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(54) Title: HIGH MELT VISCOSITY POLYESTER OR CO-POLYESTER COMPOSITIONS

(57) Abstract: Processes of decreasing the melt flow rate of a polyester selected from the group consisting of polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms, copolyester thermoplastic elastomers, and mixtures of these, by melt mixing with the polyester an alkali metal salt having a molecular weight less than 300 to provide a melt mixed composition. Processes of making a melt extruded article from such melt mixed compositions and the articles made therefrom.

TITLE

HIGH MELT VISCOSITY POLYESTER OR CO-POLYESTER COMPOSITIONS

FIELD OF THE INVENTION

[0001] The recited invention relates to the field of polyester or copolyester elastomer compositions particularly suitable for making articles by melt extrusion processes.

BACKGROUND OF THE INVENTION

[0002] Polymer compositions with high melt viscosity are ideal for making hollow structures, which involves melt extrusion processes, such as blow molding, profile extrusion and corrugated extrusion, in which molten material flows through a die assembly and is shaped into the final part. Blow molding is particularly useful for making hollow structures. Typically a parison of plastic material that has been produced by extrusion or injection molding and which is in a hot moldable condition is positioned between two halves of an open blow mold having a mold cavity of a shape appropriate to the required external shape of the article to be manufactured. During extrusion blow molding, the parison gradually moves and stretches under the influence of gravity. When the parison reaches the proper length, the mold halves are closed around it and pressurized air or other compressed gas is introduced to the interior of the parison to inflate it to the shape of the mold or to expand it against the sides of the mold cavity. After a cooling period, the mold is opened and the final article is ejected. Since the parison is suspended as it emerges from the die and must bear its own weight without being stretched or sagging in an uncontrollable fashion during this phase, polymer compositions with high melt viscosity are ideal for blow molding.

[0003] To increase the melt viscosity, that is to decrease the melt flow rate, of copolyester elastomer compositions, it is known to add an ionomer. U.S. Pat. No. 4,010,222 discloses a copolyester elastomer blend, which has an additive of an ethylene/carboxylic acid copolymer in which at least 10% of the acid groups are neutralized, the additive being termed an ionomer, and which is reported to have increased melt strength and to be more readily processable by blow molding than such a blend without the ionomer.

[0004] However, articles made of copolyester elastomer blends comprising an

ionomer may suffer from a variation of their stiffness when the article is exposed to a temperature higher than 60°C, and may exhibit phase separation, resulting in the formation of layers. The resulting layers may separate from one another, i.e. delaminate, when such nonhomogeneous articles are flexed or stretched.

[0005] U.S. Patent Application Publication No. US2010/0127434 discloses the addition of rheological additives that include solid organic and inorganic salts and aqueous solutions of these materials to compositions termed "Molecularly Self-assembling Materials", which are described as polyesteramides, copolyesteramides, copolyetheramides, copolyetherester-amides, copolyetherester-urethanes, copolyether-urethanes, copolyester-urethanes, copolyester-ureas, copolyetherester-ureas and their mixtures. The addition of the rheological additive is said to decrease melt viscosity.

[0006] U.S. Patent Application Publication No. 2007/0246867 discloses a process for introducing an additive, such as an inorganic salt or a salt of certain organic acids, such as acetic acid or propionic acid, to a polymer in the melt, wherein the additive is introduced to the molten polymer as an aqueous solution.

[0007] There remains a need for polyester or copolyester compositions that, when exposed to increased temperature, exhibit a good melt rheology while maintaining mechanical properties in the solid state.

SUMMARY OF THE INVENTION

[0008] Described herein are processes of decreasing the melt flow rate of the melt mixed compositions described herein, comprising a step of melt-mixing a) one or more polyester resins selected from polyesters being derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these described herein and b) an alkali metal salt having a molecular weight less than 300 described herein, so as to form a resin composition.

[0009] Also described herein are processes of decreasing the melt flow rate of a polyester selected from the group consisting of polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms, copolyester thermoplastic elastomers, and mixtures of these, the process

comprising melt mixing with the polyester an alkali metal salt having a molecular weight less than 300 to provide a melt mixed composition, wherein the melt mixed composition is characterized by 1) a reduction in melt flow rate of at least 40% as measured according to ISO 1133:1997(E) when compared to that of the polyester, and 2) a loss of tensile stress at 80°C of less than 40% as compared to tensile strength at 23°C when measured at 10% strain according to ISO 527-2/1A/50.

[0010] Also described herein are processes for making an article comprising shaping a melt mixed composition that comprises a polyester selected from the group consisting of polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms, copolyester thermoplastic elastomers, and mixtures of these, and which is melt mixed with an alkali metal salt having a molecular weight less than 300, such that the melt mixed composition possesses 1) a reduction in melt flow rate of at least 40% as measured according to ISO 1133:1997(E) when compared to that of the polyester; and 2) a loss of tensile stress at 80°C of less than 40% as compared to tensile strength at 23°C when measured at 10% strain according to ISO 527-2/1A/50.

