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(71) Applicant: **Polyplastics Co., Ltd.**
Tokyo 108-8280 (JP)

(72) Inventors:
- **SAITO, Itsuki**
  Fuji-shi, Shizuoka 416-8533 (JP)
- **GOSHIMA, Kazuya**
  Fuji-shi, Shizuoka 416-8533 (JP)

(74) Representative: **Winter, Brandl - Partnerschaft mbB**
Alois-Steinecker-Straße 22
85354 Freising (DE)

(54) POLYBUTYLENE TEREPHTHALATE RESIN COMPOSITION, MOLDED ARTICLE, THICKENING INHIBITOR FOR POLYBUTYLENE TEREPHTHALATE RESIN COMPOSITIONS, AND HYDROLYSIS INHIBITOR FOR MOLDED ARTICLES FORMED FROM POLYBUTYLENE TEREPHTHALATE RESIN COMPOSITIONS

(57) [Problem] The present invention addresses a problem of providing: a polybutylene terephthalate resin composition that has an excellent effect of enhancing hydrolysis resistance; a molded article; a thickening inhibitor for a polybutylene terephthalate resin composition; and a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition.

[Solution] The problem described above is solved by: a polybutylene terephthalate resin composition containing, with respect to 100 parts by mass of a polybutylene terephthalate resin (A) having a carboxylic acid terminal group of 35 meq/kg or less, 0.5 parts by mass or more and 10 parts by mass or less of an epoxy-based resin (B), and a quaternary ammonium salt (C); a molded article comprising the polybutylene terephthalate resin composition; a thickening inhibitor for a polybutylene terephthalate resin composition, the thickening inhibitor containing a quaternary ammonium salt; and a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition, the hydrolysis inhibitor containing a quaternary ammonium salt.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a polybutylene terephthalate resin composition, a molded article, a thickening inhibitor for a polybutylene terephthalate resin composition, and a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition.

BACKGROUND

[0002] Polybutylene terephthalate (hereinafter also referred to as "PBT") resin is excellent in various properties such as thermal resistance, chemical resistance, electrical properties, mechanical properties, and moldability, and is therefore applied to many uses.

[0003] Examples of specific uses include various kinds of electrical components for automobiles (various kinds of control units, various kinds of sensors, and ignition coils, etc.), connectors, switch components, relay components, and coil components.

[0004] Further, polybutylene terephthalate resin is a polyester resin and enhancing hydrolysis resistance is essential for improving durability. For this reason, enhancements by using additives such as epoxy-based resins and carbodiimide have conventionally been practiced.

[0005] Although carbodiimide has an extremely good effect of enhancing hydrolysis resistance, there is a problem of toxic isocyanates being produced. In the case of epoxy-based resins, effects of enhancing hydrolysis resistance are insufficient, and there are cases wherein carboxylic acid terminals of PBT react with epoxy groups and viscosity increases.

[0006] Note that combining a ring-opening catalyst with an epoxy-based resin is conventionally well-known (Patent Document 1). However, the only substance which actually demonstrates an effect as a ring-opening catalyst in said document is calcium stearate.

[0007] Further, Patent Document 2 discloses many examples of ring-opening catalysts. Although there is a disclosure of tetrabutylammonium bromide, etc., as a quaternary ammonium salt, it is indicated that sodium stearate is particularly preferable, and an actual evaluation of a quaternary ammonium salt is not performed.

CITATION LIST

PATENT LITERATURE

[0008]

Patent Document 1: JP H11-236492 A

Patent Document 2: JP H8-157701 A

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009] The present invention addresses a problem of providing: a polybutylene terephthalate resin composition that has an excellent effect of enhancing hydrolysis resistance; a molded article; a thickening inhibitor for a polybutylene terephthalate resin composition; and a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition.

SOLUTION TO PROBLEM

[0010] The present inventors discovered that it is possible to solve the problem described above by: a polybutylene terephthalate resin composition containing, with respect to 100 parts by mass of a polybutylene terephthalate resin (A) having a carboxylic acid terminal group of 35 meq/kg or less, 0.5 parts by mass or more and 10 parts by mass or less of an epoxy-based resin (B), and a quaternary ammonium salt (C); a molded article comprising the polybutylene terephthalate resin composition described above; a thickening inhibitor for a polybutylene terephthalate resin composition, the thickening inhibitor containing a quaternary ammonium salt; and a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition, the hydrolysis inhibitor containing a quaternary ammonium salt. This discovery led to the completion of the present invention.

