Title: NUCLEATION COMPOSITIONS FOR POLYESTER COMPOSITE, FLAME RETARDANT POLYESTER COMPOSITE MOLDING COMPOSITIONS FOR INJECTION MOLDING AND PREPARATION THEREOF

Abstract: Nucleation compositions for polyester composites, flame retardant polyester composite molding compositions, and methods of preparing flame retardant polyester composite molding compositions are provided. An exemplary terephthalate nucleation composition includes about 10 wt.% to about 60 wt.% of a nucleation agent comprising a neutralized acid copolymer or a salt of a hydrocarbon acid having 20 to 35 carbon atoms or tere or a metal stearate or a combination thereof; and about 40 wt.% to about 90 wt.% of a plasticizer comprising a polyethylene alcohol or a polyester resin or mixtures thereof. The weight percents are based on a total weight of the nucleation composition.
NUCLEATION COMPOSITIONS FOR A POLYESTER COMPOSITE, FLAME RETARDANT POLYESTER COMPOSITE MOLDING COMPOSITIONS FOR INJECTION MOLDING, AND METHODS OF PREPARING FLAME RETARDANT POLYESTER COMPOSITE MOLDING COMPOSITIONS

TECHNICAL FIELD

[0001] The technical field generally relates to polyester composites for injection molding and methods for preparing such polyester composites. More particularly, the technical field relates to nucleation compositions for polyester composite, flame retardant polyester composite molding compositions, and methods for preparing flame retardant polyester composite molding compositions.

BACKGROUND

[0002] Injection molding generally consists of high pressure injection of heated raw materials, such as a thermoplastic polymer, into a mold. During this process, raw materials are fed into a heated barrel, mixed, and forced into a mold cavity where the injected material cools and hardens to the configuration of the cavity. As a manufacturing technique, injection molding is ubiquitous in the modern world, with a variety of raw materials being suitable for the manufacture of a variety of articles. However, certain physical properties including the crystallization rate of the raw materials dictate particular injection molding conditions and affect physical properties of the resulting articles. For instance, the degree of crystallization that occurs during the cooling of an article prepared from a thermoplastic polymer resin will impact the resistance of the resulting article to deformation due to heating.

[0003] Polyethylene terephthalate (PET) has excellent chemical resistance, mechanical properties, and electrical characteristics and is relatively inexpensive compared to many polyester composites. Thus, PET finds widespread use for the production of numerous items, such as fibers, films, and bottles, by injection molding. However, PET has an extremely slow crystallization rate. To accommodate for slow crystallization rates, injection molding processes must be carefully controlled with a very narrow window of appropriate molding conditions and long cycle times in order to obtain injected molded articles with a desired set of physical properties. Furthermore, slow crystallization rates cause low
crystallinity and low heat resistance in the resulting articles. This low heat resistance limits the application of PET in a variety of industries, such as electrical & electronic (E&E) and automobile industries, which often require high heat resistance of plastic parts.

[0004] In efforts to improve crystalline rates, nucleating agents have been added to PET composites. By definition, nucleation is the first step in crystallization. Thus, a nucleating agent is an agent that facilitates crystal formation. Increased crystal formation during cooling of an article injected molded from a PET resin leads to improved heat resistance. Such agents often lead to PETs with improved crystallization rates and higher heat resistance performance in the resulting articles, but to date these efforts have not shown sufficient performance enhancements to expand use of PET into industries with high heat resistance requirements for plastics.

[0005] Other attempts to improve heat resistance of PETs have included the addition of a plasticizer with a nucleating agent in a PET composite formulation. However, plasticizers act to soften (i.e., lower the tensile strength) of injection molded articles. This reduction in tensile strength is typically so extensive that articles made from PET/plasticizer composites are not suitable for applications requiring high heat resistance and high tensile strength. Thus far, finding a PET composite formulation with a balance of satisfactory performance characteristics, including high heat resistance and satisfactory tensile strength, from formulations that include plasticizers and nucleating agents has proven elusive.

[0006] A further complication to preparation of polyester formulations for certain articles is that for some applications, the articles must be flame retardant. Flame retardance is commonly improved in polyester composite articles via the inclusion of one or more flame retardant components, several of which are known in the art. However, inclusion of flame retardant components typically reduces the effectiveness of co-present nucleating agents. Thus, as flame retardance increases, the ability of a polyester composite article to withstand elevated temperatures without deformation (i.e., heat performance) is diminished in prior art composites.