[0011] Also described herein are melt extruded articles made by the processes described herein.

[0012] Further described herein is the use of an alkali metal salt having a molecular weight less than 300 as an additive for decreasing melt flow rate of a resin composition, said resin composition being prepared by melt-mixing a mixture comprising a) one or more polyester resins selected from polyesters being derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these, with said alkali metal salt b).

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0013] The following definitions are to be used to interpret the meaning of the terms discussed in the description and recited in the claims.

As used herein, the article "a" indicates one as well as more than one and

does not necessarily limit its referent noun to the singular.

[0014] As used herein, the terms "about" and "at or about" refers to that the amount or value in question may be the value designated or some other value about the same. The phrase is intended to convey that similar values promote equivalent results or effects according to the invention.

[0015] As used herein, the term "melt extrusion processes" refers to any technique in which a molten material flows through a die and is then shaped into the final part.

[0016] As used herein, the term "melt flow rate" (MFR, also known as melt mass-flow rate) refers to the flow rate of a material through a capillary under controlled conditions of temperature and pressure/load. Thus, melt flow rate is a measure of the ability of the melt of a material to flow under pressure and is inversely proportional to the viscosity of the melt under specific test conditions.

[0017] For values recited herein, melt flow rates are measured on melted pellets that, prior to measurement, were dried under nitrogen at a temperature of at least 130°C and were tested according to ISO 1133:1997. The values of MFR are reported in grams/10 minutes. Melt flow rate is also known as melt flow index.

[0018] As used herein, the term "melt viscosity" refers to the viscosity of a molten polymer. Viscosity is the resistance of a fluid to a change in shape, or movement of neighboring portions relative to one another. In other terms, viscosity is resistance to melt flow.

[0019] Described herein are compositions made by melt-mixing a polyester selected from the group consisting of polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms, copolyester thermoplastic elastomers, and mixtures of these, with an alkali metal salt having a molecular weight less than 300 to provide a melt mixed composition that exhibits both a reduction in melt flow rate of at least 40% as measured according to ISO 1133:1997(E) when compared to that of the polyester and a loss of tensile stress at 80°C of less than 40% as compared to tensile strength at 23°C when measured at 10% strain according to ISO 527-2/1A/50.

Polyesters

[0020] The polyesters are selected from the group consisting of polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms, copolyester thermoplastic elastomers, and mixtures of these. The polyester is preferably from 90 to 99.99 weight percent, and more preferably, from 92 to 99.5 weight percent of the sum of the polyester and the alkali metal salt having a molecular weight less than 300.

[0021] The polyesters may be derived from one or more dicarboxylic acids, which include esters, and one or more diols having more than two carbon atoms. In preferred polyesters, the dicarboxylic acids comprise one or more of terephthalic acid, isophthalic acid, and 2,6-naphthalene dicarboxylic acid, and the diol component comprises one or more of $\text{HO}(\text{CH}_2)_n\text{OH}$ (I); 1,4-cyclohexanedimethanol; $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_2\text{CH}_2\text{OH}$ (II); and $\text{HO}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_z\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (III), wherein n is an integer of 3 to 10, m on average is 1 to 4, and z is on average about 7 to about 40. (II) and (III) may be a mixture of compounds in which m and z vary but are not necessarily integers as m and z are averages.

[0022] Other dicarboxylic acids that may be used to form the polyester include sebacic and adipic acids. Hydroxycarboxylic acids such as hydroxybenzoic acid may be used as comonomers. Preferably, the polyester resins are selected from poly(trimethylene terephthalate) (PTT), poly(1,4-butylene terephthalate) (PBT), poly(ethylene 2,6-naphthoate) (PEN), and poly(1,4-cyclohexyldimethylene terephthalate) (PCT) and copolymers and mixtures of these. More preferably the polyester resin is poly(trimethylene terephthalate) (PTT), poly(1,4-butylene terephthalate) (PBT), poly(1,4-cyclohexyldimethylene terephthalate) (PCT), and copolymers and blends of the same. Still more preferably are poly(trimethylene terephthalate) (PTT), poly(1,4-butylene terephthalate) (PBT) and copolymers and blends of the same.

Copolyester Thermoplastic Elastomers

[0023] Copolyester thermoplastic elastomers (TPCs) include copolyester ester elastomers, copolycarbonate ester elastomers, and copolyether ester elastomers, the latter preferred.

