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(54) **METHOD FOR FORMING AN INSERT INJECTION-MOLDED ARTICLE EXHIBITING IMPROVED RESISTANCE TO HEAT SHOCK UTILIZING A SPECIFICALLY DEFINED POLYBUTYLENE TEREPHTHALATE COMPOSITION**

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(56) **References Cited**

U.S. PATENT DOCUMENTS

4,859,741 A 8/1989 Takahashi et al.  
 6,512,027 B2 \* 1/2003 Kanai et al. .... 523/511  
 2001/0016263 A1 \* 8/2001 Doteguchi et al. .... 428/458

FOREIGN PATENT DOCUMENTS

CN	1268530 A	10/2000
GB	1386548	3/1975
JP	60210659 A	10/1985
JP	633055 A	1/1988
JP	3-285945 A	12/1991
JP	069861 A	1/1994
JP	0841302 A	2/1996
JP	09124908 A	5/1997
JP	09216997 A	8/1997
JP	1143593 A	2/1999
JP	2000336258 A	12/2000
JP	2001234046 A	8/2001
JP	2005290176 A	10/2005
JP	2006111693 A	4/2006
JP	2007091978 A	4/2007
JP	2007112858 A	5/2007
JP	2007126509 A	5/2007

OTHER PUBLICATIONS

Technical Data Sheet "STABAXOL P", [online], Jul. 2008, Rhein Chemie Rheinau GmbH, Searched on Oct. 31, 2014, <URL : <http://www.rheinchemie.com/handle-downloads.php?pid=7608>>.

HOME >> Products >> TOYOBO Engineering Plastics Families "Grades & Material properties of PELPRENETM", [online], Toyobo Co., Ltd., Searched on Oct. 31, 2014, <URL, <http://www.toyobo.co.jp/seihin/xj/enpla/pelprene/grade.htm>>.

Declaration filed in U.S. Appl. No. 12/996,461 on Jun. 19, 2012. International Search Report for PCT/JP2009/002608 dated Sep. 8, 2009.

Machine translation of JP 2007-112858, May 2007.\*

Machine translation of JP 09-124908, May 1997.\*

International Search Report (PCT/ISA/210) dated Sep. 8, 2009.

\* cited by examiner

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(57) **ABSTRACT**

The present invention provides a polybutylene terephthalate resin composition, having performance of high durability and the like in a cold cycle environment, and having high strength. Specifically, relative to 100 parts by weight of a polybutylene terephthalate resin (A) having 30 meq/kg or less of the amount of terminal carboxyl groups, there are added a carbodiimide compound (B) in an amount of 0.3 to 1.5 equivalents of the carbodiimide functional group when the amount of carboxyl terminal group in the polybutylene terephthalate resin (A) is set as 1, 20 to 100 parts by weight of a fibrous filler (C), and 5 to 15 parts by weight of an elastomer (D).

**8 Claims, No Drawings**

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**METHOD FOR FORMING AN INSERT  
INJECTION-MOLDED ARTICLE  
EXHIBITING IMPROVED RESISTANCE TO  
HEAT SHOCK UTILIZING A SPECIFICALLY  
DEFINED POLYBUTYLENE  
TEREPHTHALATE COMPOSITION**

**Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue; a claim printed with strikethrough indicates that the claim was canceled, disclaimed, or held invalid by a prior post-patent action or proceeding.**

TECHNICAL FIELD

The present invention relates to a polybutylene terephthalate resin composition and a molded article thereof which are excellent in high strength and resistance to heat shock.

BACKGROUND ART

Polybutylene terephthalate resins are used as engineering plastics in wide fields including automobile parts, electric and electronic parts, or the like owing to their excellent mechanical properties, electric properties, and other physical and chemical properties, and their good workability. In particular, since their heat resistance and strength can be increased by adding a fibrous filler such as glass fiber thereto, polybutylene terephthalate resins are often used by reinforcing thereof by the fibrous filler.

Specifically in the automobile field, polybutylene terephthalate is often used as the material of sensor for electric control and of ECU housing. In that case, for the parts (insert molded articles) being mounted in an environment of severe temperature increase/decrease, such as engine room of automobile, the toughness of the parts is often improved by adopting an elastomer and the like to prevent crack generation caused by strain resulting from the difference in linear expansion between metal and resin. Many kinds of compositions have been proposed for that purpose.

For example, JP-A 3-285945 discloses the improvement in the resistance to heat shock by adding an elastomer such as ethylene-alkyl acrylate to polybutylene terephthalate. The resin, however, does not exhibit satisfactory resistance to heat shock and does not exhibit satisfactory resistance to hot water, although the improvement effect of those resistances is recognized in comparison with that of non-additive resin.

JP-A 60-210659 discloses the improvement of the resistance to hot water by adding an elastomer such as ethylene-alkyl acrylate and carbodiimide to polybutylene terephthalate. That kind of composition, however, does not exhibit satisfactory resistance to heat shock, although the resistance to hot water is improved.

