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(54) Title: CONCENTRATES FOR IMPROVING POLYESTER COMPOSITIONS AND METHOD OF MAKING SAME			
(57) Abstract Disclosed is a concentrate useful as an additive in a polyester composition comprising a polyolefin and a polyfunctional carboxylic acid or polyol branching agent. Also disclosed is a method of preparing a polyester composition having increased melt viscosity and melt strength, and improved impact strength which comprises the steps of: A) melt compounding a polyolefin and a polyfunctional carboxylic acid or polyol branching agent, B) dry blending the melt compounded mixture formed in A) with a polyester, and C) molding or extruding the dry blended mixture formed into B) to form an article.			

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CONCENTRATES FOR IMPROVING POLYESTER
COMPOSITIONS AND METHOD OF MAKING SAME

Technical Field

5 The present invention relates to improved polyester compositions prepared from a concentrate containing a branching agent and a polyolefin, and to the method for preparing the improved polyester compositions. These compositions have improved melt viscosity, melt strength
10 and impact strength, and are particularly useful in preparing foamed articles although they are also useful in non-foamed polyester compositions.

Background of the Invention

15 Many polymeric materials are foamed to provide low density articles such as films, cups, food trays, decorative ribbons, and furniture parts. For example, polystyrene beads containing low boiling hydrocarbons such as pentane are formed into lightweight foamed cups
20 for hot drinks such as coffee, tea, hot chocolate, and the like. Polypropylene can be extruded in the presence of blowing agents such as nitrogen or carbon dioxide gas to provide decorative films and ribbons for package wrappings. Also, polypropylene can be injection molded
25 in the presence of these blowing agents to form lightweight furniture parts such as table legs and to form lightweight chairs.

 Polyesters such as poly(ethylene terephthalate) have a much higher density (e.g. about 1.3 g/cc) than
30 other polymers. Therefore, it would be desirable to be able to foam polyester materials to decrease the weight of molded parts, films, sheets, food trays, and the like. Such foamed articles also have better insulating properties than unfoamed parts. However, it is
35 difficult to foam such polyester materials because of

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the low melt viscosity and low melt strength of typical poly(ethylene terephthalate) and related polyester polymers. The low melt viscosity and low melt strength of the polyesters is a problem because the polymer melt will not adequately retain the bubbles of an expanding gas. It would be desirable therefore to be able to provide polyester polymers which could be foamed with conventional foaming systems.

One approach to provide polyesters with high melt strength involves treating preformed polyesters with multifunctional carboxylic acids or polyols to provide branched polyesters. Such compositions are disclosed in U.S. Patent Nos. 4,132,707; 4,145,466; 4,999,388; 5,000,991; 5,110,844; 5,128,383; and 5,134,028. The branching agents used include tri- and tetracarboxylic acids and anhydrides such as trimesic acid, pyromellitic acid, and pyromellitic dianhydride or polyols such as trimethylolpropane and pentaerythritol. These branching agents will provide polyesters with increased melt viscosities and melt strengths but their use is often disadvantageous. For one thing, the branching agent cannot be put into the initial reaction mixture of polyester reagents because this will lead to crosslinked structures. If added after the polyester is formed, an additional processing step is required and the branching action is hard to control. The usual method of adding the branching agent is to melt the polyester in an extruder and to add the branching agent into the melt in the barrel of the extruder. It is difficult to control the amount of branching agent used and to get adequate mixing and reaction before the melt exits the die. It would be advantageous therefore to provide a method whereby the branching agent and possibly other additives could be dry blended with the polyester pellets prior to the extrusion operation.

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Other patent references of interest with regard to foaming polymers include U.S. Patent Nos. 3,879,505; 4,149,485; 4,176,101; 4,761,256; 4,284,596; 4,351,911; 4,462,947; 4,466,933; 4,473,665; 4,626,183; 4,728,673; 5 4,734,304; 4,737,523; 4,746,478; 4,751,250; 4,981,631; and 5,182,307.

