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(54) Title: METHODS AND COMPOSITIONS TO PROVIDE IMPROVED PROCESSABILITY AND FLAME RETARDANCE IN POLY(TRIMETHYLENE TEREPHTHALATE) FIBERS

(57) Abstract: Poly(trimethylene terephthalate) compositions, and articles made therefrom, having improved flame retardancy are provided. The compositions can be used to make carpets that are suitable for installation where flame retardancy is desired. The compositions contain particulate flame retardants having an average particle size of less than about 10 micrometers.

Methods and Compositions to Provide Improved Processability and Flame Retardance in Poly(trimethylene terephthalate) Fibers

FIELD OF THE INVENTION

The present invention relates to poly(trimethylene terephthalate) compositions having improved flame retardancy and to articles made from the compositions.

BACKGROUND

Poly(trimethylene terephthalate) (PTT) is potentially useful in a variety of applications that require flame retardancy. However, a need remains for improved flame retardancy in PTT. Specifically, it is desirable to provide improved radiant panel performance of PTT in carpet such that a class 1 carpet tile, (> 0.45 Watts/cm2, as measured by ASTM 648) as known in the art, can be obtained.

SUMMARY OF THE INVENTION

One aspect of the invention is a poly(trimethylene terephthalate)-based composition comprising: (a) from about 75 to about 99.9 weight percent of a resin component, based on the total composition weight, wherein the resin component comprises at least about 70 weight percent of a poly(trimethylene terephthalate), based on the weight of the resin component; and (b) from about 0.1 to about 25 weight percent of an additive package, based on the total composition weight, wherein the additive package comprises from about 0.1 to about 15 weight percent of a flame retardant comprising at least one of: melamine cyanurate, melamine pyrophosphate, a zinc salt of diethyl phosphinic acid, or blends thereof, based on the total composition weight, wherein the flame retardant is granular with an average particle size of less than about 10 micrometers.

DETAILED DESCRIPTION

The compositions disclosed herein contain a resin component, comprising PTT and optionally one or more other polymers, and one or more flame retarding compounds selected from: melamine phosphates, melamine cyanurates and diethyl phosphinic acid zinc salts. Other polymers that can be in the resin component, include polyethylene terephthalate, polybutylene terephthalate, nylon, polypropylene and blends thereof. Thus, the term "PTT-based composition", as used herein, is intended to encompass compositions wherein the resin component contains one or more other polymers in addition to PTT. The amount of other polymer in the resin component, based on the total weight of the resin component, can vary and can be, for example, 5, 10, 15, 20, or 25 weight percent, or greater. In some preferred embodiments wherein one or more other polymer is present in the resin component with the PTT, the resin component contains from 75 to 99 weight percent of PTT and 1 to 25 weight percent of the other polymer(s), based on the total weight of the resin component.

In some embodiments, the resin component comprises a poly poly(trimethylene terephthalate) made from 1,3-propanediol that is biologically derived.

It has been surprisingly found that improvements in both processing and properties of fibers made from PTT and containing flame retardants such as those disclosed herein can be obtained when the flame retardants are in particulate form and have average diameters of 10 microns or less. The particles can be irregular or can have defined shape with a median particle size, d50, of 10 micron or less. Particles can be further characterized using laser diffraction techniques known in art to provide d10 and d90 as representative of sizes below which 10% or 90% sample population lies. Further, the particles are preferably non-melting and remain as particulates during fiber spinning, subsequent processing into carpet and end-use.

In some embodiments, the particulate flame retardant has a particle size of 6 microns or less, or 3 microns or less. In some embodiments, the particles can have sizes of 2 microns or less, or one microns or less, which can be obtained using techniques such as fracturing the particles, subsequently taking steps to prevent the particles from reagglomerating during compounding or spinning.

Specifically, it has been found that, when PTT contains a flame retardant having a particle size as disclosed herein, processing of the PTT into fibers can be more easily carried out than with PTT compositions containing the same flame retardant of larger particle size.

In some embodiments the additive package contained in the resin component contains, in addition to the specified flame retardant, one or more additives such as delusterants (such as TiO_2, zinc sulfates or zinc oxide), a dye or pigment. The additive package can further contain one or more additives such as antioxidants, residual catalyst, colorants (such as dyes), stabilizers, fillers (such as calcium carbonate), antimicrobials agents, antistatic agents, optical brighteners, extenders, processing aids, and/or other functional additives, commonly referred to as “chip additives”.