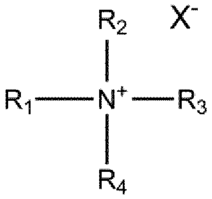
[0011] That is, the present invention relates to (1)-(10) below.

(1) A polybutylene terephthalate resin composition containing, with respect to 100 parts by mass of a polybutylene terephthalate resin (A) having a carboxylic acid terminal group of 35 meq/kg or less, 0.5 parts by mass or more and 10 parts by mass or less of an epoxy-based resin (B), and a quaternary ammonium salt (C).

(2) The polybutylene terephthalate resin composition described in (1), wherein the content of the quaternary ammonium salt (C) is 0.1 parts by mass or more and 3.0 parts by mass or less with respect to 100 parts by mass of the polybutylene terephthalate resin (A).

(3) The polybutylene terephthalate resin composition described in (1) or (2), wherein the quaternary ammonium salt (C) is represented by the following chemical formula, wherein: R_{1-4} are C_{1-5} alkyl groups or zero or more one or less of R_{1-4} is an aryl group or an aralkyl group; and the quaternary ammonium salt (C) has an anion X^- that is a bromide ion.

Chem. 1



(4) The polybutylene terephthalate resin composition described in any one of (1)-(3) further containing a filler.

(5) The polybutylene terephthalate resin composition described in (4), wherein the filler is glass fibers.

(6) A molded article comprising the polybutylene terephthalate resin composition described in any one of (1)-(5).

(7) A thickening inhibitor for a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin, the thickening inhibitor containing a quaternary ammonium salt.

(8) The thickening inhibitor described in (7), wherein the quaternary ammonium salt is the quaternary ammonium salt (C) indicated in (3), wherein: R_{1-4} are C_{1-5} alkyl groups or zero or more one or more of R_{1-4} is an aryl group or an aralkyl group; and the quaternary ammonium salt (C) has an anion X^- that is a bromide ion.

(9) A hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin, the hydrolysis inhibitor containing a quaternary ammonium salt.

(10) The hydrolysis inhibitor described in (9), wherein the quaternary ammonium salt is the quaternary ammonium salt (C) indicated in (3), wherein: R_{1-4} are C_{1-5} alkyl groups or zero or more one or more of R_{1-4} is an aryl group or an aralkyl group; and the quaternary ammonium salt (C) has an anion X^- that is a bromide ion.

EFFECTS OF INVENTION

[0012] According to the present invention, it is possible to provide: a polybutylene terephthalate resin composition that has an excellent effect of enhancing hydrolysis resistance; a molded article; a thickening inhibitor for a polybutylene terephthalate resin composition; and a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition.

DESCRIPTION OF EMBODIMENTS

[0013] Hereinafter, an embodiment of the present invention shall be described in detail. The present invention is not limited to the following embodiment and can be implemented with changes added, as appropriate, as long as the effects of the invention are not inhibited. Further, in the present description, the expression "X-Y" means "X or more and Y or less'.

Polybutylene terephthalate resin composition

Polybutylene terephthalate resin

[0014] Polybutylene terephthalate resins (PBT resins) are obtained by condensation polymerizing a dicarboxylic acid component comprising at least terephthalic acid or an ester-forming derivative thereof (a C_{1-6} alkylester, an acid halide, etc.) and at least of a glycol component comprising an alkylene glycol with a carbon number 4 (1,4-butanediol) or an ester-forming derivative thereof (an acetylate, etc.). In the present embodiment, the polybutylene terephthalate resin is not limited to homopolybutylene terephthalate resins and may be a copolymer containing 60 mol% or more of butylene terephthalate units.

[0015] The terminal carboxyl group amount of the polybutylene terephthalate resin is 35 meq/kg or less but is not particularly limited thereto as long as the objective of the present invention is not hindered, and is preferably 30 meq/kg or less and more preferably 25 meq/kg or less.