Furthermore, JP-A 2001-234046 discloses that a resin composition composed of polybutylene terephthalate, a material providing impact resistance, and an aromatic polyvalent carboxylic acid ester compound exhibits excellent resistance to heat shock. However, the addition of the aromatic polyvalent carboxylic acid ester compound raises a problem of deteriorating the strength and the toughness, and also raises a problem of inducing bleeding at high temperatures.

As described above, although the addition of elastomer in order to improve the toughness is known, the addition

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thereof at an amount necessary for improving the toughness raises a problem of deteriorating the strength.

DISCLOSURE OF THE INVENTION

The present invention has been made to solve the above technical problems, and an object of the present invention is to provide a polybutylene terephthalate resin composition having performance of high durability and the like in cold cycle environment, and further having high strength, and to provide a molded article thereof.

The inventors of the present invention have conducted detail studies to obtain a polybutylene terephthalate resin composition capable of achieving the above object, and have found that a composition which is made up mainly of a polybutylene terephthalate resin having 30 meq/kg or less of terminal carboxyl groups and to which a specific amount of a carbodiimide compound, a fibrous filler, and an elastomer are added in combination gives extremely high resistance to heat shock and resistance to hydrolysis without significant deterioration in the mechanical properties, thus having completed the present invention.

That is, the present invention provides a polybutylene terephthalate resin composition, obtained by blending 100 parts by weight of a polybutylene terephthalate resin (A) having 30 meq/kg or less of terminal carboxyl groups with a carbodiimide compound (B) in an amount of 0.3 to 1.5 equivalents of the carbodiimide functional group when the amount of terminal carboxyl groups in the polybutylene terephthalate resin (A) is set as 1; 20 to 100 parts by weight of a fibrous filler (C), and 5 to 15 parts by weight of an elastomer (D), and provides a molded article obtained by molding the resin composition, specifically an insert-molded article thereof.

The present invention also provides a polybutylene terephthalate resin composition including: 100 parts by weight of a polybutylene terephthalate resin (A) having 30 meq/kg or less of terminal carboxyl groups; a carbodiimide compound (B) in an amount of 0.3 to 1.5 equivalents of the carbodiimide functional group when the amount of terminal carboxyl groups in the polybutylene terephthalate resin (A) is set as 1; 20 to 100 parts by weight of a fibrous filler (C); and 5 to 15 parts by weight of an elastomer (D).

The present invention further provides an insert-molded article composed of a resin material of the above polybutylene terephthalate resin composition.

The present invention further provides a method of manufacturing the above polybutylene terephthalate resin composition, including blending 100 parts by weight of a polybutylene terephthalate resin (A) having 30 meq/kg or less of terminal carboxyl groups with a carbodiimide compound (B) in an amount of 0.3 to 1.5 equivalents of the carbodiimide functional group, when the amount of terminal carboxyl groups in the polybutylene terephthalate resin (A) is set as 1; 20 to 100 parts by weight of a fibrous filler (C); and 5 to 15 parts by weight of an elastomer (D).

The present invention further provides a method of manufacturing a molded article or an insert-molded article containing the step of performing injection-molding of the above polybutylene terephthalate resin composition having 120 MPa or higher tensile strength in accordance with ISO 527.

The present invention provides a polybutylene terephthalate resin composition having excellent performance of high durability and the like in a cold cycle environment and having excellent resistance to hydrolysis. The polybutylene

terephthalate resin composition of the present invention is useful as varieties of molded articles, specifically as insert-molded articles.

#### DETAILED DESCRIPTION OF THE INVENTION

The structural components of the resin material of the present invention will be described in detail in the following. The (A) polybutylene terephthalate resin which is the basic resin of the resin composition of the present invention is a polybutylene terephthalate-based resin which is obtained by polycondensation of a dicarboxylic acid component containing at least terephthalic acid or an ester-forming derivative thereof (such as lower alcohol ester) and a glycol component containing at least a C<sub>4</sub> alkylene glycol (1,4-butane diol) or an ester-forming derivative thereof. The polybutylene terephthalate resin is not limited to the homo-polybutylene terephthalate resin, and may be a copolymer containing 60% by mole or more, specifically about 75 to 95% by mole, of butylene terephthalate unit.

The polybutylene terephthalate resin in the present invention is produced by dissolving a crushed polybutylene terephthalate sample in benzyl alcohol for 10 minutes at 215° C., followed by titrating the solution by using an aqueous solution of 0.01N sodium hydroxide to thereby be used as the polybutylene terephthalate resin having 30 meq/kg or less of the amount of terminal carboxyl groups measured, preferably 25 meq/kg or less thereof.

The use of a polybutylene terephthalate resin having more than 30 meq/kg of the amount of terminal carboxyl groups deteriorates the effect of improving the resistance to heat shock even by controlling the amount to be added of carbodiimide compound, and increases the lowering of the strength by hydrolysis in a moist-heat environment.

The lower limit of the amount of terminal carboxyl groups is not specifically limited. However, the polybutylene terephthalate resin having less than 5 meq/kg of the amount of terminal carboxyl groups is generally difficult to be produced, and the resin having less than 5 meq/kg thereof does not allow the reaction with carbodiimide compound to proceed sufficiently, which may result in insufficient effect of improving the resistance to heat shock. Accordingly, the amount of terminal carboxyl groups in the polybutylene terephthalate resin is preferably 5 meq/kg or more, and specifically preferably 10 meq/kg or more.