The closest prior art of which we are aware concerning polyester/polyolefin blends include U.S. Patent Nos. 4,981,631, 3,960,807, 4,572,852 and 10 5,229,432 but none of these patents are related to a master batch concept for incorporating some other agents into a polyester composition.

It has now been found that branching agents such as trimellitic acid, pyromellitic dianhydride and the like 15 can be melt compounded with polyolefin polymers to provide concentrates. These concentrates can be dry blended with polyesters such as poly(ethylene terephthalate), dried in vacuum or conventional ovens, and then extruded and foamed with conventional inert 20 gases, volatile organic compounds, or chemical blowing agents. During the melt compounding, the branching agent reacts with the polyester to provide branching and thus to increase the melt viscosity and the melt strength of the polyester. The effect of this is to 25 significantly improve the foamability and blow molding characteristics of the polyester. The polyolefin of the concentrate component is also beneficial for improving the impact properties of the polyester.

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Description of the Invention

According to one embodiment of the present invention, there is provided a concentrate useful as an additive in a polyester composition comprising

- 5 A) about 50 to about 99 wt % of a polyolefin
 selected from (1) ethylene polymers having a
 melt index of about 0 to about 100 at 190°C
 and (2) propylene polymers, 1-butene polymers,
10 having a melt flow rate of about 0 to about
 100 at 230°C, and
- B) about 1 to about 50 wt % of a polyfunctional
 carboxylic acid or polyol branching agent
 having at least 3 carboxylic or hydroxyl
15 groups or combinations thereof.

According to another embodiment of the present invention there is provided a method of preparing a polyester composition having increased melt viscosity and melt strength, and improved impact strength which
20 comprises the steps of

- A) melt compounding
- 1) about 50 to about 99 wt % of a polyolefin
 selected from (1) ethylene polymers
 having a melt index of about 0 to about
25 100 at 190°C and (2) propylene polymers,
 1-butene polymers, and copolymers of
 propylene and/or 1-butene, having a melt
 flow rate of about 0 to about 100 to
 230°C, and
- 30 2) about 1 to about 50 wt % of a
 polyfunctional carboxylic acid or polyol
 branching agent having at least 3
 carboxylic or hydroxyl groups or
 combinations thereof to form a melt
35 compounded concentrate,

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- 5 B) dry blending the melt compounded mixture formed in A) with about 80 to about 99.9 wt % of a polyester having repeat units from an aromatic, aliphatic or cycloaliphatic dicarboxylic acid having 6-40 carbon atoms and an aliphatic or cycloaliphatic glycol having 2-10 carbon atoms, said polyester having an I.V. of about 0.4-1.1, and
- 10 C) molding or extruding the dry blended mixture formed into B) to form an article.

The concentrates of this invention are useful with a wide range of polyesters such as polyesters derived from glycols containing about 2 to about 10 carbon atoms and dibasic acids containing about 6 to about 40 carbon atoms. Preferred polyesters include those derived from terephthalic acid, isophthalic acid, naphthalene-15 dicarboxylic acid, cyclohexanedicarboxylic and the like or their alkyl esters. Preferred glycols include ethylene glycol, 1,4-butanediol, 1,4-cyclohexane-20 dimethanol and the like. The polyesters may be homopolymers or copolymers containing up to about 50 mol % of other dibasic acids or glycols. Also, blends of polyesters may be used. Modifying dibasic acids (in addition to those named above) include oxalic, 25 succinic, glutaric, adipic, sebacic, suberic, dimer, sulfoisophthalic, or its metal salts, and the like. When naphthalenedicarboxylic acid is used, it may be any of the various isomers but the preferred ones include the 2,6-, 2,7-, 1,5-, and 1,6- isomers. Mixtures of the 30 various isomers may also be used. When cyclohexanedicarboxylic acid is used, it may be the 1,3-, or 1,4-isomers, and may be cis-, trans-, or a mixture of cis/trans isomers. Modifying glycols (in addition to those named above) include 1,6-hexanediol, neopentyl 35 glycol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol and the

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like. When cyclohexanedimethanol is used, it may be the 1,3- or 1,4-isomers and may be cis-, trans-, or a mixture of cis/trans isomers. These polyesters are readily made by conventional melt phase or solid state polycondensation techniques well known in the art. These polymers will generally have inherent viscosity (I.V.) values in the range of about 0.4 to about 1.1 and may be crystallizable or amorphous.