[0016] The intrinsic viscosity (IV) of the polybutylene terephthalate resin is not particularly limited as long as the objective of the present application is not hindered, and is preferably 0.60 dL/g or more and 1.2 dL/g or less, and more preferably 0.65 dL/g or more and 0.9 dL/g or less. When a polybutylene terephthalate resin with an intrinsic viscosity in such a range is used, the obtained polybutylene terephthalate resin composition has particularly excellent moldability. Further, the intrinsic viscosity can be adjusted by blending polybutylene terephthalate resins having different intrinsic viscosities. For example, by blending a polybutylene terephthalate resin having an intrinsic viscosity of 1.0 dL/g with a polybutylene terephthalate resin having an intrinsic viscosity of 0.7 dL/g, a polybutylene terephthalate resin having an intrinsic viscosity of 0.9 dL/g can be prepared. The intrinsic viscosity of the polybutylene terephthalate resin can be measured under conditions of, for example, a temperature of 35°C in o-chlorophenol.

[0017] In preparing the polybutylene terephthalate resin, when using an aromatic dicarboxylic acid other than terephthalic acid or an ester-forming derivative thereof as a comonomer component, for example, a C_{8-14} aromatic dicarboxylic acid such as isophthalic acid, phthalic acid, 2,6-naphthalenedicarboxylic acid, or 4,4'-dicarboxydiphenylether; a C_{4-16} alkanedicarboxylic acid such as succinic acid, adipic acid, azelaic acid, or sebacic acid;

a C_{5-10} cycloalkanedicarboxylic acid such as cyclohexanedicarboxylic acid; or an ester-forming derivative of these dicarboxylic acid components (a C_{1-6} alkylester derivative, an acid halide, etc.) can be used. These dicarboxylic acid components may be used alone or in a combination of two or more.

[0018] Among these dicarboxylic acid components, a C_{8-12} aromatic dicarboxylic acid such as isophthalic acid and a C_{6-12} alkanedicarboxylic acid such as adipic acid, azelaic acid, or sebacic acid are more preferred.

[0019] In preparing the polybutylene terephthalate resin, when using a glycol component other than 1,4-butanediol as a comonomer component, for example, a C_{2-10} alkylene glycol such as ethylene glycol, propylene glycol, trimethylene glycol, 1,3-butylene glycol, hexamethylene glycol, neopentyl glycol, or 1,3-octanediol; a polyoxyalkylene glycol such as diethylene glycol, triethylene glycol, or dipropylene glycol; an alicyclic diol such as cyclohexanedimethanol or hydrogenated bisphenol A; an aromatic diol such as bisphenol A or 4,4'-dihydroxybiphenyl; a C_{2-4} alkylene oxide adduct of bisphenol A such as an ethylene oxide 2-mol adduct of bisphenol A or a propylene oxide 3-mol adduct of bisphenol A; or an ester-forming derivative of these glycols (an acetylate, etc.) can be used. These glycol components may be used alone or in a combination of two or more.

[0020] Among these glycol components, a C_{2-6} alkylene glycol such as ethylene glycol or trimethylene glycol, a polyoxyalkylene glycol such as diethylene glycol, an alicyclic diol such as cyclohexanedimethanol, etc. is more preferred.

[0021] As comonomer components that can be used beyond the dicarboxylic acid component and the glycol component, there are, for example, aromatic hydroxycarboxylic acids such as 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, and 4-carboxy-4'-hydroxybiphenyl; aliphatic hydroxycarboxylic acids such as glycolic acid and hydroxycaproic acid; C_{3-12} lactones such as propiolactones, butyrolactones, valerolactones, and caprolactones (ε-caprolactone, etc.); and ester-forming derivatives of these comonomer components (C_{1-6} alkylester derivatives, acid halides, acetylates, etc.).

[0022] The content of the polybutylene terephthalate resin is preferably 20-90 mass% of the total mass of the resin composition, more preferably 30-80 mass%, and still more preferably 40-70 mass%.

Epoxy-based resin

[0023] Examples of epoxy-based compounds constituting the epoxy-based resin of the present invention include aromatic epoxy compounds such as biphenyl-type epoxy compounds, bisphenol A-type epoxy compounds, phenol novolak-type epoxy compounds, and cresol novolak-type epoxy compounds. Two or more epoxy compounds may be used in any arbitrary combination. The epoxy equivalent weight is preferably 150-1500 g/equivalent (g/eq).