[0007] Accordingly, it is desirable to provide nucleation compositions for flame retardant polyester resin compositions that result in injected molded articles that have a balance of physical properties, including improved high heat resistance without significant loss of tensile strength, to meet the requirements of E&E and automobile industry. It is also
desirable to provide such flame retardant polyester composite molding compositions and methods for preparing such flame retardant polyester composite molding compositions. Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the foregoing technical field and background.

**BRIEF SUMMARY**

[0008] Nucleation compositions for polyester composites, flame retardant polyester composite molding compositions, and methods for preparing flame retardant polyester composite molding compositions are provided. In one exemplary embodiment, a terephthalate nucleation composition comprises about 10 wt.% to about 60 wt.% of a nucleation agent comprising a neutralized acid copolymer or a salt of a hydrocarbon acid having 20 to 35 carbon atoms or talc or a metal stearate or a combination thereof; and about 40 wt.% to about 90 wt.% of a plasticizer comprising a polyethylene alcohol or a polyester resin or mixtures thereof. The weight percents are based on a total weight of the nucleation composition.

[0009] In another exemplary embodiment, a flame retardant polyester composite molding composition is provided. In this embodiment, the flame retardant polyester composite molding composition comprises about 40% to about 80% by weight of a polyester resin, about 10% to about 20% by weight of a flame retardant, about 0% to 40% by weight of a filler, and about 0.5% to about 5% by weight of a nucleation composition, with all weights based on the total weight of the flame retardant polyester composite molding composition. In this embodiment, the nucleation composition comprises about 10 wt.% to about 60 wt.% of a nucleation agent comprising a neutralized acid copolymer or a salt of a hydrocarbon acid having 20 to 35 carbon atoms or talc or a metal stearate or a combination thereof, and about 40 wt.% to about 90 wt.% of a plasticizer comprising a polyethylene alcohol or a polyester resin or mixtures thereof. The weight percents are based on a total weight of the nucleation composition.

[0010] In another exemplary embodiment, a method for preparing a flame retardant polyester composite molding composition is provided. The method includes mixing about 40% to about 80% by weight of a polyester resin, about 10% to about 20% by weight of a flame retardant, about 0% to 40% by weight of a filler, and about 0.5% to about 5% by
weight of a nucleation composition, with all weights based on the total weight of the flame retardant polyester composite molding composition. In this embodiment, the nucleation composition comprises about 10 wt.% to about 60 wt.% of a nucleation agent comprising a neutralized acid copolymer or a salt of a hydrocarbon acid having 20 to 35 carbon atoms or talc or a metal stearate or a combination thereof, and about 40 wt.% to about 90 wt.% of a plasticizer comprising a polyethylene alcohol or a polyester resin or mixtures thereof. The weight percents are based on a total weight of the nucleation composition.

DETAILED DESCRIPTION

[0011] The following detailed description is merely exemplary in nature and is not intended to limit the exemplary compositions of methods described herein. Furthermore, there is no intention to be bound by any theory presented in the preceding background or the following detailed description.

[0012] Nucleation compositions comprising mixtures of a nucleation agent and a plasticizer for preparing a flame retardant polyester composite molding composition are provided herein. Also provided herein are flame retardant polyester composite molding compositions and methods of making the same. Nucleation compositions provided herein allow for preparation of articles derived from flame retardant polyester composite molding compositions that exhibit high heat resistance without excessive loss of tensile strength.

[0013] In particular, the nucleation compositions described herein may be combined with one or more polyester resins, referred to herein as a polyester composite, and one or more flame retardants to prepare a flame retardant polyester composite molding composition that may serve as the raw material for injection molding flame retardant polyester articles. In some embodiments, the nucleation compositions are combined with a polyethylene terephthalate (PET) resin and/or polybutylene terephthalate (PBT), one or more flame retardant agents, and optionally a filler material, to prepare a flame retardant polyester composite molding composition suitable for injection molding. Articles prepared via injection molding of the flame retardant polyester composite molding composition described herein are flame retardant and exhibit high heat performance characteristics without the normally accompanying degree of reduction in tensile strength.