Polyolefins useful in preparing concentrates containing the branching agents include linear low density polyethylene, conventional low density polyethylene, high density polyethylene, ethylene copolymers with α -olefins containing 2 to about 10 carbon atoms, polypropylene, propylene copolymers with α -olefins containing 2 to about 10 carbon atoms, poly-1-butene, 1-butene copolymers with α -olefins containing 2 to about 10 carbon atoms, poly-4-methyl-1-pentene, 4-methyl-1-pentene copolymers with α -olefins containing 2 to about 10 carbon atoms and the like. The ethylene polymers will have melt index values (measured by ASTM Method No. D1238-56T) of about 0 to about 100 at 190°C with preferred melt index values of about 0.1 to about 20. Propylene and 1-butene polymers will have melt flow rate values (measured by ASTM Method No. D1238-56T) of about 0 to about 100 at 230°C with preferred melt flow rates of about 0.1 to about 20 at 230°C. These olefin polymers are readily prepared by conventional methods and many of them are commercially available.

The branching agent preferably has a molecular weight of about 50-5000, more preferably, 92-3000 and a functionality of about 3-6. The branching agent may be a polyol having 3-6 hydroxyl groups, a polycarboxylic acid having 3 or 4 carboxyl groups or a hydroxy acid having a total of 3-6 hydroxyl and carboxyl groups.

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Representative polyols that function as branching agents include glycerol, trimethylolpropane, pentaerythritol, 1,2,6-hexanetriol, sorbitol, 1,1,4,4-tetrakis (hydroxymethyl)cyclohexane, tris(2-hydroxyethyl) isocyanurate, and dipentaerythritol. In addition to those low molecular weight polyols, higher molecular weight polyols (MW 400-3000), particularly triols derived by condensing alkylene oxides having 2-3 carbons, e.g., ethylene oxide, propylene oxide with polyol initiators, which have 3-6 carbons, e.g., glycerol, can also be used as branching agents.

Representative polycarboxylic acids that can be used as branching agents include hemimellitic or trimellitic acid, trimesic acid, pyromellitic acid, 1,1,2,2-ethanetetracarboxylic acid, 1,1,2-ethanetricarboxylic acid, 1,3,5-pentanetricarboxylic acid, and 1,2,3,4-cyclopentanetetracarboxylic acid. Although the acids may be used as such, preferably they are used in the form of their lower alkyl esters or (most preferably) as their cyclic anhydrides in those instances where cyclic anhydrides can be formed.

Representative hydroxy acids that can be used as branching agents include malic acid, citric acid, tartaric acid, 3-hydroxyglutaric acid, mucic acid, trihydroxyglutaric acid, and 4-(beta-hydroxyethyl)-phthalic acid. Such hydroxy acids contain a combination of 3 or more hydroxyl and carboxyl groups.

Especially preferred branching agents include trimellitic anhydride, trimesic acid, oxypropylated triols (optionally capped with ethylene oxide) having molecular weight of 400-3000 and tris(2-hydroxyethyl) isocyanurate.

An antioxidant may be added to the composition in an amount of up to 2 percent by weight of the polyester.

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Generally, the amount of antioxidant that is added to and incorporated in the polyester is from about 0.1-1% by weight of the polyester. The antioxidants can be added with the monomers prior to the formation of the polyester polymer or, if desired, they can be added to the molten polymer after polymerization has been completed. Preferably, the antioxidant is added with the monomers before polymerization is initiated.