TiO_2 and other compounds such as zinc sulfide or zinc oxide, which can function as pigments and/or delusterants, can be used in amounts that are commonly used in the art for making PTT compositions. For example, the total amount of pigments/delusterants can be about 5 weight percent or more, based on the total weight of the PTT-based composition, for making fibers, with relatively larger amounts typically being used for other applications. Examples of materials that can be used as pigments and/or delusterants include TiO_2, ZnO, and zinc sulfates. In some embodiments, TiO_2 is preferred. When used in polymer for fibers and film, TiO_2 is added in an amount of preferably at least about 0.01 weight percent, and preferably up to 3 weight percent more preferably up to about 2 weight percent (based on total composition weight).

The term “pigment” is used herein in reference to those substances commonly referred to as pigments in the art. Pigments are substances usually in the form of a dry powder, that impart color to a polymer or article made from the polymer (e.g., chip or fiber). Pigments can be inorganic or organic and can be natural or synthetic. Generally, pigments are inert (i.e., electronically neutral and do not react with the polymer) and are substantially insoluble in the medium to which they are added, such as a poly(trimethylene terephthalate) composition. However, pigments can also be soluble or partially soluble in some materials.

Preferably the resin components, the flame retardant(s) and any other additive(s) are melt blended. Preferably, the resin components and additive(s), including flame retardant, are mixed and heated at a temperature sufficient to form a melt blend composition. The compositions can be spun into fibers or formed into other shaped articles, preferably in a continuous manner.

The resin components and additives can be formed into a blended composition in a variety of different ways known to those skilled in the art. For example, they can be (a) heated and mixed simultaneously, (b) pre-mixed in a separate apparatus before heating, or (c) heated then mixed. The mixing, heating, and forming can be carried out by conventional equipment designed for that purpose such as, for example extruders and Banbury® mixers. The temperature is preferably above the melting points of each of the components but below the lowest decomposition temperature, and can be adjusted for any particular composition of PTT and flame retardant additive. The temperature is typically in the range of about 180 °C to about 270 °C.

The amount of flame retardant compound used in the PTT-based compositions is preferably from 0.1 percent to 15 weight percent, based on total composition weight. More preferably, the amount is from about 0.5 to about 10 weight percent, more preferably from about 1 to about 6 weight percent, still more preferably from about 2 to about 6 weight percent, on total PTT-based composition weight.

Also provided in some embodiments are articles, such as fibers, films and molded parts, comprising the PTT composition, such articles having improved flame retardant properties.

The compositions can be spun into fibers such as bulked continuous filaments (BCF). The BCF can be made into yarns and formed into carpets. Carpets made from the BCF yarns can be made using any method known to those skilled in the art. Typically, a number of yarns are cable twisted together to form a carpet yarn and heat-set in a device such as an autoclave. Alternatively, continuous processes such as dry heat-setting, using, for example, a Suessen heat setting machine, or steam-autoclave heat setting, such as with a Superba® autoclave, can be used to impart structural stability to yarns. Yarns are then tufted into a primary backing, also referred to as the tufting substrate.

BCF can be made using any methods known to those skilled in the art, for example, as disclosed in US Patent No. 7013628, which discloses BCF made from fiber bearing a delta cross section and having a total denier of approximately 1450 denier and a denier per filament of about 20.8. Fiber tenacities range from 1.5 to 2.5 grams/denier and fiber elongations ranging from 35 to 75 percent. The fiber can have a variety of cross-section shapes, depending on the desired properties of the yarn and end product (e.g., carpet) made therefrom. For example, the cross-section can be delta, trilobal, round, or other shapes commonly used in the trade. The total denier of yarns made from the fibers can range from 1000 to 3000 and denier per filament (dpf) can range from 10 to 30.

In some embodiments wherein the PTT-based compositions are used in making fibers and the fibers are used to make carpets, an adhesive material, commonly referred to as the precoat, is used to bind the fibers to the tufting substrate. Common precoats are latex-derived or derived from a hot melt adhesive. The latex-derived precoat or hot melt adhesive precoat contains a binding polymeric resin and may also contain a filler, such as

calcium carbonate. In some cases, the precoat can also contain additives such as dispering agents and/or thickener.

Typical polymeric resins used in latex-derived precoats include a polymeric component such as vinyl acetate-ethylene (VAE), styrene-butadiene rubber (SBR), polyvinyl chloride (PVC), polyesters, poyurethanes, and polyolefins, particularly polypropylene. Conventional hot melt adhesives or other non-aqueous adhesives such as ethylene vinyl acetate (EVA), polyolefins and polyethylenes ,which sometimes are used instead of latex for a stronger bond than that provided by latex adhesives, can be utilized as the precoat.