Copolyesterester elastomers

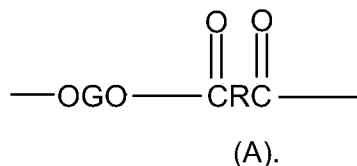
[0024] Copolyesterester elastomers are block copolymers containing a) hard polyester segments and b) soft and flexible polyester segments. Examples of hard polyester segments are polyalkylene terephthalates, poly(cyclohexanedicarboxylic acidcyclohexanemethanol). Examples of soft polyester segments are aliphatic polyesters, including polybutylene adipate, polytetramethyladipate and polycaprolactone. The copolyesterester elastomers contain blocks of ester units of a high melting polyester and blocks of ester units of a low melting polyester which are linked together through ester groups and/or urethane groups. Copolyesterester elastomers comprising urethane groups may be prepared by reacting the different polyesters in the molten phase, after which the resulting copolyesterester is reacted with a low molecular weight polyisocyanate, such as diphenylmethane diisocyanate.

Copolycarbonateester Elastomers

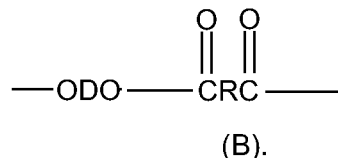
[0025] Copolycarbonateester elastomers are block copolymers containing a) hard segments consisting of blocks of an aromatic or semi-aromatic polyester and b) soft segments consisting of blocks of a polycarbonate containing polymeric component. Suitably, the copolycarbonateester elastomer is made of hard polyester segments made up of repeating units derived from an aromatic dicarboxylic acid and an aliphatic diol, and of soft segments made up of repeating units of an aliphatic carbonate, and/or soft segments made up of randomly distributed repeating units of an aliphatic carbonate and either an aliphatic diol and an aliphatic dicarboxylic acid or a lactone, and a combination of these, wherein the hard segments and the soft segments can be connected with a urethane group. These elastomers and their preparation are described in EP Pat. No. 0846712, for example.

Copolyetherester Elastomers

[0026] Copolyetherester elastomers are the preferred thermoplastic polyesters in these compositions and have a multiplicity of recurring long-chain ester units and short-chain ester units joined head-to-tail through ester linkages. The long-chain ester units are represented by formula (A):



The short-chain ester units are represented by formula (B):



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

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 less than about 250.

[0027] As used herein, the term “long-chain ester units” as applied to units in a polymer chain refers to the reaction product 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 can be used.

[[0028] As used herein, the term “short-chain ester units” as applied to units in a polymer chain of copolyetheresters refers to low molecular weight compounds or polymer chain units having molecular weights less than about 550. These units 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 (B) above. Included among the low molecular weight diols that react to form suitable short-chain ester units are acyclic, alicyclic and aromatic dihydroxy compounds. Preferred 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 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.

[0029] As used herein, the term "diols" includes equivalent ester-forming derivatives such as those mentioned. However, any molecular weight requirements refer to the corresponding diols, not their derivatives.

[0030] Dicarboxylic acids that can react with the foregoing long-chain glycols and low molecular weight diols to produce the copolyetheresters are aliphatic, cycloaliphatic or aromatic dicarboxylic acids of a low molecular weight, i.e., having a molecular weight of less than about 300. The term "dicarboxylic acids" as used herein includes functional equivalents of dicarboxylic acids that have two carboxyl functional groups that perform substantially like dicarboxylic acids in reaction with glycols and diols in forming copolyetherester polymers. These 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.

[0031] Thus, an ester of a dicarboxylic acid having a molecular weight greater than 300 or a functional equivalent of a dicarboxylic acid having a molecular weight greater than 300 are included provided the corresponding acid has a molecular weight below about 300. The dicarboxylic acids can contain any substituent groups or combinations that do not substantially interfere with copolyetherester polymer formation.

[0032] As used herein, the term "aliphatic dicarboxylic acids" refers to carboxylic acids having two carboxyl groups, each group attached to a saturated carbon atom. If the carbon atom to which the carboxyl group is attached is saturated and is 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, can be used.

[0033] As used herein, the term “aromatic dicarboxylic acids” refers to dicarboxylic acids having two carboxyl groups, each group 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 and where more than one ring is present, they can be joined by aliphatic or aromatic divalent radicals or divalent radicals such as $-O-$ or $-SO_2-$. Representative useful aliphatic and cycloaliphatic acids that can be used include sebacic acid; 1,3-cyclohexane dicarboxylic acid; 1,4-cyclohexane dicarboxylic acid; adipic acid; glutaric acid; 4-cyclohexane-1,2-dicarboxylic acid; 2-ethylsuberic 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.

[0034] Representative aromatic dicarboxylic acids include 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 C_1 - C_{12} alkyl and ring substitution derivatives thereof, such as halo, alkoxy, and aryl derivatives. Hydroxyl acids such as p-(beta-hydroxyethoxy)benzoic acid can also be used provided an aromatic dicarboxylic acid is also used.

[0035] Aromatic dicarboxylic acids are preferred for making the copolyetherester elastomers. Among the aromatic acids, those with 8-16 carbon atoms are preferred, particularly terephthalic acid alone or with a mixture of phthalic and/or isophthalic acids.