[0014] In an exemplary embodiment, the nucleation composition for a flame retardant polyester composite molding composition comprises a nucleation agent and a plasticizer. It
is believed that the nucleation composition contemplated herein induces small and regular crystalline structure of the polyester composite during cooling after injection molding and suppresses large crystalline growth that results in brittleness. In some embodiments, the nucleation composition for the flame retardant polyester composite molding composition consists essentially of a nucleation agent and a plasticizer. In some embodiments, the nucleation composition contains about 10 weight percent (wt.%) to about 60 wt.% nucleation agent, for example, about 20 wt.% to about 60 wt.%, for example, about 30 wt.% to about 60 wt.%, for example, about 40 wt.% to about 60 wt.%, for example, about 10 wt.% to about 50 wt.%, for example, about 10 wt.% to about 40 wt.%, for example, about 10 wt.% to about 30 wt.%, for example, about 20 wt.% to about 50 wt.%, for example, about 30 wt.% to about 40 wt.% nucleation agent. In some embodiments, the nucleation agent contains about 40 wt.% to about 90 wt.% plasticizer, for example, about 50 wt.% to about 90 wt.%, for example, about 60 wt.% to about 90 wt.%, for example, about 70 wt.% to about 90 wt.%, for example, about 40 wt.% to about 80 wt.%, for example, about 40 wt.% to about 70 wt.%, for example, about 40 wt.% to about 60 wt.%, for example, about 40 wt.% to about 50 wt.%, for example, about 50 wt.% to about 60 wt.%, for example, about 60 wt.% to about 70 wt.%, for example, about 70 wt.% to about 80 wt.%, for example, about 80 wt.% to about 90 wt.%, for example, about 50 wt.% to about 70 wt.%, for example, about 50 wt.% to about 80 wt.%, for example, about 50 wt.% to about 90 wt.% for example, about 60 wt.% to about 80 wt.%, for example, about 60 wt.% to about 90 wt.% plasticizer.

[0015] In some embodiments, the nucleating agent is an ionomer. In some embodiments, the ionomer comprises a neutralized acid copolymer. Examples of neutralized acid copolymers suitable for use herein include neutralized ethylene/acrylic acid copolymers, neutralized ethylene/methacrylic copolymers, and mixtures thereof. In some embodiments, the ionomer comprises a neutralized ethylene/acrylic acid copolymer, where the ethylene to acrylic ratio is about 95:5 to about 80:20. In some embodiments, the ionomer comprises a neutralized ethylene/methacrylic acid copolymer, where the ethylene to methacrylic ratio is about 95:5 to about 85:15. The neutralized acid copolymer may be neutralized with one or more alkali, alkaline earth, or transition metals, such as lithium (Li), sodium (Na), potassium (K), calcium (Ca), zinc (Zn), and magnesium (Mg). In some particular embodiments, the neutralized acid copolymer has been neutralized with sodium. In some related embodiments, the neutralized acid copolymer has been neutralized with
sodium, such that about 25% to about 100%, such as about 50% to about 100%, of the carboxylic groups in the acid copolymer have been neutralized by sodium.

[0016] In some embodiments, the nucleating agent comprises a salt of a hydrocarbon acid having from 20 to 35 carbon atoms. Exemplary salts of hydrocarbon acids include salts of arachidic acids, hencosanoic acids, behenic acids, tricosanoic acids, lignoceric acids, pentacosanoic acids, cerotinic acids, heptacosanoic acids, montanic acids, melissic acids, lacceroic acids, ceromelissic acids, geddic acids, ceroplastic acids, and mixtures thereof. In some embodiments, the salt is a sodium or potassium salt. An example of a salt of a hydrocarbon acid suitable for use as a nucleating agent herein includes a sodium salt of a montanic acid.

[0017] In some embodiments, the nucleating agent is a magnesium-comprising compound, particularly, hydrated magnesium silicate with the chemical formula Mg$_3$Si$_3$O$_8$(OH)$_2$ (hereinafter referred to as "talc"). In an exemplary embodiment, the talc has particle size distribution D50 in the range of from about 1 micrometer ($\mu$m) to 50 $\mu$m.

[0018] In some embodiments, the nucleating agent is a metal stearate, for example, calcium stearate, magnesium stearate, sodium stearate, zinc stearate, or combinations thereof. In an exemplary embodiment, the nucleating agent is magnesium stearate (Mg(Ci8H$_{17}$O$_2$)2). In another exemplary embodiment, the magnesium stearate has a particle size distribution D50 in the range of from 1 $\mu$m to 100 $\mu$m.

