 99 weight percent of the copolyetherester and said long chain ester units comprise about 1 to about 85 weight percent of the copolyetherester; and

(ii) about 0.25 to about 15 weight percent of one or more polyhydric alcohols having more than two hydroxyl groups,

wherein weight percentages are based on the total weight of the copolyetherester composition;

wherein the article has been molded or extruded, and

wherein 2 mm test bars

made from said copolyetherester composition,

exposed in an atmosphere of air at a test temperature of 150° C. for a test period of about 120 hours, and

tested according to according to ISO 527-2/5A method have, on average, a retention of tensile strain at break of at least 50 percent as compared with that of an unexposed control having identical composition and shape; and

b) utilizing the article of step (a) so that it is exposed in air at a temperature of 150° C. for a period of about 120 hours and, during utilization, exhibits high heat stability.

17. A method of using the article of claim 9, comprising: utilizing the article in the engine compartment of a motorized vehicle.

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