[0024] The content of the epoxy-based resin in the polybutylene terephthalate resin composition of the present invention is 0.5 parts by mass or more and 10 parts by mass or less with respect to 100 parts by mass of the polybutylene terephthalate resin, but is preferably 0.5 parts by mass or more and 8 parts by mass or less, more preferably 0.5 parts by mass or more and 6 parts by mass or less, still more preferably 0.5 parts by mass or more and 5 parts by mass or less, and particularly preferably 0.5 parts by mass or more and 4 parts by mass or less.

Quaternary ammonium salt

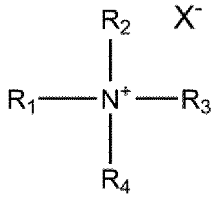
[0025] The quaternary ammonium cation constituting the quaternary ammonium salt contained in the polybutylene terephthalate resin composition of the present invention is a polyatomic ion which has a positive charge and is represented by a molecular formula NR_4^+. The four Rs are each a C_{1-16} alkyl group, aryl group, aralkyl group, or a combination thereof.

[0026] The number of carbon atoms of each of the four Rs is preferably 1-10, more preferably 1-8, still more preferably 1-7, particularly preferably 2-4, and most preferably 4 (butyl). The four Rs may have a number of carbon atoms that differs from one another. Further, the total number of carbon atoms of the four Rs is preferably 30 or less, more preferably 26 or less, still more preferably 22 or less, particularly preferably 18 or less, and most preferably 16 or less.

[0027] The anion X^- constituting the quaternary ammonium salt contained in the polybutylene terephthalate resin composition of the present invention has a monovalent negative charge. That anion is preferably a halide ion, more preferably an ion selected from the group consisting of a chloride ion, a bromide ion, and an iodide ion, still more preferably an ion selected from the group consisting of a chloride ion and a bromide ion, and particularly preferably a bromide ion.

[0028] Further, the quaternary ammonium salt according to the present invention may be represented by the following chemical formula.

Chem. 1



$$R_1-\overset{\displaystyle R_2}{\underset{\displaystyle R_4}{N^+}}-R_3 \quad X^-$$

[0029] In the chemical formula above, it is preferable that R_{1-4} are C_{1-5} alkyl groups or zero or more one or less of R_{1-4} is an aryl group or an aralkyl group. Further, the anion $X^-$is preferably a bromide ion. Note that "zero or more one or less of R_{1-4} is an aryl group or an aralkyl group" means that R_{1-4} may include an alkyl group that is not an aryl group or an aralkyl group.

[0030] Examples of a quaternary ammonium salt which is particularly preferably contained in the polybutylene terephthalate resin composition of the present invention include tetrabutylammonium bromide, tetraethylammonium bromide, benzyltrimethylammonium bromide, and benzyltriethylammonium bromide.

[0031] The content of the quaternary ammonium salt contained in the polybutylene terephthalate resin composition of the present invention is, with respect to 100 parts by mass of the polybutylene terephthalate resin (A), preferably 0.1 parts by mass or more and 3.0 parts by mass or less, more preferably 0.15 parts by mass or more and 2.0 parts by mass or less, and still more preferably 0.2 parts by mass or more and 1.0 parts by mass or less.

Thickening inhibitor for polybutylene terephthalate resin composition

[0032] Further, by using, as the quaternary ammonium salt, a quaternary ammonium cation represented by NR_4^+ wherein, among the four Rs, three Rs are methyl groups and the other R is a functional group that has a number of carbon atoms of six or more and is selected from an alkyl group, an aryl group, and an aralkyl group, it is possible to obtain a thickening inhibitor for a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin. Examples of a quaternary ammonium salt which is preferably used as the thickening inhibitor of the present invention include benzyltrimethylammonium bromide and dodecyltrimethylammonium bromide.

Hydrolysis inhibitor for molded article comprising polybutylene terephthalate resin composition

[0033] Furthermore, by using, as the quaternary ammonium salt, a quaternary ammonium cation represented by NR_4^+ wherein the four Rs are each a C_{1-15} alkyl group, a C_{1-15} aryl group, a C_{1-15} aralkyl group, or a combination thereof, it is possible to obtain a hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin.

Filler

[0034] A filler may be used, as necessary, in the polybutylene terephthalate resin composition of the present invention. Such a filler is preferably blended in order to obtain excellent properties in performance such as mechanical strength, thermal resistance, dimensional stability, and electrical properties and is particularly effective with the objective of increasing rigidity. In accordance with the objective, a fibrous, granular, or tabular filler is used.