[0019] In an exemplary embodiment, the plasticizer comprises one or more polymeric polyols, such as one or more polyethylene alcohols, polyester resins, or combinations thereof. An example of a polyethylene alcohol suitable for use as a plasticizer herein includes a polyethylene glycol (PEG). In some related embodiments, the plasticizer comprises a PEG with a number average molecular weight from about 200 to 20,000 Daltons. An example of a polyester resin suitable for use as a plasticizer herein includes polybutylene succinate (PBS). In some embodiments, the PBS has a number average molecular weight of from about 50,000 to about 200,000 Daltons. In some embodiments, the plasticizer comprises PEG and PBS. In some embodiments, the plasticizer consists essentially of PEG and PBS. In some embodiments, the plasticizer comprises one or more PEGs with a number average molecular weight from about 200 to 20,000 Daltons, and polybutylene succinate (PBS) with a number average molecular weight of from about
50,000 to about 200,000 Daltons. In some embodiments, the plasticizer comprises about 5 wt.% to about 75 wt.% PEG, for example, about 10 wt.% to about 75 wt.%, for example, about 20 wt.% to about 75 wt.%, for example, about 30 wt.% to about 75 wt.%, for example, about 40 wt.% to about 75 wt.%, for example, about 50 wt.% to about 75 wt.%, for example, about 60 wt.% to about 75 wt.%, for example, about 5 wt.% to about 65 wt.%, for example, about 5 wt.% to about 55 wt.%, for example, about 5 wt.% to about 45 wt.%, for example, about 5 wt.% to about 35 wt.%, for example, about wt.% to about 25 wt.% of a PEG. In some embodiments, the plasticizer contains 0 to about 65 wt.% PBS, for example, 0 to about 55 wt.%, for example, 0 to about 45 wt.%, for example, 30 to about 55 wt.%, of a PBS.

[0020] The nucleating composition is prepared by blending the nucleating agent and plasticizer by any suitable means, such as by dry blending or melt blending, blending in extruders, heated rolls or other types of mixers. In some embodiments, the nucleating composition is prepared by melt-blending by extrusion. In such embodiments, the extrusion may be carried out in a suitable extruder such as for example a twin screw extruder with down-stream feeding capability. Such extruders are widely known by those of skill in the art. The extruder is fed with the nucleating agent and plasticizer and temperatures are kept at a suitable level, for example, from about 100°C to about 200°C, such as about 120°C to about 150°C, during the extrusion process. In some embodiments, the nucleating composition is formed by extrusion and pelletized. Extruded pellets may then be heated to an elevated temperature, such as about 50°C, and held for a sufficient period of time, such as about 2 hours, to dry.

[0021] In another exemplary embodiment, a flame retardant polyester composite molding composition includes the nucleation composition, a polyester resin, one or more flame retardant agents, and optionally one or more fillers and/or other additives known in the art, such as antioxidants, stabilizers, lubricants, colorants, mold release agents, ultraviolet light stabilizers, and the like. One exemplary antioxidant is N,N'-hexane-1,6-diylbis(3-(3,5-di-tert-butyl-4-hydroxyphenylpropionamide)), although other antioxidants known in the art can be used. The flame retardant polyester composite molding composition may serve as the raw material for an injection molding process to prepare flame retardant polyester composite articles.
In some embodiments, a flame retardant polyester composite molding composition comprises about 40 weight percent (wt.%) to about 80 wt. % of a polyester resin, about 10 wt.% to about 20 wt.% of a flame retardant, and about 0.5 wt.% to about 5 wt.% of a nucleation composition, all weights based on the total weight of the flame retardant polyester composite molding composition. Some particular embodiments include about 0 wt.% to about 40 wt.% of a filler. Some particular embodiments include about 0 wt.% to about 1 wt.% of an antioxidant.

In some embodiments, the polyester composite comprises a terephthalate resin, for example, PET, PBT, or combinations thereof. As used herein "polyethylene terephthalate resin," "PET," "PET resin" and so forth refers to a polymeric resin composed of at least about 85 percent of recurring ester units of terephthalic acid and ethylene glycol. In some embodiments, the polyester resin has an intrinsic viscosity of about 0.4 dL/g to about 1.2 dL/g, such as about 0.6 dL/g to about 0.8 dL/g.