[0036] The copolyetherester elastomer preferably comprises from 15 to 99 weight percent, more preferably 20 to 95 weight percent, and still more preferably 50 to 90 weight percent, of short-chain ester units corresponding to Formula (B), with the remainder being long-chain ester units corresponding to Formula (A) above. More preferably, at least about 70% of the groups represented by R in Formulae (A) and (B) above are 1,4-phenylene radicals and at least about 70% of the groups represented by D in Formula (B) above are 1,4-butylene radicals

and the sum of the percentages of R groups which 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. If a second low molecular weight diol is used, ethylene glycol, 1,3-propanediol, cyclohexanedimethanol, or hexamethylene glycol are preferred.

[0037] Since a mixture of two or more copolyetherester elastomers may be used, the weight percent of short-chain ester units of each copolyetherester elastomer in the mixture need not be within the values disclosed herein. Rather, it is the total weight percent of short-chain ester units for the elastomer mixture that must fall within the values disclosed above, and is calculated as a weighted average. For example, in a mixture that contains equal amounts of two copolyetherester elastomers, one copolyetherester elastomer can contain 60 weight percent short-chain ester units and the other resin can contain 30 weight percent short-chain ester units for a weighted average of 45 weight percent short-chain ester units.

[0038] Preferred copolyetherester elastomers include, but are not limited to, those prepared from: (1) monomers selected the group consisting of poly(tetramethylene oxide) glycol, poly(trimethylene oxide) glycol, and ethylene oxide-capped poly(propylene oxide) glycol; (2) a dicarboxylic acid selected from isophthalic acid, terephthalic acid, and mixtures of these; and (3) a diol selected from 1,4-butanediol, 1,3-propanediol, and mixtures of these.

[0039] Preferably, the copolyetherester elastomers are made from esters or mixtures of esters of terephthalic acid and/or isophthalic acid, 1,4-butanediol and poly(tetramethylene ether)glycol or poly(trimethylene ether) glycol or ethylene oxide-capped polypropylene oxide glycol, or are prepared from esters of terephthalic acid, e.g. dimethylterephthalate, 1,4-butanediol and poly(ethylene oxide)glycol. More preferably, the copolyetheresters are prepared from esters of terephthalic acid, e.g. dimethylterephthalate, 1,4-butanediol and poly(tetramethylene ether)glycol. Examples of suitable copolyetherester elastomers are commercially available under the trademark Hytre[®] from E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Alkali Metal Salt

[0040] The alkali metal salt having a molecular weight less than 300 is used in the melt mixed compositions described herein to decrease the melt flow rate of the polyester. Preferably, the alkali metal salt having a molecular weight less than 300 is selected from the group consisting of lithium salts, sodium salts, potassium salts, and mixtures of these—of which sodium is more preferred—and more preferably, selected from the group consisting of alkali metal carbonates, alkali metal benzoates, and mixtures of these. The term “sodium carbonate” refers to a compound defined by the nominal formula $\text{Na}_2\text{CO}_3 \cdot x \text{H}_2\text{O}$, wherein x is greater than or equal to zero. Examples of sodium carbonate are anhydrous sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 0 \text{H}_2\text{O}$), sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot 1 \text{H}_2\text{O}$), sodium carbonate heptahydrate ($\text{Na}_2\text{CO}_3 \cdot 7 \text{H}_2\text{O}$), sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$).

[0041] The compositions described herein are prepared by melt mixing one or more of the polyesters described herein with preferably from 0.1 to 10 weight percent, and more preferably from 0.5 to 8 weight percent, of the alkali metal salt having a molecular weight less than 300, the weight percent based on the sum of the polyester and the alkali metal salt.

Additives

[0042] The melt mixed compositions described herein may further comprise one or more heat stabilizers, antioxidants, and fillers. Examples of suitable heat stabilizers and antioxidants include diphenylamines, amides, thioesters, phenolic antioxidants, and phosphites. When used, the heat stabilizer or antioxidant are preferably from 0.01 to 5 weight percent, more preferably from 0.01 to at or about 2 weight percent, of the total weight of the sum of the polyester and the alkali metal salt.

[0043] The melt mixed compositions described herein may also comprise one or more salts of fatty acids. Fatty acids comprise a chain of alkyl groups that contains from about 2 to about 80 carbon atoms and has a terminal methyl group and a terminal carboxyl group. Fatty acids can be saturated, unsaturated or multi-unsaturated fatty acids. Examples of suitable salts of fatty acids include, but are not limited to, salts of caproic acid, caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, palmitic acid, margaric acid, stearic acid, oleic acid, arachidic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid,

and melissic acid, with the salt of stearic acid and of montacid acid being preferred. The one or more salts of fatty acids are preferably sodium or calcium salts of fatty acids. When used, the one or more salts of fatty acids are from 0.1 to 10 weight percent of the of the total weight of the melt mixed composition.

[0044] Additional additives include one or more of the following components as well as combinations of these: lubricants, UV light stabilizers, antistatic agents, coloring agents, fillers, fillers and reinforcing agents, flame retardants, impact modifiers, viscosity modifiers, nucleating agents and other processing aids known in the polymer compounding art. When used, additional additives are from 0.1 to about 50 weight percent of the total weight of the melt mixed composition.