[0035] Examples of fibrous fillers include glass fibers, silica fibers, silica/alumina fibers, zirconia fibers, boron nitride fibers, silicon nitride fibers, and boron fibers, etc. Highmelting point organic fibrous substances such as polyamides, fluorine resins, and acrylic resins can also be used.

[0036] Examples of granular fillers include quartz powder, glass beads, glass powder, silicates (excluding talc) such as calcium silicate, aluminum silicate, kaolin, clay, diatomaceous earth, and wollastonite, etc., silicon carbide, silicon nitride, and boron nitride, etc.

[0037] Further, examples of tabular inorganic fillers include mica and glass flakes, etc.

[0038] The type of the filler is not particularly limited and one or more types of filler can be added. In particular, using glass fibers or glass flakes is preferred.

[0039] The amount of the filler added is not particularly specified but is preferably 200 parts by mass or less with respect to 100 parts by mass of the polybutylene terephthalate resin composition. When the filler is added excessively, inferior moldability and decreases in toughness are observed.

Other components

[0040] In a range that does not hinder the effects of the present invention, in order to impart desired properties in accordance with the objective thereof, the polybutylene terephthalate resin composition according to an embodiment of the present invention may have blended therein publicly-known substances that are generally added to thermoplastic resins and thermosetting resins, including, for example, stabilizers such as antioxidants and ultraviolet absorbers, etc., antistatic agents, impact modifiers such as elastomers, etc., colorants such as dyes and pigments, etc., mold release agents, lubricants, crystallization promoters, and crystal nucleating agents, etc.

Molded Article

[0041] A molded article according to an embodiment of the present invention is formed by molding the polybutylene terephthalate resin composition of the present invention. The molding method is not particularly limited and a publicly-known molding method may be employed. For example, production may be performed by: (1) a method involving mixing the components, kneading and extruding with a single-screw or twinscrew extruder to prepare pellets, and then molding; (2) a method involving firstly preparing pellets (masterbatch) having different compositions, mixing (diluting) the pellets at predetermined amounts, and subjecting to molding to obtain a molded article having a prescribed composition; or (3) a method involving directly loading one or more of the components into a molder. The pellets may be prepared, for example, by melt-mixing components other than brittle components (glass-based reinforcing material, etc.) and thereafter mixing in the brittle components. Further, the method for molding other molded articles comprising a thermoplastic resin is not particularly limited and a publicly-known molding method may be employed.

[0042] The molded product may be produced by melt-kneading the resin composition and molding using a conventional method such as extrusion molding, injection molding, compression molding, blow molding, vacuum molding, rotation molding, and gas injection molding, etc., but is normally molded by injection molding. The mold temperature at the time of injection molding is normally approximately 40-90°C, preferably approximately 50-80°C, and more preferably approximately 60-80°C.

[0043] The molded article may include a colorant. Examples of the colorant include inorganic pigments {black pigments such as carbon black [for example, acetylene black, lamp black, thermal black, furnace black, channel black, and ketjen black, etc.], red pigments such as iron oxide red, etc., orange pigments such as molybdate orange, etc., and white pigments such as titanium oxide, etc.}, and organic pigments (yellow pigments, orange pigments, red pigments, blue pigments, and green pigments, etc.). The average particle diameter of the carbon black is normally approximately 10-1000 nm, and preferably, may be approximately 10-100 nm. The ratio of the colorant with respect to the entire molded article is approximately 0.1-10 weight% and preferably approximately 0.3-5 weight% (for example, 0.3-3 weight%).

Examples

[0044] The present invention will be explained in detail below by using the following examples, but the present invention is not limited by these examples so long as the gist thereof is not exceeded.

Materials

[0045] The materials used in the examples are as shown in Tables 1-3.