In some embodiments, the flame retardant polyester composite molding composition comprises a flame retardant material. Numerous flame retardant materials for use with polyester composite formulations are known by those of skill in the art, and include brominated flame retardants such as brominated phthalic acid ester, tetradecabromodiphenoxybenzene, brominated epox resin, polydibromostyrene, polytribromostyrene, polypentabromostyrene, and 1,2-bis(pentabromophenyl)ethane. In some embodiments, the flame retardant polyester composite molding composition comprises a plurality of flame retardant materials, including a primary flame retardant material and a synergistic flame retardant material. In such embodiments, the primary flame retardant may comprise a brominated flame retardant material, and the synergistic flame retardant material may comprise a non-brominated flame retardant material, such as antimony trioxide or sodium antimonite.

In embodiments where the flame retardant polyester composite molding composition comprises a filler, numerous filler materials known in the art may be used. Exemplary fillers include alumina, aluminum hydrates, feldspar, asbestos, talc, calcium carbonates, clay, carbon black, quartz, novaculite, other forms of silica, kaolinite, bentonite, garnet, mica, saponite, beidellite, calcium oxide, calcium hydroxide, glass fiber, carbon fiber, ceramic fiber, fibrous potassium titanate, iron whiskers, and the like. In some embodiments, the filler is glass fiber.
In an exemplary embodiment, a method for preparing a flame retardant polyester composite molding composition includes blending about 40% to about 80% by weight of a polyester resin, about 10% to about 20% by weight of a flame retardant, and about 0.5% to about 5% by weight of a pre-formed nucleation composition as provided above (all weights based on the total weight of the flame retardant polyester composite molding composition) by any suitable means, such as by dry blending or melt blending, blending in extruders, heated rolls or other types of mixers. In some embodiments, the flame retardant polyester composite molding composition further comprises about 0% to 40% by weight of a filler. In some embodiments, the polyester composite formulation further comprises about 0% to about 1% by weight of an antioxidant. The method for preparing the flame retardant polyester composite molding composition is not limited to any particular sequence for the addition of the above ingredients and the ingredients can be added at once in their required entire amounts or can be divided and added in increments.

Alternatively, methods for preparing a flame retardant polyester composite molding composition may not utilize a pre-formed nucleation composition as provided above, but rather utilize individual constituents of the nucleation composition. Thus, in some embodiments, the methods include blending a flame retardant polyester composite molding composition comprising about 40% to about 80% by weight of a polyester resin, about 10% to about 20% by weight of a flame retardant; one or more of: a neutralized acid copolymer, a salt of a hydrocarbon acid having from 20 to 35 carbon atoms, talc, and a metal stearate; and a polyethylene alcohol and/or a polyester resin. The one or more of: a neutralized acid copolymer, a salt of a hydrocarbon acid having from 20 to 35 carbon atoms, talc, and a metal stearate (the components that otherwise constitute the nucleation agent as described above) and the polyethylene alcohol and/or a polyester resin (the components that otherwise constitute the plasticizer as described above) together comprise about 0.5 wt.% to about 5 wt.% of the flame retardant polyester composite molding composition. Of this 0.5 wt.% to about 5 wt.% of the component(s) that otherwise constitute the nucleation agent as described above, and about 40 wt.% to about 90 wt.% is/are the component(s) that otherwise constitute the plasticizer as described above. In these embodiments, the flame retardant polyester composite molding composition may be blended by any suitable means, such as by dry blending or melt blending, blending in extruders, heated rolls or other types of mixers. In some embodiments, the flame retardant polyester composite molding composition further comprises about 0% to 40% by weight of
a filler. In some embodiments, the flame retardant polyester composite composition further
comprises about 0% to about 1% by weight of an antioxidant.

[0028] In some embodiments, the flame retardant polyester composite composition is
blended by melt-compounding by extrusion. In such embodiments, blending by extrusion
may be carried out in a suitable extruder such as for example a twin screw extruder with
down-stream feeding capability. Such extruders are conventional in the art. The extruder is
fed with the components of the flame retardant polyester composite molding composition
and temperatures within the extruder are kept at a suitable level, for example, from about
80°C to about 300°C. In some embodiments, certain regions within an extruder may be kept
at temperatures such as about 80°C to about 140°C. In some embodiments, certain regions
within an extruder may be kept at temperatures such as about 225°C to about 275°C. In
some embodiments, the flame retardant polyester composite molding composition is formed
by extrusion and pelletized. Extruded pellets may then be heated to an elevated temperature,
such as about 100°C, for a sufficient period of time, such as about 2 hours, to dry. Articles
made from the flame retardant polyester composite molding composition may then be
produced by injection molding the pelletized extrudate.