Properties of these polyester compositions can also be modified by incorporation of various conventional organic fillers, such as carbon black, silica gel, alumina, clays and chopped fiber glass. Improvement in light stability is possible by the addition of small amounts of pigments or the incorporation of a light stabilizer, such as ultraviolet light absorbers. Flame retardants, lubricants and extenders can also be added to the compositions.

The concentrate is prepared by melt blending the polyolefin and branching agent by well known means until a homogeneous blend is obtained. Other conventional additives can be melt blended at this time. The concentrates are readily prepared by melt mixing the polyolefin and the branching agent in an extruder, Banbury mixer or other conventional melt mixing device and the master batch is then extruded and pelletized. The concentration of the branching agent is generally in the range of about 1 to about 50 weight % based on the weight of the concentrate but the preferred range is about 5 to about 20%. In addition to the branching agent, other components such as nucleating agents, colorants, pigments, fillers, antioxidants and the like may also be incorporated in the polyolefin master batch.

When the concentrates are mixed with polyesters in the melt at elevated temperatures, the resulting branched polyesters are useful in a variety of end uses

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including the manufacture of films, tubes, foams, blow
molded objects, extrusion coated materials, food
packaging containers, injection molded parts and the
like. The blend is dried in conventional or vacuum
5 ovens and extruded or molded by conventional techniques.

Although the concentrate and method according to
the present invention can be used in many molding or
extrusion applications, i.e., such as injection molding,
injection blow molding, extrusion, extrusion blow
10 molding, etc., to form non-foamed products, a preferred
product is a foamed article. Foaming polymers is a
process well known in the art.

Extrusion techniques common to those skilled in the
art can be used to foam the polyester and concentrate of
15 the present invention, preferably to densities less than
1.1 g/cc more preferably, densities of less than about
0.9 g/cc are achieved.

In a typical foam extrusion process, the basic
apparatus comprises a single extruder (preferably a
20 length to diameter ratio of at least about 30:1), a
liquid injection pump or gas cylinder with injector
valves, a die to form the desired object, a cooling
device and a device to collect the expanded, extruded
product.

25 In such a process a two-stage screw is typically
used but is not critically necessary. The polyester and
concentrate are preferably added to the extruder feed
hopper and fed to the feed section of the screw. The
polyester and concentrate are melted in the transition
30 section of the screw and the blowing agent added either
in the transition section of the screw or near the
beginning of the metering section.

Suitable blowing agents for the present invention
include inert gases, such as nitrogen and carbon
35 dioxide, hydrocarbons boiling about -40°C to about 45°C ,

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such as propane, butane and pentane; hydrofluorocarbons and hydrochlorofluorocarbons; and gas liberating chemical blowing agents, such as sodium bicarbonate, a combination of citric acid and sodium bicarbonate, a
5 combination of citric acid and sodium carbonate, azodicarbonamid and various endothermic blowing agents which release CO₂. Mixtures of blowing agents can also be used. Blowing agents are used in amounts of about 0.1 to about 20% (by weight based upon the weight of the
10 polyester and blowing agent) to obtain the desired high expansion ratios. Concentrations of about 0.1 to about 5 percent are typical.

The resin melt containing dissolved and/or dispersed blowing agent is metered by the screw to the
15 die. Upon exiting the die, the melt is expanded, optionally shaped, cooled and collected. The temperature profile on the extruder and die is adjusted to melt the polyester in the extruder prior to the injection of the blowing agent and adequately cool the
20 melt/blowing agent composition to allow for expansion without coalescence.

Another typical foam extrusion process employs two tandem extruders. In this process the polyester is mixed, melted and the blowing agent injected in the
25 first extruder. The melt/blowing agent composition is transferred by means of a conventional transfer tube to the feed section of the second extruder which is used to transfer the melt blend to the die and to bring the melt temperature and pressure in the die to the values
30 necessary for optimum foam formation. Typically the two extruders are of different sizes. The tandem extruder process allows for excellent control of process variables.