(A) Polybutylene terephthalate resin (PBT)

[0046]

- (A-1) PBT: polybutylene terephthalate resin, manufactured by Polyplastics Co., Ltd., terminal carboxyl group amount 12 meq/kg, intrinsic viscosity 0.87 dl/g
- (A-2) PBT: polybutylene terephthalate resin, manufactured by Polyplastics Co., Ltd., terminal carboxyl group amount 23 meq/kg, intrinsic viscosity 0.69 dl/g

(B) Epoxy-based resin

[0047]

- Epoxy resin: Epikote JER1004K, manufactured by Mitsubishi Chemical Corporation

(C) Quaternary ammonium salt

[0048]

- (C-1) Tetrabutylammonium bromide
- (C-2) Tetraethylammonium bromide
- (C-3) Tetrapropylammonium bromide
- (C-4) Tetrapentylammonium bromide
- (C-5) Tetrahexylammonium bromide
- (C-6) Tetraheptylammonium bromide
- (C-7) Tetraoctylammonium bromide
- (C-8) Tetrabutylammonium chloride
- (C-9) Tetrabutylammonium iodide
- (C-10) Tetrabutylammonium tetraphenylborate
- (C-11) Benzyltrimethylammonium bromide
- (C-12) Benzyltriethylammonium bromide
- (C-13) Benzyltriethylammonium chloride
- (C-14) Dodecyltrimethylammonium bromide
- (C-15) Phenyltrimethylammonium chloride
- (C-16) Cetyldimethylethylammonium bromide
- (C-17) Stearyltrimethylammonium bromide
- (C'-1) Phenylboronic acid
- (C'-2) Calcium stearate
- (C'-3) Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate

Filler

[0049]

- Glass fibers: EC SO3T-127, manufactured by Nippon Electric Glass Co., Ltd. Other components
- Antioxidant: Irganox 1010, manufactured by BASF Japan, Ltd.
- Lubricant: Rikemal B74, diglycerin fatty acid ester, manufactured by Riken Vitamin Co., Ltd.

Evaluation Method

Examples 1-20 and Comparative Examples 1-12

[0050] The components were mixed at the proportions shown in Tables 1-3 and thereafter melt-kneaded and extruded using TEX-30 manufactured by The Japan Steel Works, Ltd., at a cylinder temperature of 260°C, a discharge rate of 15 kg/h, and a screw rotation speed of 130 rpm to obtain pellets comprising a polybutylene terephthalate resin composition, and the following properties were evaluated.

Melt viscosity

[0051] The obtained pellets were dried at 140°C for three hours and thereafter a capilograph manufactured by Toyoseiki Seisaku-sho, Ltd. was used, employing a flat die with a 1 mm ø × 20 mmL capillary, to measure melt viscosity (Pa·s) at a barrel temperature of 260°C, a residence time of nine minutes, and a shear rate of 1000 sec^{-1}. The results are shown in Tables 1-3.

Hydrolysis resistance

[0052] The obtained pellets were dried at 140°C for three hours, then injection-molded at a cylinder temperature of 260°C and a mold temperature of 80°C to produce type 1A tensile test pieces compliant with ISO 3167, and the tensile strength of the obtained test pieces was measured in compliance with ISO 527-1 and 2.

[0053] Next, other test pieces produced in the same manner were processed in a pressure cooker test (121°C × 100 %Rh × 203 kPa × 75 hr, 100 hr, 120 hr), thereafter the tensile strength thereof was measured in compliance with ISO 527-1 and 2, and respective strength retention rates (%) were calculated from ratios relative to the tensile strength of unprocessed pieces. The results are shown in Tables 1-3.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example8	Example 9	Example 10	Example 11	Example 12
A-1 PBT resin	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
B Epoxy-based resin	1.33	2.69	2.69	2.69	2.70	2.70	2.70	2.70	2.69	2.69	2.70	2.69
C-1 Tetrabutylammonium bromide	0.20	0.41										
C-2 Tetraethylammonium bromide			0.30									
C-3 Tetrapropylammonium bromide				0.38								
C-4 Tetrapentylammonium bromide					0.55							
C-5 Tetrahexylammonium bromide						0.62						
C-6 Tetraheptylammonium bromide							0.71					
C-7 Tetraoctylammonium bromide								0.79				
C-8 Tetrabutylammonium chloride									0.40			
C-9 Tetrabutylammonium iodide										0.53		
C-10 Tetrabutylammonium tetraphenylborate											0.37	
C-11 Benzyltrimethylammonium bromide												0.33
Antioxidant	0.20	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Lubricant	0.20	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Melt viscosity (Pa·s)	142	140	172	150	167	194	198	184	155	168	164	134
Tensile strength retention rate (%) after 75 hr PCT	102	98	102	100	98	96	85	72	84	90	101	100
Tensile strength retention rate (%) after 100 hr PCT	103	98	103	91	91	91	78	65	75	76	93	101
Tensile strength retention rate (%) after 120 hr PCT	70	96	98	90	87	61	55	37	56	68	69	100