[0029] In another exemplary embodiment, methods of making flame retardant polyester
composite articles are provided. In some embodiments, the methods include: (a) providing
a polyester composite molding composition comprising about 40% to about 80% by weight
of a polyester resin, about 10% to about 20% by weight of a flame retardant, about 0.5% to
about 5% by weight of a nucleation composition as defined above, about 0% to 40% by
weight of a filler, and about 0% to about 1% by weight of an antioxidant, all weights based
on the total weight of the polyester composite molding composition; and (b) injection
molding the polyester composite molding composition into a predetermined shape with an
injection molding system to form a flame retardant polyester article, wherein one or more
surfaces of the injection molding system that are contacted by the polyester composite
molding composition are maintained at a temperature of about 180°C to about 270°C, such
as about 225°C to about 270°C, such as about 250°C to about 270°C. In these embodiments,
the mold temperature is typically about 100°C.

[0030] Alternatively, some embodiments include blending a polyester composite
molding feed mixture comprising about 40% to about 80% by weight of a polyester resin,
about 10% to about 20% by weight of a flame retardant, a nucleation agent, a plasticizer,
about 0% to 40% by weight of a filler, and about 0% to about 1% by weight of an antioxidant; wherein the nucleation agent comprises a neutralized acid copolymer, a salt of a hydrocarbon acid having from 20 to 35 carbon atoms, talc, metal stearate, or a combination thereof; the plasticizer comprises a polyethylene alcohol, a polyester resin, or mixtures thereof; the combined weight of the nucleation agent and plasticizer account for about 0.5% to about 5% by weight of the flame retardant polyester composite molding composition, with all weights based on the total weight of the polyester composite molding composition. The polyester composite molding feed mixture is heated to form a flame retardant polyester composite molding composition, which is then injection molded into a predetermined shape with an injection molding system to form a flame retardant polyester article. In these embodiments, one or more surfaces of the injection molding system that are contacted by the polyester composite molding composition are maintained at a temperature of about 180°C to about 270°C, such as about 225°C to about 270°C, such as about 250°C to about 270°C. In these embodiments, the mold temperature is typically about 100°C.

[0031] EXAMPLES

[0032] The following are examples of flame retardant polyester composite molding compositions with each of the components set forth in grams, unless otherwise noted. The examples are provided for illustration purposes only and are not meant to limit in any way the various embodiments of the nucleation compositions or the flame retardant polyester composite molding compositions contemplated herein.

[0033] Cylindrical samples were prepared according to the formulas below. The Comparative Example was prepared according to a prior art formula. Examples 1-9 were flame retardant polyester composite molding compositions as contemplated herein. Examples 10-13 are flame retardant polyester composite molding compositions with nucleation agent and/or plasticizer weight percents outside the ranges contemplated in the various embodiments herein. The samples had diameters in the range of about 1 to about 1.5 millimeters (mm). The heights of the samples were in the range of about 3 to 4 mm. The ingredients used in the examples were as follows: Aclyn® 285P, ethylene/acrylic acid copolymer neutralized with sodium, from Honeywell International, Inc., Morristown, New Jersey; Surlyn® 8920, ethylene/methylacrylic acid copolymer neutralized with sodium, from DuPont of Wilmington, Delaware; Licomont® NaV1Ol, sodium salt of montanic acid, from Clariant of Switzerland; PEG 200, PEG 1500 and PEG 6000, from Sinopharm
Chemical Reagent Co., Ltd. of China; PBS Z101, polybutylene succinate, from Anqing Hexing Chemical Co. of China; PET, polyethylene terephthalate with intrinsic viscosity of about 0.6 to 0.68, from Sinopec Yizheng Chemical Fibre Co., Ltd. of China; KBE-2025, brominated epoxy resin, from Kaimei Chemical Science and Technology (Nantong) Co., Ltd. of China; Irganox 1098, antioxidant containing \( \text{N,N'}-\text{hexane-l,6-dihylbis(3-(3,5-di-tert-butyl-4-hydroxyphenylpropionamide))} \), from BASF of Florham Park, New Jersey; talc, particle size 1.2 \( \mu \text{m} \), from Specialty Mineral Inc. of New York, New York; and magnesium stearate, type S, from FACI SPA of Italy.