In preferred embodiments, the precoat contains a flame retardant additive such as aluminum trihydrate (ATH) or magnesium hydroxide ($Mg(OH)_2$). ATH is preferred.

In a latex-derived precoat, the amount of flame retardant additive used in the precoat depends in part on the nature and quantity of the binding polymer or of the polymeric component present,and also on the amount of precoat used, and can vary up to 600 parts per hundred of the polymeric resin in the precoat-(phr). (The polymeric component in the precoat is separate and apart from the resin component of the compositions disclosed herein that comprises PTT). Typically loadings up to 400 phr, such as 1 to 400 phr, are employed. Preferably, loadings from 100 to 400, and more preferably 100 to 300 parts per hundred of flame retardant are employed.

For a precoat based on a hot melt adhesive, the amount of flame retardant additive, such as ATH, used in the precoat is based on the amount of adhesive and fillers , such as calcium carbonate, and can vary up to about 35 weight %, e.g., from 1 to 35 weight %. Preferably, loadings of 1 to 25 weight % of flame retardant are employed. Most preferably, 10-25% of flame retardant is employed,

Some carpet includes a secondary backing in addition to the precoat. The secondary backing adheres to the precoat and is the portion of the carpet structure that contacts the surface being carpeted. In some applications, the

carpet has a self-stick and self-release sticky secondary backing; in other applications a cement or glue is used on the secondary backing. Secondary backings derived from polyolefins typically require higher flame retardant loadings in the face fiber and precoat as compared to secondary backings derived from vinyl polymers such as PVC.

It has been found that the amount of flame retardant in the precoat can advantageously be adjusted based on the weight of the face fiber in the carpet, as well as the basis weight and type of the secondary backing if present. "Basis weight" is a term known to those skilled in the art and is used to refer to the weight (in ounces) of carpet, secondary backing, or precoat, per unit area (in square yards). Thus, typically, basis weight for carpet or for precoat is reported in ounces per square yard. Face fiber refers to the fiber content of the carpet including that is visible to the observer. The face fiber is primarily made up of yarns, and those yarns may be styled as cut, loop, cut and loop or any number of styles known to those skilled in the art. Fiber face weight is also typically reported in units such as ounces per square yard. The secondary backing can be a heavy latex, as is the case for carpets commonly referred to as broadloom. Alternatively, the secondary backing can be olefin or vinyl derived as is the case for tile based carpets. The secondary backing can contain multiple layers separated, for example, by fiberglass scrim, and one or more of the multiple layers can contain fillers.

For many applications, it is desired that carpet meet a "Class 1" rating in the ASTM 648E (Radiant Panel) test. However, merely increasing the content of flame retardant in the carpet fibers has been found to produce inconsistent results. Moreover, merely using a higher content of flame retardant in the precoat has limited success because too high a content can adversely affect adhesion properties of the precoat and lead to delamination of the tufted substrate from the secondary backing.

In preferred embodiments, the carpet contains 2 weight % or less flame retardant in the fiber, at a carpet basis weight of 28 oz/yd^2 or less and in some embodiments 24 oz/yd^2 or less.

EXAMPLES

Ingredients

The PTT used in the examples was SORONA® "semi-bright" PTT available from E.I. du Pont de Nemours and Company (Wilmington, DE). Melamine pyrophosphate with two particle size distributions, shown in Table 1, was purchased from Hummel Croton, New Jersey, USA.

Table 1

MPP Type	D10, µm	D50, µm	D90, µm
A	2.03	7.39	19.16
B	1.03	2.87	6.14

The specifications for the two MPP types were similar except for the particle size distribution (PSD)

1) TGA weight loss 0.05% @ 300°C; 6% @ 350°C
2) P content 14.4%
3) N content 39.0%
4) Water solubility 0.06%
5) Moisture < 500 ppm
6) pH 3.8 ± 0.4 (25% slurry)
7) Chlorides <100ppm

The approach to determining improvement in spinning performance and radiant panel testing was to produce MPP concentrate masterbatch that was

added to PTT resin at the spinning machine screw melter to achieve desired MPP level in the bulked continuous filaments (BCF). BCF thus produced was converted into carpet tiles by first tufting onto a primary backing that was adhered to two extruded layers of secondary backings with an intervening glass scrim layer. Carpet tiles thus produced were tested for critical radiant flux using ASTM 648-03 radiant panel test method