Table 2

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex.6
A-1 PBT resin	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
B Epoxy-based resin	2.69	2.69	2.69	2.69	2.70	2.70		1.32	2.68	2.68	2.68	2.69
C-12 Benzyltriethylammonium bromide	0.39											
C-13 Benzyltriethylammonium chloride		0.33										
C-14 Dodecyltrimethylammonium bromide			0.45									
C-15 Phenyltrimethylammonium chloride				0.25								
C-16 Cetyldimethylethylammonium bromide					0.55							
C-17 Stearyltrimethylammonium bromide						0.57						
C'-1 Phenylboronic acid										0.07		
C'-2 Calcium stearate											0.17	
C'-3 Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate												0.28
Antioxidant	0.21	0.21	0.21	0.21	0.21	0.21	0.20	0.20	0.21	0.21	0.21	0.21
Lubricant	0.21	0.21	0.21	0.21	0.21	0.21	0.20	0.20	0.21	0.21	0.21	0.21
Melt viscosity (Pa·s)	143	140	91	135	83	65	142	133	116	132	184	130
Tensile strength retention rate (%) after 75 hr PCT	99	98	99	61	93	71	69	102	101	55	99	96
Tensile strength retention rate (%) after 100 hr PCT	86	95	64	40	46	39	24	50	68	23	47	59
Tensile strength retention rate (%) after 120 hr PCT	97	69	37	22	26	20	0	13	0	0	0	0

Table 3

	Example 19	Example 20	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12
A-2 PBT resin	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
B Epoxy-based resin	1.47	1.45		1.46				1.46
C-1 Tetrabutylammonium bromide	0.88				0.14	0.43	0.87	
C-11 Benzyltrimethylammonium bromide		0.65						
C'-2 Calcium stearate								0.10
Antioxidant	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Lubricant	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Glass fibers	44.00	43.00	43.00	44.00	43.00	43.00	43.00	43.00
Melt viscosity (Pa·s)	181	103	176	172	174	173	172	200
Tensile strength retention rate (%) after 75 hr PCT	66	47	46	59	46	45	45	63
Tensile strength retention rate (%) after 100 hr PCT	40	35	30	30	30	30	30	28

[0054] As shown in Tables 1-3, in the examples, a high tensile strength retention rate was shown even after the PCT treatment. From a comparison with the comparative examples, in particular, it was confirmed in the examples that remarkable superiority can be observed after PCT processing of 100 hr or 120 hr. This shows that the quaternary ammonium salt specified in the present invention improves the hydrolysis properties of a molded article comprising a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin.

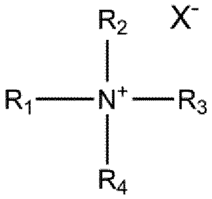
Claims

1. A polybutylene terephthalate resin composition containing, with respect to 100 parts by mass of a polybutylene terephthalate resin (A) having a carboxylic acid terminal group of 35 meq/kg or less, 0.5 parts by mass or more and 10 parts by mass or less of an epoxy-based resin (B), and a quaternary ammonium salt (C).

2. The polybutylene terephthalate resin composition according to claim 1, wherein the content of the quaternary ammonium salt (C) is 0.1 parts by mass or more and 3.0 parts by mass or less with respect to 100 parts by mass of the polybutylene terephthalate resin (A).

3. The polybutylene terephthalate resin composition according to claim 1 or 2, wherein the quaternary ammonium salt (C) is represented by the following chemical formula, wherein: $R_{1\text{-}4}$ are $C_{1\text{-}5}$ alkyl groups or zero or more one or less of $R_{1\text{-}4}$ is an aryl group or an aralkyl group; and the quaternary ammonium salt (C) has an anion X^- that is a bromide ion.

Chem. 1



$$R_1 - \overset{\displaystyle R_2}{\underset{\displaystyle R_4}{N^+}} - R_3 \quad X^-$$

4. The polybutylene terephthalate resin composition according to any one of claims 1-3, further containing a filler.

5. The polybutylene terephthalate resin composition according to claim 4, wherein the filler is glass fibers.

6. A molded article comprising the polybutylene terephthalate resin composition according to any one of claims 1-5.

7. A thickening inhibitor for a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin, the thickening inhibitor containing a quaternary ammonium salt.