[0045] The additives described herein may be present in these in amounts and in forms known in the art, including in the form of so-called nano-materials where at least one of the dimensions of the particles is in the range of 1 to 1000 nm.

Preparation of The Melt Mixed Compositions

[0046] The compositions described herein are melt mixed blends, wherein all of the polymeric components are well dispersed within each other and all of the non-polymeric ingredients are well-dispersed in and bound by the polymer matrix, such that the blend forms a unified whole. Any melt mixing method may be used to combine the polymeric components and non-polymeric ingredients of the present invention.

[0047] For example, 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 single or twin-screw kneader; or a Banbury mixer, either all at once through a single step addition, or in a stepwise fashion, and then melt mixed. When adding the polymeric and the non-polymeric ingredients in a stepwise fashion, a portion of the polymeric and/or the non-polymeric ingredients are added first and then melt-mixed, with the remaining polymeric and non-polymeric ingredients subsequently added and further melt-mixed until a well mixed composition is obtained. Preferably, an extruder, and more preferably, a twin-screw extruder, melt mixes these compositions. The extruder may preferably comprise a vent port and more preferably a vacuum vent port, especially when the alkali metal salt is a hydrated alkali metal salt. When long fillers, such as long

glass fibers, are present in these compositions, pultrusion may prepare a reinforced composition.

Decreasing Melt Flow Rate

[0048] Described herein are processes of decreasing the melt flow rate of the melt mixed compositions described herein, comprising a step of melt-mixing a) the one or more polyester resins selected from the group consisting of polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers; and mixtures of these described herein and b) an alkali metal salt having a molecular weight less than 300 described herein, so as to form a resin composition.

[0049] Also described herein are processes for decreasing the melt flow rate of the melt mixed compositions described herein, comprising melt mixing with the polyesters described herein an alkali metal salt having a molecular weight less than 300 to provide a melt mixed composition, wherein the melt mixed composition is characterized by 1) a reduction in melt flow rate of at least 40% as measured according to ISO 1133:1997(E) when compared to that of the polyester, and 2) a loss of tensile stress at 80°C of less than 40% as compared to tensile strength at 23°C when measured at 10% strain according to ISO 527-2/1A/50.

Articles

[0050] Compared with polyester compositions that do not comprise an alkali metal salt of molecular weight less than 300, the melt mixed compositions described herein exhibit a 40% reduction in melt flow rate (as measured according to ISO 1133:1997(E)) and a loss of tensile stress at 80°C of less than 40% as compared to tensile strength at 23°C (when measured at 10% strain according to ISO 527-2/1A/50). Consequently, these melt mixed compositions are particularly suitable for making a melt extruded article.

[0051] Thus, also described herein are processes of making an article comprising a step of shaping the melt mixed compositions described herein. As used herein, the term "shaping", refers to any technique that imparts form to an article and comprises extrusion, extrusion coating, injection molding, compression molding or blow molding. Preferably, shaping is conducted by a

melt extrusion process including blow molding, which is preferred, profile extrusion and corrugated extrusion.

[0052] The melt mixed compositions described herein are particularly suited to shaping processes in which a tube of molten resin called a parison moves under the influence of gravity, for example, in blow molding. Blow molding processes include, for example, extrusion blow molding and injection blow molding, among others, and typically begin with a step that provides a parison by extrusion or injection molding. While still in a hot moldable condition, the parison is positioned between two halves of an open mold having a mold cavity of the desired, external shape of the article. When the parison reaches the proper length, the mold halves are closed around it, the end of the hollow parison are sealed and the article made either by a) introducing pressurized air or other compressed gas into the parison, thereby inflating it to the shape of mold or expanding it against the sides of the mold cavity or by b) vacuum expansion against the surface of the mold cavity. After a cooling period, the mold is opened and the blow molded article ejected. During injection blow molding, the parison is formed by injection molding, the inner core of the mold is removed and the parison is quickly inflated while being enclosed in two mold halves as described above.

[0053] Other variants of the blow molding process are well-known in the art and include without limitation suction blow molding, coextrusion blow molding, sequential blow molding, processes involving parison manipulation or laying down, and combinations of these. In suction blow molding, the mold is closed and the parison enters it through an opening at its top surface and moves through the mold cavity by suction, generally with the help of an additional flow of gas. In coextrusion blow molding, the parison is made with layers of different materials. In sequential blow molding process, the parison is made of different materials alternating along its length.

[0054] Profile extrusion and corrugated extrusion are conventional techniques of making hollow plastic articles of arbitrary lengths. In both, the composition is extruded in a hot moldable state through the gap between the pin and the die of an extrusion head.