Compounding

The PTT polymer (SORONA®) was dried in a vacuum oven at 120°C for 16 hours to obtain the dried PTT. Flame retardant additive MPP was used as is, without drying. The dry PTT was fed at a rate of 80.5 lb/hr into the throat of a twin-screw, co-rotating, intermeshing, Coperion MEGA type extruder (26 mm screw, Stuttgard, Germany) with a temperature profile of 280 °C in the first four barrels and 240 °C in rest of the barrels. MPP powder was fed into the fifth extruder barrel using a twin screw side feeder at a rate of 23 lb/hr. Another stream of dried Sorona® PTT pellets was introduced into the fifth barrel at a rate of 11.5 lb/hr to prevent packing of MPP in the side feeder. The strand was cooled in a 6 ft tap water trough prior to being pelletized to give a pellet count of 100-120 pellets per gm. The extruder was purged with dried PTT for at least 5 min. prior to introduction of MPP. Following concentrates were produced:

MasterBatch A - 20% MPP A in Sorona® PTT
MasterBatch B - 20% MPP B in Sorona® PTT

Spinning

The masterbatch compositions mentioned above can be spun into fibers such as bulked continuous filaments (BCF). BCF can be made in any of the manners known to those skilled in the art. Such a manner can be found as described in US 7013628. The BCF produced in this application contain fiber bearing a delta cross section having a total denier of approximately 1400.

Before spinning, Sorona® PTT as well as masterbatch pellets was dried for 16 hrs at 100°C in a vacuum oven with a dry nitrogen sweep. The dried polymer and masterbatch pellets were metered, mixed and introduced into a single screw extruder and spun through a 70-hole spinneret orifice. The extruder was heated in the feed zone at 245°C, melt zones at 250°C to 255°C, transfer zones at 255°C and pump zone at 255°C. Molten polymer was pushed and transferred to the spinneret pack block at 255°C. The polymer stream was filtered through a pack screen assembly consisting of a 325 mesh screen sandwiched between two 120 mesh screens. After filtration, a total of 70 individual filaments were created that were cooled in ambient air quench zone and given an aqueous emulsion (0.7%) finish. The 70 filament yarn was pulled away from the spinneret orifices and through the guide by an inlet roll at approximately 1000 m/min. From these rolls the yarn was taken to a pair of rolls at 1070 m/min, then through draw rolls at 2800 m/min to produce fibers with a draw ratio of 2.8. The drawn fibers then pass through a bulking unit to produce carpet quality fibers. The fiber identification is shown in Table 2 below. Feed and draw roll temperatures were at 70°C and 140°C, respectively. Bulking jet temperature and pressure were 180°C and 8.5 bars, respectively. Interlace jet pressure was at 6.5 bar. The BCF thus produced had tenacity greater than 2.0 gm/denier and elongation in the range of 55 to 75%.

Table 1

Example	PTT feed rate (%)	Masterbatch feed rate (%)
Fiber 1 (control)	100	0
Fiber 2 (3% MPP A)	85	15 (Masterbatch A)
Fiber 3 (3% MPP B)	85	15 (Masterbatch B)
Fiber 4 (2% MPP B)	90	10 (Masterbatch B)

Pack pressure rise observed during fiber spinning is an indication of polymer quality and provides assessment of quality of MPP dispersion during compounding and subsequent dispersion of MPP rich masterbatch into PTT during single screw extrusion. The pressure rise information during spinning of the different grades of MPP is shown in Table 3. These results indicate slower pressure rise (1.4 bar in 90 min and 5.4 bar in 180 min) in the case of type B MPP having smaller particle size (d50 = 2.87 μm). In contrast, spinning of PTT with larger particle size type A MPP (d50 = 7.39 μm) demonstrated much faster pressure rise (85 bar in 85 min).

Table 3: Pressure Rise during spinning

Example	Spinning Time (min)	Pressure Increase (bars)
Fiber 1 (control)	80	0
Fiber 2 (3% MPP A)	85	85
Fiber 3 (3% MPP B)	90	1.4
	180	5.4
Fiber 4 (2% MPP B)	90	0.7
	180	2.3

Carpet Preparation

Two 1400 denier BCF yarn bundles, each having 70 filaments of nominally 20 denier per filament, were twisted at 4.75 twist per inch and Sussen heat-set. Fibers were then tufted into a 3.5 ounces per square yard nonwoven primary substrate known as Colback® form Colbond. Tuft settings were 5/64th gauge, 0.18 in pile height to achieve 24 oz/sq yd fiber face weight.