As is apparent to those of ordinary skill in the
35 art, various screw configurations and designs typical

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for this application can be used to prepare foamed polyesters. Mixers can be added to the screw or as independent components to disperse additives, nucleation agents, and blowing agents. Twin screw extruders can be used.

The following examples are submitted for a better understanding of the invention:

Example 1 - Preparation of Concentrate Based on Linear Low Density Polyethylene - A physical blend is prepared using 15.66 lb of linear low density polyethylene (melt index 0.9; density 0.919), 2.0 lb of pyromellitic dianhydride branching agent, 2.0 lb of sodium carbonate, 0.34 lb talc, and 0.1 lb of Ethanox 330 antioxidant. The blend is tumbled in a stainless steel vessel and purged with nitrogen to exclude air. The blend is then melt blended at 400°F (204°C) in a Werner and Pfleiderer extruder using mixing type 30 mm twin screws. The extrudate in the shape of a rod (2-3 mm in diameter) is quenched in a cold water trough, chopped into pellets, and then the pellets are air dried. The sodium carbonate and talc are present to act as foam nucleating agents.

Example 2 - Preparation of Concentrate Based on Linear Low Density Polyethylene - The procedure of Example 1 is repeated using 17.66 lb of linear low density polyethylene (melt index 0.9; density 0.919), 2.0 lb of pyromellitic dianhydride, 0.34 lb of TiO₂ nucleating agent and 0.05 lb of Ethanox 330 antioxidant.

Example 3 - Preparation of Concentrate Based on Linear Low Density Polyethylene - The procedure of Example 1 is repeated using 15.66 lb of linear low density polyethylene (melt index 0.9; density 0.919), 2.0 lb of pyromellitic dianhydride, 2.0 lb of sodium carbonate, 0.34 lb of TiO₂, and 0.02 lb of Ethanox 330 antioxidant.

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Example 4 - Preparation of Concentrate Based on Conventional Low Density Polyethylene - The procedure of Example 1 is repeated using 17.66 lb of conventional low density polyethylene (melt index 4.0; density 0.917),
5 2.0 lb of pyromellitic acid, 0.34 lb of TiO_2 and 0.02 lb of Irganox 1076 antioxidant.

Example 5 - Preparation of Concentrate Based on High Density Polyethylene - The procedure of Example 1 is repeated using 16.62 lb of high density polyethylene
10 (melt index 0.1; density 0.965), 3.0 lb of trimellitic anhydride branching agent, 0.34 lb of china talc nucleating agent, and 0.04 lb of Irganox 1010 antioxidant.

Example 6 - Preparation of Concentrate Based on Polypropylene - The procedure of Example 1 is repeated
15 using 17.66 lb of polypropylene (melt flow rate 1.2), 3.0 lb of pyromellitic dianhydride branching agent, 0.34 lb of TiO_2 nucleating agent, 0.04 lb of dilauryl thiodipropionate and 0.02 lb of Irganox 1010. The
20 latter two compounds are present as heat stabilizers and antioxidants.

Example 7 - Preparation of Concentrate Based on a Propylene Copolymer - The procedure of Example 1 is
repeated using 17.66 lb of propylene copolymer
25 containing 3 mol % ethylene (melt flow rate 0.5), 2.0 lb of pentaerythritol branching agent, 0.34 lb of TiO_2 , 0.04 lb of dilauryl thiodipropionate, 0.02 lb of Irganox 1010, and 0.02 lb of Weston 619 stabilizer.

Example 8 - Preparation of Concentrate Based on a Propylene Copolymer - The procedure of Example 1 is
30 repeated using 17.66 lbs. of propylene copolymer containing 5 mol % 1-butene (melt flow rate 3.5), 3.0 lbs. of pyromellitic dianhydride, 0.34 lbs. of TiO_2 , 0.04 lbs. of dilauryl thiodipropionate, and 0.02 lbs. of
35 Irganox 1010.