[0055] In profile extrusion, a hollow article is made having the same cross section

over a long length. The pin and die are shaped to produce the desired cross-section. For example, an annular die-gap between the concentric circular pin and die is used to make tubes and pipes. After exiting the die assembly, the melt may be drawn to a thinner cross section through an air gap, then cooled and the shape maintained, which results, upon solidification, in an extruded hollow body.

[0056] In corrugated extrusion, the hollow article comprises corrugated regions interrupted by smooth regions. Here, the pin and the die are positioned inside the halves of the mold blocks of the equipment. When the melt from the extrusion head reaches and enters the mold blocks, it is drawn up to the shape of the mold either by heated air or by vacuum expansion against the surface of the mold cavity. Such a process is described in U.S. Pat. No. 6,764,627, U.S. Pat. No. 4,319,872 or Int'l. Pat. App. Pub. No. WO 03/055664.

[0057] Melt extruded articles made of the melt mixed compositions described herein include fibers, filaments, containers, films and hollow bodies such as pipes, ducts, conduits, jounce bumpers, tubes/ tubing including air ducts, and constant velocity joint boots (CVJ boots). A jounce bumper (also called a bump stop, rebound bumper, end-of-travel bumper, strike-out bumper, suspension bumper, or compression bumper) is a shock-absorbing device ordinarily positioned on the top of vehicle suspensions. Jounce bumpers are elongated, generally cylindrical or conical, members with or without convolutes, made of a compressible and elastomeric material that extends around the piston rod. As taught in U.S. Patent No. 4,681,304, convoluted bumpers function by a progressive stacking of the convolutions to provide resistance to jounce forces.

[0058] The invention is further directed to the use of the alkali metal salts described herein having a molecular weight less than 300 as additives for decreasing melt flow rate of a polyester resin composition. When used as an additive for this purpose, a polyester composition that comprises the alkali metal salt is prepared by melt-mixing a mixture comprising a) one or more polyester resins selected from polyesters derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these, with said alkali metal salt b). Suitable polyester resins are those described hereinabove and wherein poly(trimethylene terephthalate) (PTT), poly(1,4-butylene terephthalate) (PBT) and copolymers and

blends of these resins are preferred. Especially preferred are copolyetherester thermoplastic elastomers are copolymers that have a multiplicity of recurring long-chain ester units and short-chain ester units joined head-to-tail through ester linkages, as described hereinabove.

[0059] The use of the alkali metal salts described herein is preferably carried out using the quantities and preferred quantities of components described herein for the processes of the invention, i.e. for the preparation of the resin compositions of the invention and the processes for making articles from the melt mixed compositions described herein. Thus, the use of the salt to manufacture articles by shaping methods that may comprise extrusion, extrusion coating, injection molding, compression molding or blow molding. Preferably, the shaping will be conducted using a melt extrusion process, for example blow molding.

EXAMPLES

[0060] The Examples provide greater detail for the processes described herein.

Materials

[0061] The materials below were used to prepare the melt mixed compositions of the Examples and Comparative Examples.

Copolyester thermoplastic elastomer 1 (TPC1): a copolyetherester elastomer containing about 40 weight percent poly(tetramethylene oxide) terephthalate and having an average molecular weight of about 1000 g/mol as copolymerized long-chain ester units, the weight percentage based on the total weight of the copolyetherester elastomer. The short-chain ester units are polybutylene terephthalate segments.

Copolyester thermoplastic elastomer 2 (TPC2): a copolyetherester elastomer containing about 77 weight percent poly(tetramethylene oxide) terephthalate and having an average molecular weight of about 2000 g/mol as copolymerized long-chain ester units, the weight percentage based on the total weight of the copolyetherester elastomer. The short-chain ester units are polybutylene terephthalate segments.

Poly(1,4-butylene terephthalate) (PBT): commercially available from E.I. du Pont de Nemours and Company, Wilmington, Delaware, USA under the trademark Crastin® 6130.

Sodium stearate: commercially available from Fluka.

Ionomer: a copolymer comprising copolymerized units of ethylene, 11 weight percent methacrylic acid, wherein about 58% of the available carboxylic acid moieties are neutralized with sodium cations.

Sodium benzoate: commercially available from Sigma-Aldrich.

Sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$): commercially available from Fluka (puriss. p.a. > 99%).

Sodium carbonate monohydrate ($\text{Na}_2\text{CO}_3 \cdot 1\text{H}_2\text{O}$): commercially available from Fluka (puriss. p.a. > 99%).

Anhydrous sodium carbonate (Na_2CO_3): commercially available from Sigma-Aldrich.

Preparation of Samples and Measurements

Compounding Method

[0061] The compositions of Examples (abbreviated as “E”) and Comparative Examples (abbreviated as “C”) were prepared by melt mixing the ingredients shown in Table 1 in a 30 mm twin screw extruder. The extruder was fitted with a vacuum vent port in the barrel. Compositions comprising a copolyester thermoplastic elastomer were prepared in the extruder operating with barrel temperature settings at about 220°C using a screw speed of about 250 rpm. Compositions comprising a poly(1,4-butylene terephthalate) were prepared in the extruder operating with barrel temperatures set at about 250°C using a screw speed of about 250 rpm.