Latex adhesive used as a precoat was obtained from BizMax Solutions Inc. The precoat was VAE based and contained 400 parts per hundred

aluminum trihydrate. Precoat was applied to carpet samples at a basis weight of approximately 20 oz/yard^2.

Secondary backing was an extrusion grade thermoplastic polyolefin TKP 882D TPO merge containing 65% by weight, based on the weight of TPO, of calcium carbonate as filler, obtained from the LyondellBasell company. Two extruded layers, each approximately 28 oz/sq yd, with a 2.1 oz/ yard^2 fiberglass in between, were applied to the precoated primary substrate.

Radiant Panel Testing

Carpet tile samples were produced and submitted for radiant panel testing according to ASTM 648E. The critical radiant flux (CRF) was determined and the results for samples that either did not contain melamine pyrophosphate as flame retardant additive in the fiber or contained Type A melamine pyrophosphate having larger size and are captured in Table 4 below. All tile samples contain aluminum trihydrate in backing.

Table 4

Example Number	MPP Type	Weight of flame retardant (%)	CRF Avg (watts/cm^2)
Comparative Ex. 1	None	0	0.48
Comparative Ex. 2	A	2	0.49
Comparative Ex. 3	A	3	0.57

These results indicate that 3% type A MPP with aluminum trihydrate in backing is needed to clearly exceed Class 1 CRF requirement of 0.45 w/sq cm. It should be noted that, in general, a CRF value of 0.55 w/sq cm is required in the trade to ensure consistent performance at Class 1 level.

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The CRF results for tiles containing type B MPP with a nominal D50 of about 3 μm are shown in Table 5 below. As before, all tile constructions contain 400 parts ATH.

Table 5

Example Number	MPP Type	Weight of flame retardant (%)	CRF Avg (watts/cm^2)
Ex. 1	B	1	0.51
Ex. 2	B	2	0.67
Ex. 3	B	3	0.61
Ex. 4	B	4	0.66

By comparing Ex. 2 and Ex.3 with Comparative Ex. 2 and Comparative Ex. 3 we find that Type B MPP is surprisingly more effective at a lower loading level of 2% versus Type A that requires 3% loading. Type B MPP is therefore advantageous from the points of view of cost of flame retardant and ease of compounding and spinning. As shown in Table 4 below, type B MPP has additional benefit of improving carpet texture retention, an indication of carpet durability or wear resistance in use, as measured by Hexapod Tumbler Test ASTM D5252-05 and Vettermann Drum Test ASTM D5417-05 on a subjective scale of 1 (very poor to 5 (excellent) over a wider range of type A MPP loading level as compared to type B MPP. Whereas a full unit loss in Hexapod test (4 = good to 3 = fair) is seen for type A MPP, loss in texture for type B MPP is within the increment of ranking scale.

Table 2

Example Number	MPP Type	Weight of flame retardant (%)	Vettermann Drum Test rating after 22,000 cycles	Hexapod Tumbler Test rating after 15,000 cycles
Comperative Ex. 1	None	0	3.5	4.0

Comperative Ex. 2	A	3	3.0	3.0
Ex. 1	B	1	3.5	3.5
Ex. 2	B	2	3.5	3.5
Ex. 3	B	3	3.5	3.5
Ex. 4	B	4	3.5	3.5

CLAIMS:

1. A poly(trimethylene terephthalate)-based composition comprising: (a) from about 75 to about 99.9 weight percent of a resin component, based on the total composition weight, wherein the resin component comprises at least about 70 weight percent of a poly(trimethylene terephthalate), based on the weight of the resin component; and (b) from about 0.1 to about 25 weight percent of an additive package, based on the total composition weight, wherein the additive package comprises from about 0.1 to about 15 weight percent of a flame retardant comprising at least one of: melamine cyanurate, melamine pyrophosphate, a zinc salt of diethyl phosphinic acid, or blends thereof, based on the total composition weight, wherein the flame retardant is granular with an average particle size of less than about 10 micrometers.
2. The composition of claim 1 wherein the average particle size is 6 microns or less.
3. The composition of claim 1 wherein the average particle size is 3 microns or less.
4. The composition of claim 1 wherein the flame retardant composition comprises a blend of particles having two or more different average particle sizes.
5. A fiber made from the poly(trimethylene terephthalate)-based composition of claim 1.
6. A carpet comprising fibers of claim 5.