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Example 9 - Foaming of Poly(ethylene terephthalate)
(PET) - Dried pellets of poly(ethylene terephthalate)
(I.V 0.90) and dried pellets of the linear low density
polyethylene concentrate from Example 1 are thoroughly
5 mixed in a 20:1 ratio (wt/wt) in a stainless steel
vessel and the blend is fed manually into a tandem
extruder consisting of a 2-inch primary extruder capable
of injecting a gaseous blowing agent under high pressure
into the polymeric melt and a 2.5-inch secondary
10 extruder which allows the melt to foam under reduced
pressure and then extrudes it through an annular die
(3-inch diameter) located at the end of the second
extruder. The two extruders are connected through a
well-known low pressure crossover zone. The gaseous
15 blowing agent used in this example is isopentane. The
extruders, the crossover zone, and the annular die are
heated at 500-525°F (260-274°C) through their entire
length as noted below:

20 2-inch primary extruder = 500°F (260°C)
 Crossover Zone = 500°F (260°C)
 2.5-inch secondary extruder = 500°F (260°C)
 Annular 3-inch die = 525°F (274°C)

25 Other relevant extrusion conditions and parameters
are as follows:

Pressures (psi)

2-inch extruder	5600 - 6000
30 Crossover Zone	3740 - 3860
2.5-inch extruder	2210 - 2230
Isopentane injection	3250 - 5600

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Extrusion Rates

	2-inch extruder	87 rpm
	2.5-inch extruder	16.4 rpm
	Polymer output	66 lb/hr
5	Isopentane injected	1.6 lb/hr

Under these conditions, the PET concentrate mixture described above extrudes with the desired characteristics needed to produce good foam. The foam coming from the annular die has a dry hand and good melt strength so that it can be readily stretched over a water cooled mandrel. The foam is slit and collected as a sheet 36 inches wide. The thickness and density of the foam respond well to changes in the line-speed and isopentane level. The foam produced has a density of 0.19 g/cc at a thickness of 56 μm . It has an I.V. of 0.79 and a GPC weight average molecular weight of 71898 and a M_z/M_n ratio of 8.94. It also has a crystallinity of 14.78% as measured by DSC. Scanning Electron Microscopy and Confocal Light Microscopy show the cell structure to be well formed with all cells being closed and of 100-200 μm diameter in size. The foam shows good post-expansion properties as described below.

25 Post Expansion:

(a) A small piece of the foam produced above is immersed in boiling water for 2 minutes and then cooled to room temperature. Its thickness is measured using a FOWLER micrometer at several points along the foam surface and the average thickness is 89 μm , which is a 59% increase from the as-produced foam. The density of this post-expanded foam is measured to be 0.096 g/cc. It has a crystallinity of 31.21% as measured by DSC.

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Scanning Electron Microscopy and Confocal Light Microscopy show the cell structure to be well formed with all cells being closed and of 200-400 μm diameter in size.

5

(b) A small piece of the foam is also post-expanded in a conventional air-oven at 175°C for 3 minutes. This foam has an average thickness of 73 μm , and a density of 0.135 g/cc. It has a crystallinity of 31.74% as measured by DSC. Scanning Electron Microscopy and Confocal Light Microscopy show the cell structure to be well formed with all cells being closed and of 200-300 μm diameter in size.

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Similarly good foaming results are achieved using PET/concentrate blends which are mixed at ratios of 25:1 and 15:1.

20

Similarly good results are also obtained when nitrogen or carbon dioxide gas is used instead of the isopentane as the blowing agent.

25

Similarly good foaming results are achieved when the polyester/master batch is dusted with 2 wt % of the chemical blowing agent azodicarbonamide prior to the extrusion process instead of using the isopentane blowing agent.