[0062] All ingredients were introduced into the first barrel and the melt temperature of the resin composition measured with a hand-held probe was about 245°C as it exited the die. Upon exiting the extruder, the compounded mixture was extruded in the form of laces or strands, cooled, chopped into granules and placed into sealed aluminum lined bags in order to prevent moisture pick up. Ingredient quantities shown in Table 1 are given in weight percent on the basis of the total weight of the ingredients before melt-mixing them.

Melt Flow Rate

[0063] Melt flow rate was measured (Zwick 4105 instrument) on pellets according to the method of International Standard ISO 1133:1997(E) under the following conditions:

- for compositions comprising copolyester thermoplastic elastomer 1:

- temperature of 230°C under a 5 kg load,
- for compositions comprising copolyester thermoplastic elastomer 2: temperature of 220°C under a 5 kg load, and
 - for compositions comprising poly(1,4-butylene terephthalate): temperature of 250°C under a 2.16 kg load. Prior to melt flow rate measurements, the granules were dried under nitrogen for one hour at 135°C. Table 1 gives average values obtained from two samples.

Tensile properties

[0064] Prior to injection molding, the granules of the melt mixed compositions were dried to a moisture level below 0.05 percent. Tensile strength was measured according to ISO 527-2/1A/50. Measurements were made on injection molded ISO tensile bar 1A samples according to ISO 527. The thickness of the test specimen was 4 mm and the width was 10 mm.

[0065] For compositions comprising a copolyester thermoplastic elastomer, barrel temperature was 250°C; mold temperature was 80°C and hold pressure was 60 MPa. For compositions comprising a poly(1,4-butylene terephthalate), barrel temperature was 250°C; mold temperature was 80°C and hold pressure was 60 MPa.

[0066] The term tensile strength is defined in ISO 527-1 section 4.3.4 as the stress at which the strain reached the value 10 expressed in percentage using a Zwick tensile instrument. The average values of tensile strength obtained from 5 specimens are given in Table 1. Tensile stress at 10% strain was measured at 23°C and at 80°C. Tensile stress at 10% strain results and the loss of tensile stress at 10% strain from 23°C and at 80°C strain are shown in Table 1.

Table 1

	C0	C1	C2	C3	C4	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12
TPC 1	100	95.7	81.2			98.0	99.26	98.0	99.13	98.0	99.5	98	96	92			
TPC 2				100											98	95	
PBT					100												98
Na stearate		4.3															
Ionomer			18.8														
Na benzoate						2.0											
Na ₂ CO ₃							0.74	2.0									
Na ₂ CO ₃ ·1H ₂ O									0.87	2.0							
Na ₂ CO ₃ ·10H ₂ O											0.5	2	4	8	2	5	2
Na content [%]	-	0.32	0.32	-	-	0.32	0.31	0.87	0.32	0.74	0.08	0.32	0.64	1.29	0.32	0.84	0.32
MFR [g/10 min]	32.6	52.2	8.6	42.6	19.6	15.8	2.4	2.4	6.3	2.1	18.9	5.8	2.9	2.1	15.2	6.3	2.0
Tensile stress at 10% at 23°C / Mpa	10.9	10.6	10.6	1.7	54.8	13.2	11.8	-	11.7	-	-	11.1	11.5	-	1.7	1.8	58.8
Tensile stress at 10% at 80°C / Mpa	6.8	6.6	5.8	1.2	18.5	8.6	7.8	-	7.2	-	-	7.1	7.5	-	1.1	1.3	27.6
Loss of tensile stress from 23°C to 80°C	38%	38%	45%	29%	55%	35%	34%	-	38%	-	-	36%	35%	-	35%	28%	53%

Compositions of the Examples are "E" and Compositions of Comparative Examples are "C".

[0067] The data shown in Table 1 indicates that the composition prepared by melt-mixing a copolyetherester elastomer with sodium stearate (C1) exhibited greater melt flow rate relative to the copolyetherester elastomer alone (C0). Such a composition is not ideal for melt-extrusion processes, because a parison descends too rapidly.

[0068] The composition prepared by melt-mixing a copolyetherester elastomer with an ionomer (C2) according to U.S. Pat. No. 4,010,222 exhibited a reduced melt flow rate relative to the copolyetherester elastomer alone (C0). A similar decrease of melt flow rate was obtained for compositions prepared by melt-mixing a copolyetherester elastomer with sodium benzoate or sodium carbonate (E1-E11).

[0069] The composition prepared by melt-mixing a copolyetherester elastomer with an ionomer (C2) exhibited a reduced melt flow rate relative to the copolyetherester elastomer alone (C0), however, such compositions showed a relatively high loss of tensile stress when the temperature was raised from 23°C to 80°C.