[0034] Each sample was tested for tensile strength using a universal test machine. The samples had a flame retardant level of V0 (as measured by testing method UL94). Heat distortion temperature was determined for each sample by applying a fiber stress of 1.82 MPa according to ASTM D648. Samples that exhibited tensile strength of 120 MPa or greater were considered acceptable. Samples that exhibited tensile strengths less than 120 MPa were considered failed samples. Samples that exhibited heat distortion temperatures of 220°C or greater were considered acceptable samples. Samples that exhibited heat distortion temperatures below 220°C were considered failures.

<table>
<thead>
<tr>
<th>Ingrid.</th>
<th>Comp. Ex.</th>
<th>Ex. 1</th>
<th>Ex. 2</th>
<th>Ex. 3</th>
<th>Ex. 4</th>
<th>Ex. 5</th>
<th>Ex. 6</th>
<th>Ex. 7</th>
<th>Ex. 8</th>
<th>Ex. 9</th>
<th>Ex.10</th>
<th>Ex.11</th>
<th>Ex.12</th>
<th>Ex.13</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>51.3</td>
<td>51.3</td>
<td>51.8</td>
<td>51.3</td>
<td>51.8</td>
<td>51.3</td>
<td>51.8</td>
<td>51.8</td>
<td>51.8</td>
<td>52.8</td>
<td>51.3</td>
<td>51.8</td>
<td>51.3</td>
<td>52.7</td>
</tr>
<tr>
<td>Glass Fiber</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>NaV101</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulyn 8920</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AClynp 285P</td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>Mg Stearate</td>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Talc</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG1500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEG6000</td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBS Z101</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

12
Accordingly, nucleation compositions comprising mixtures of a nucleation agent and a plasticizer for preparing a flame retardant polyester composite molding composition, flame retardant polyester molding compositions containing such nucleation compositions, and methods of making the flame retardant polyester composite molding compositions have been provided herein. The nucleation compositions provided herein allow for preparation of articles derived from a flame retardant polyester composite molding composition that exhibit high heat resistance without excessive loss of tensile strength. While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.
CLAIMS

What is claimed is:

1. A terephthalate nucleation composition comprising:

   about 10 wt.% to about 60 wt.% of a nucleation agent comprising a neutralized acid copolymer or a salt of a hydrocarbon acid having 20 to 35 carbon atom or talc or a metal stearate or a combination thereof; and

   about 40 wt.% to about 90 wt.% of a plasticizer comprising a polyethylene alcohol or a polyester resin or mixtures thereof;

   wherein the weight percents are based on a total weight of the nucleation composition.

2. The nucleation composition of claim 1, wherein the neutralized acid copolymer comprises a sodium neutralized acid copolymer.

3. The nucleation composition of claim 1, wherein the neutralized acid copolymer comprises a neutralized ethylene/acrylic acid copolymer or a neutralized ethylene/methacrylic copolymer or mixtures thereof.

4. The nucleation composition of claim 1, wherein the salt of the hydrocarbon acid comprises a salt of an acid chosen from an arachidic acid, a henicosanoic acid, a behenic acid, a tricosanoic acid, a lignoceric acid, a pentacosanoic acid, a cerotinic acid, a heptacosanoic acid, a montanic acid, a melissic acid, a lacceroic acid, a ceromelissic acid, a geddic acid, a ceroplastic acid, and a mixture thereof.

5. The nucleation composition of claim 1, wherein the nucleation agent comprises magnesium stearate.

6. The nucleation composition of claim 1, wherein the plasticizer comprises:

   about 5 wt.% to about 75 wt.% of a polyethylene alcohol; and

   about 5 wt.% to about 45 wt.% of a polyester resin,
wherein the weight percents are based on a total weight of the nucleation composition.

7. The nucleation composition of claim 6, wherein the plasticizer comprises about 5 wt.% to about 75 wt.% of a polyethylene glycol (PEG) and about 5 wt.% to about 45 wt.% of a polybutylene succinate (PBS), wherein the weight percents are based on a total weight of the nucleation composition.

8. The nucleation composition of claim 7, wherein the plasticizer comprises a PEG with a molecular weight from about 200 to 20,000.