30

Similarly good foaming results are also achieved when a combination of a chemical blowing agent and a gas blowing agent is used. Thus, the polyester/master batch blend is dusted with 0.5 wt % of the chemical blowing agent azodicarbonamide prior to the extrusion process, and then the isopentane blowing agent is used during the extrusion process as described above.

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Example 10 - Foaming of Branched Poly(ethylene terephthalate) Polymer - The procedure of Example 9 is repeated using a 20:1 blend of a branched poly(ethylene terephthalate) copolyester containing 0.3 mol %
5 trimellitic anhydride (I.V. 0.68) and the concentrate of Example 2. The foam produced has a dry hand and good cell structure.

Similarly good results are achieved when poly(ethylene terephthalate) copolyester containing
10 0.2 mol % of either trimellitic acid or pyromellitic dianhydride is foamed using the master batch of Example 2.

Example 11 - Foaming of a Poly(ethylene terephthalate) Copolyester - The procedure of Example 9
15 is repeated using a 20:1 blend of a poly(ethylene terephthalate) copolyester containing 3.5 mol % of 1,4-cyclohexanedimethanol (I.V. 0.80) and the concentrate of Example 3. The foam produced has a dry hand and good, uniform cell structure.

20 Similarly good results are achieved when the concentrates of Examples 4, 5, and 6 are used instead of the master batch from Example 3.

Example 12 - Foaming of Poly(1,4-cyclohexylene-dimethylene terephthalate) - The procedure of Example 9
25 is repeated using a 20:1 blend of poly(1,4-cyclohexylenedimethylene terephthalate) (I.V. 0.77) and the concentrate of Example 7. The foam produced has a dry hand and a good, uniform cell structure.

Similarly good results are achieved when the
30 concentrates of Example 1 and Example 8 are used instead of the concentrate of Example 7.

Example 13 - Foaming of a Poly(ethylene terephthalate) Copolyester - The procedure of Example 9
is repeated using a 20:1 blend of a poly(ethylene
35 terephthalate) copolyester containing 31 mol %

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1,4-cyclohexanedimethanol (I.V. 0.75) and the concentrate of Example 1. The foam produced has a dry hand and good, uniform cell structure.

Similarly good results are achieved using
5 poly(ethylene terephthalate) copolyesters containing 17 mol % diethylene glycol (I.V. 0.74) or 37 mol % diethylene glycol (I.V. 0.74).

Example 14 - Foaming of a Poly(1,4-Cyclohexylene-
dimethylene terephthalate) Copolyester - The procedure
10 of Example 9 is repeated using a 20:1 blend of a poly(1,4-cyclohexylenedimethylene terephthalate) copolyester containing 34 mol % ethylene glycol (I.V. 0.75) and the concentrate of Example 1. The foam
15 produced has a dry hand and good, uniform cell structure.

Similarly good results are achieved when
poly(1,4-cyclohexylenedimethylene terephthalate)
copolymers containing 5 mol % isophthalic acid (I.V.
0.95), 17 mol % isophthalic acid (I.V. 0.77) or 10 mol %
20 2,6-naphthalenedicarboxylic acid (I.V. 0.72) are used.

Example 15 - Foaming of Poly(ethylene
2,6-naphthalenedicarboxylate) - The procedure of Example
9 is repeated using a 20:1 blend of poly(ethylene
2,6-naphthalenedicarboxylate) (I.V. 0.70) and the
25 concentrate of Example 1. The foam produced has a dry
hand and good, uniform cell structure.

Similarly good foaming results are achieved when
the polyester/master batch blend is dusted with 2 wt. %
of the chemical blowing agent azodicarbonamide prior to
the extrusion process instead of using the isopentane
30 blowing agent.

The foamed compositions described in the above
examples have improved melt viscosity. For example, a
0.9 I.V. PET has a melt viscosity of about 19,000 poise
35 at 280°C. When branched with 0.6% pyromellitic

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dianhydride from the concentrate, the melt viscosity is about 117,000 poise at 280°C.