[0070] In contrast, the compositions prepared by melt-mixing a copolyetherester elastomer with sodium benzoate or sodium carbonate (E1-E11) exhibited a reduced melt flow rate relative to the copolyetherester elastomer alone (C0) while maintaining good mechanical performance in terms of having a low loss of tensile stress when the temperature was raised from 23°C to 80°C related to C2.

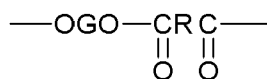
[0071] The composition prepared by melt-mixing poly(1,4-butylene terephthalate) with sodium carbonate (E12) exhibited reduced melt flow rate relative to the poly(1,4-butylene terephthalate) alone (C4) and maintained a good mechanical performance in terms of having a low loss of tensile stress when the temperature was raised from 23°C to 80°C.

[0072] The compositions prepared by melt-mixing a copolyetherester elastomer or a polyester resin with an alkali metal salt (e.g. sodium salt) having a molecular weight of less than 300 combine good melt rheology by exhibiting low melt flow rates and a good retention of mechanical properties in the solid state upon increase of temperature, especially from 23°C to 80°C.

CLAIMS

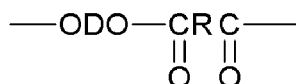
What is claimed is:

1. A use of an alkali metal salt having a molecular weight less than 300 as an additive for decreasing melt flow rate of a resin composition, said resin composition being prepared by melt-mixing a mixture comprising a) one or more polyester resins selected from polyesters being derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these, with said alkali metal salt b).
2. The use of claim 1, wherein the one or more polyester resins a) are selected from poly(trimethylene terephthalate) (PTT), poly(1,4-butylene terephthalate) (PBT) and copolymers and blends of the same.
3. The use of claim 1, wherein the one or more polyester resins a) are selected from copolyetherester thermoplastic elastomers.
4. The use of claim 3, wherein the copolyetherester thermoplastic elastomers are copolymers 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 (A):



(A)

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



(B)

wherein:

G is a divalent radical remaining after the removal of terminal hydroxyl groups from poly(alkylene oxide)glycols having preferably a number average molecular weight of between about 400 and 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 preferably less than about 250.

5. The use of claim 3 or 4, wherein the copolyetherester thermoplastic elastomers are selected from copolyetherester resins prepared from monomers comprising (1) poly(tetramethylene oxide) glycol; (2) a dicarboxylic acid selected from isophthalic acid, terephthalic acid and mixtures of these; and (3) a diol selected from 1,4-butanediol, 1,3-propanediol and mixtures of these.
6. The use of claim 3 or 4, wherein the copolyetherester thermoplastic elastomers are selected from copolyetherester resins prepared from monomers comprising (1) poly(trimethylene oxide) glycol; (2) a dicarboxylic acid selected from isophthalic acid, terephthalic acid and mixtures of these; and (3); and a diol selected from 1,4-butanediol, 1,3-propanediol and mixtures of these.
7. The use of claim 3 or 4, wherein the copolyetherester thermoplastic elastomers are selected from copolyetherester resins prepared from monomers comprising (1) ethylene oxide-capped poly(propylene oxide) glycol; (2) dicarboxylic acid selected from isophthalic acid, terephthalic acid and mixtures of these; and (3) a diol selected from 1,4-butanediol, 1,3-propanediol and mixtures of these.
8. The use of any preceding claim, wherein the alkali metal salt is present in an amount from at or about 0.1 to at or about 10 weight percent, the weight percentage being based on the total weight of the one or more resins selected from polyesters being derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these (a) and the alkali metal salt (b), i.e. the sum of components (a) and (b).
9. The use of any preceding claim, wherein the alkali metal salt having a molecular weight less than 300 is selected from lithium salts having a molecular weight less than 300, sodium salts having a molecular weight less than 300, potassium salts having a molecular weight less than 300 and mixtures of these.
10. The use of claim 9, wherein the alkali metal salt having a molecular weight less than 300 is selected from alkali metal carbonates, alkali metal benzoates and mixtures of these.
11. The use of claim 9 or 10, wherein the alkali metal salt having a molecular weight less than 300 is selected from sodium carbonates, sodium benzoates and mixtures of these.

12. The use of the resin composition recited in any preceding claim, to shape an article made by a process selected from melt extrusion, blow molding, extrusion blow molding, injection blow molding, profile extrusion and corrugated extrusion .
13. The use of the resin composition recited in any preceding claim, to make a CVJ boot or a jounce bumper.
14. A jounce bumper made substantially or entirely from a resin composition prepared by melt-mixing a composition comprising a) one or more polyester resins selected from polyesters being derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these, with said alkali metal salt b).
15. A CVJ boot made substantially or entirely from a resin composition prepared by melt-mixing a composition comprising a) one or more polyester resins selected from polyesters being derived from one or more dicarboxylic acids and one or more diols having more than two carbon atoms; copolyester thermoplastic elastomers and mixtures of these, with said alkali metal salt b)