9. A method for preparing a flame retardant polyester composite molding composition, the method comprising:

mixing:

about 40% to about 80% by weight of a polyester resin;

about 10%, to about 20% by weight of a flame retardant;

about 0% to 40%, by weight of a filler; and

about 0.5% to about 5% by weight of a nucleation composition;

wherein the weight percents are based on a total weight of the flame retardant polyester composite molding composition, and

wherein the nucleation composition comprises about 10 wt.% to about 60 wt.% of a nucleation agent comprising a neutralized acid copolymer or a salt of a hydrocarbon acid having 20 to 35 carbon atoms or talc or a metal stearate or a combination thereof, and about 40 wt.% to about 90 wt.% of a plasticizer comprising a polyethylene alcohol or a polyester resin or mixtures thereof, wherein the weight percents are based on a total weight of the nucleation composition.

10. The method of claim 9, wherein the polyester resin comprises polyethylene terephthalate (PET) or polybutylene terephthalate (PBT) or combinations thereof.

11. The method of claim 9, wherein the plasticizer comprises:
about 5 wt.% to about 75 wt.% of a polyethylene alcohol; and

about 5 wt.% to about 45 wt.% of a polyester resin,

wherein the weight percents are based on a total weight of the nucleation composition.

12. The method of claim 11, wherein the plasticizer comprises:

about 5 wt.% to about 75 wt.% of a polyethylene glycol (PEG); and

about 5 wt.% to about 45 wt.% of a polybutylene succinate (PBS),

wherein the weight percents are based on a total weight of the nucleation composition.

13. The method of claim 9, wherein the salt of the hydrocarbon acid comprises a salt of an acid chosen from an arachidic acid, a henicosanoic acid, a behenic acid, a tncosanoic acid, a lignoceric acid, a pentacosanoic acid, a cerotinic acid, a heptacosanoic acid, a montanic acid, a melissic acid, a lacceroic acid, a ceromelissic acid, a gaddic acid, a ceroplastic acid, and a mixture thereof.

14. The method of claim 9, wherein the neutralized acid copolymer comprises a neutralized ethylene/acrylic acid copolymer or a neutralized ethylene/methacrylic copolymer or mixtures thereof.

15. The method of claim 9, wherein the nucleating agent comprises magnesium stearate.
### INTERNATIONAL SEARCH REPORT

**International application No.**

PCT/CN2015/078450

---

#### A. CLASSIFICATION OF SUBJECT MATTER

C08K 5/06(2006.01)i; C08K 5/09(2006.01)i; C08K 5/10(2006.01)i; C08K 5/098(2006.01)i; C08L 67/02(2006.01)i

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

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08L 67/02, C08L 67/00, C08K5/

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 practicable, search terms used)

WPI, EPDOC, CA, CNPAT, CNKI: PET, terephthalate, nucleat+, talc, stearate, plasticizer, polyethylene, alcohol, PEG, polyester, ethylene, +acrylic

#### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>CN 103275468 A (FOSHAN PLASTIC TECHNOLOGY GROUP CO., LTD.) 04 September 2013 claims 1, 5, 6</td>
<td>1-15</td>
</tr>
<tr>
<td>X</td>
<td>CN 101747596 A (WANG, SHIHE) 23 June 2010 (2010-06-23) paragraphs 0013-0025</td>
<td>1-15</td>
</tr>
<tr>
<td>X</td>
<td>CN 102504500 A (HUEHOU WOTE ADVANCEDMATERIALS CO., LTD.) 20 June 2012 (2012-06-20) paragraphs 0019-0029</td>
<td>1-15</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. [See patent family annex.]

* Special categories of cited documents:

  - **A** - document defining the general state of the art which is not considered to be of particular relevance
  - **E** - earlier application or patent but published on or after the international filing date
  - **L** - document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - **O** - document referring to an oral disclosure, use, exhibition or other means
  - **P** - document published prior to the international filing date but later than the priority date claimed

---

Date of the actual completion of the international search

16 July 2015

Date of mailing of the international search report

29 July 2015

Name and mailing address of the ISA/CN

**STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA**

6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China

Facsimile No. (86-10)62019451

Authorized officer

REN, Weihua

Telephone No. (86-10)82246917

Form PCT/ISA/210 (second sheet) (July 2009)
<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date (day/month/year)</th>
<th>Patent family member(s)</th>
<th>Publication date (day/month/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN 103275468 A</td>
<td>04 September 2013</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>CN 101747596 A</td>
<td>23 June 2010</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>CN 102504500 A</td>
<td>20 June 2012</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>