Inherent viscosity is measured in a 60/40 solution of phenol/tetrachloroethane at a concentration of
5 0.5 gram polymer per 100 ml, at 25°C.

Molecular weight is measured by gel permeation chromatography (GPC).

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

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CLAIMS

1. A concentrate useful as an additive in a polyester composition comprising
 - 5 A) about 50 to about 99 wt % of a polyolefin selected from (1) ethylene polymers having a melt index of about 0 to about 100 at 190°C and (2) propylene polymers, 1-butene polymers and copolymers of propylene and/or 1-butene
10 having a melt flow rate of about 0 to about 100 at 230°C, and
 - B) about 1 to about 50 wt % of a polyfunctional carboxylic acid or polyol branching agent having at least 3 carboxylic or hydroxyl
15 groups or combinations thereof.
2. The concentrate according to Claim 1 wherein said polyolefin is polyethylene or copolymers of
20 ethylene with α -olefins having 2 to 10 carbon atoms.
3. The concentrate according to Claim 1 wherein said branching agent is selected from trimesic acid, pyromellitic acid, pyromellitic dianhydride,
25 trimellitic anhydride, 1,2,3,4-benzenetetra-carboxylic acid, glycerine, trimethylolpropane and pentaerythritol.
4. The method of preparing a polyester composition
30 having increased melt viscosity and melt strength, and improved impact strength which comprises the steps of
 - A) melt compounding
 - 35 1) about 50 to about 99 wt % of a polyolefin selected from (1) ethylene polymers

- 20 -

- 5 having a melt index of about 0 to about 100 at 190°C and (2) propylene polymers, 1-butene polymers, and copolymers of propylene and/or 1-butene, having a melt flow rate of about 0 to about 100 at 230°C, and
- 10 2) about 1 to about 50 wt % of a polyfunctional carboxylic acid or polyol branching agent having at least 3 carboxylic or hydroxyl groups or combinations thereof to form a melt compounded concentrate,
- 15 B) dry blending the melt compounded mixture formed in A) with about 80 to about 99.9 wt % of a polyester having repeat units from an aromatic, aliphatic or cycloaliphatic dicarboxylic acid having 6-40 carbon atoms and an aliphatic or cycloaliphatic glycol having 2-10 carbon atoms, said polyester having an I.V. of about 0.4-1.1, and
- 20 C) molding or extruding the dry blended mixture formed in B) to form an article.
- 25 5. The method according to Claim 4 wherein said polyolefin is polyethylene or copolymers of ethylene with α -olefins having 2 to 10 carbon atoms.
- 30 6. The method according to Claim 4 wherein said branching agent is selected from trimesic acid, pyromellitic acid, pyromellitic dianhydride, trimellitic anhydride, 1,2,3,4-benzenetetracarboxylic acid, glycerine, trimethylolpropane and pentaerythritol.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/10640

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J3/22 C08K5/53 C08K5/09 //C08L23:02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J C08K

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 76-87888X[47] & JP,A,51 114 447 (ASAHI CHEMICAL IND. KK.) 9 October 1976 see abstract ---	1,2
A	EP,A,0 552 813 (SEKISUI KASEIHIN KOGYO KK.) 28 July 1993 see page 5, line 38 - line 41 see claims 1,13-15 ---	1
A	GB,A,2 172 601 (THE GOODYEAR TIRE & RUBBER COMPANY) 24 September 1986 see claims 1,4 --- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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

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Date of the actual completion of the international search

12 January 1995

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INTERNATIONAL SEARCH REPORT

Int. l. Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE,A,24 35 294 (GENERAL ELECTRIC CO.) 13 February 1975 see claims 1,8,11-13 see example 9 ---	1
P,A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93-392867[49] & JP,A,5 295 241 (DENKI KAGAKU KOGYO KK.) 9 November 1993 see abstract -----	1

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