8. The thickening inhibitor according to claim 7, wherein the quaternary ammonium salt is the quaternary ammonium salt (C) indicated in claim 3, wherein: $R_{1\text{-}4}$ are $C_{1\text{-}5}$ alkyl groups or zero or more one or less of $R_{1\text{-}4}$ is an aryl group or an aralkyl group; and the quaternary ammonium salt (C) has an anion X^- that is a bromide ion.

9. A hydrolysis inhibitor for a molded article comprising a polybutylene terephthalate resin composition containing a polybutylene terephthalate resin and an epoxy-based resin, the hydrolysis inhibitor containing a quaternary ammonium salt.

10. The hydrolysis inhibitor according to claim 9, wherein the quaternary ammonium salt is the quaternary ammonium salt (C) indicated in claim 3, wherein: $R_{1\text{-}4}$ are $C_{1\text{-}5}$ alkyl groups or zero or more one or less of $R_{1\text{-}4}$ is an aryl group or an aralkyl group; and the quaternary ammonium salt (C) has an anion X^- that is a bromide ion.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/046881

A. CLASSIFICATION OF SUBJECT MATTER
C08K 5/19(2006.01)i; C08K 7/14(2006.01)i; C08L 67/02(2006.01)i; C09K 3/00(2006.01)i; C08L 63/00(2006.01)i
FI: C08L67/02; C08L63/00 Z; C08K5/19; C08K7/14; C09K3/00 103Z
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)
C08K3/00-13/08; C08L67/00-67/08; C09K3/00; C08L63/00-63/10

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2021
Registered utility model specifications of Japan	1996-2021
Published registered utility model applications of Japan	1994-2021

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CAplus/REGISTRY (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2018/174129 A1 (TOYOBO CO., LTD.) 27 September 2018 (2018-09-27) claims, paragraphs [0006]-[0010], [0029], [0048], [0060]-[0063], [0067], examples	1-10
X	JP 2-274717 A (GENERAL ELECTRIC CO.) 08 November 1990 (1990-11-08) claims, examples	1-3, 6
X	JP 5-209117 A (GENERAL ELECTRIC CO.) 20 August 1993 (1993-08-20) claims, paragraphs [0002], [0043], [0047], [0052], examples	1-10
X	JP 5-222279 A (GENERAL ELECTRIC CO.) 31 August 1993 (1993-08-31) claims, paragraphs [0001], [0038], [0042], [0047], examples	1-10
X Y	JP 2002-194184 A (DICEL CHEMICAL INDUSTRIES, LTD.) 10 July 2002 (2002-07-10) claims, paragraphs [0001], [0022], [0024], examples	7-10 1-6

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"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)	"&"	document member of the same patent family
"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 17 February 2021 (17.02.2021)	Date of mailing of the international search report 02 March 2021 (02.03.2021)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2020/046881

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 1465621 A (BEIJING CHONYGAO NANO SCIENCE) 07 January 2004 (2004-01-07) claims, examples 13, 14	1-3, 6
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Y	JP 2010-132930 A (MITSUBISHI CHEMICAL CORP.) 17 June 2010 (2010-06-17) claims, paragraph [0018]	1-6
Y	JP 2019-156891 A (TORAY INDUSTRIES, INC.) 19 September 2019 (2019-09-19) claims, paragraph [0022]	1-6

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application no.
PCT/JP2020/046881

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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JP 5-209117 A	20 Aug. 1993	US 5300546 A claims, column 1, lines 24-29, column 6, lines 52-65, column 7, lines 40-44, column 8, lines 28-30, examples WO 1993/002132 A1 KR 10-1993-0702439 A	
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JP 2002-194184 A	10 Jul. 2002	US 2005/0245646 A1 claims, paragraphs [0001], [0057], [0062], examples WO 2004/005399 A1 CN 1639259 A	
CN 1465621 A	07 Jan. 2004	(Family: none)	
WO 2012/147811 A1	01 Nov. 2012	US 2014/0058015 A1 claims, paragraph [0024] CN 103492485 A	
JP 2010-132930 A	17 Jun. 2010	CN 1980996 A claims, page 7, lines 7-15	
JP 2019-156891 A	19 Sep. 2019	(Family: none)	

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- JP H8157701 A **[0008]**