Furthermore, the intrinsic viscosity (IV) of the applied (A) polybutylene terephthalic resin is preferably within the range of 0.67 to 0.90 dL/g. If the intrinsic viscosity exceeds 0.90 dL/g, the flowability at the time of molding necessary for the insert-molding article cannot be attained in some cases. The intrinsic viscosity of 0.90 dL/g or less can also be attained by blending polybutylene terephthalate resins having different intrinsic viscosities from each other, for example, the one having an intrinsic viscosity of 1.00 dL/g and the one having an intrinsic viscosity of 0.70 dL/g. The intrinsic viscosity can be determined, for example, in o-chlorophenol at 35° C.

In the polybutylene terephthalate resin, examples of the dicarboxylic acid component (comonomer component) other than terephthalic acid and an ester-forming derivative thereof are: an aromatic dicarboxylic acid component (such as C<sub>6</sub>-C<sub>12</sub> aryl dicarboxylic acid including isophthalic acid, phthalic acid, naphthalene dicarboxylic acid or diphenyl ether dicarboxylic acid); an aliphatic dicarboxylic acid component (such as C<sub>4</sub>-C<sub>16</sub> alkyl dicarboxylic acid including succinic acid, adipic acid, azelaic acid, and sebacic acid, and

C<sub>5</sub>-C<sub>10</sub> cycloalkyl dicarboxylic acid including cyclohexane dicarboxylic acid); and an ester-forming derivative thereof. Those dicarboxylic acid components can be used alone or in combination of two or more thereof.

5 Preferable dicarboxylic acid component (comonomer component) includes an aromatic dicarboxylic acid component (specifically C<sub>6</sub>-C<sub>10</sub> aryl dicarboxylic acid such as isophthalic acid) and an aliphatic dicarboxylic acid component (specifically C<sub>6</sub>-C<sub>12</sub> alkyl dicarboxylic acid such as adipic acid, azelaic acid, and sebacic acid).

10 Examples of glycol component (comonomer component) other than 1,4-butane diol are: an aliphatic diol component (such as alkylene glycol (including C<sub>2</sub>-C<sub>10</sub> alkylene glycol such as ethylene glycol, propylene glycol, trimethylene glycol, 1,3-butylene glycol, hexamethylene glycol, neopentyl glycol, and 1,3-octane diol, or polyoxy C<sub>2</sub>-C<sub>4</sub> alkylene glycol such as diethylene glycol, triethylene glycol or dipropylene glycol), and alicyclic diol such as cyclohexane dimethanol or hydrogenated bisphenol A); an aromatic diol component (such as aromatic alcohol including bisphenol A and 4,4-dihydroxybiphenyl, and C<sub>2</sub>-C<sub>4</sub> alkyleneoxide adduct of bisphenol A (for example, 2-mole adduct of ethylene oxide of bisphenol A and 3-mole adduct of propylene oxide of bisphenol A)); and an ester-forming derivative thereof. These glycol components can also be used alone or in combination of two or more thereof.

25 Preferred glycol component (Comonomer component) includes an aliphatic diol component (specifically C<sub>2</sub>-C<sub>6</sub> alkylene glycol, polyoxy C<sub>2</sub>-C<sub>3</sub> alkylene glycol such as diethylene glycol, and alicyclic diol such as cyclohexane dimethanol).

Any of the polybutylene terephthalate-based polymers obtained by polycondensation of above compounds as the monomer components can be used as the (A) component of the present invention. The combined use of homo-polybutylene terephthalate polymer and polybutylene terephthalate copolymer is also useful.

40 The (B) carbodiimide compound used in the present invention is a compound having carbodiimide group (—N=C=N—) in the molecule. Applicable carbodiimide compound includes an aliphatic carbodiimide compound having the aliphatic main chain, an alicyclic carbodiimide compound having the alicyclic main chain, and an aromatic carbodiimide compound having the aromatic main chain, and a preferred one is an aromatic carbodiimide compound in terms of resistance to hydrolysis.

50 Examples of the aliphatic carbodiimide compound include diisopropyl carbodiimide, dioctyldecyl carbodiimide, or the like. An example of the alicyclic carbodiimide compound includes dicyclohexyl carbodiimide, or the like.

55 Examples of aromatic carbodiimide compound include: a mono- or di-carbodiimide compound such as diphenyl carbodiimide, di-2,6-dimethylphenyl carbodiimide, N-tolyl-N'-phenyl carbodiimide, di-p-nitrophenyl carbodiimide, di-p-aminophenyl carbodiimide, di-p-hydroxyphenyl carbodiimide, di-p-chlorophenyl carbodiimide, di-p-methoxyphenyl carbodiimide, di-3,4-dichlorophenyl carbodiimide, di-2,5-dichlorophenyl carbodiimide, di-o-chlorophenyl carbodiimide, p-phenylene-bis-di-o-tolyl carbodiimide, p-phenylene-bis-dicyclohexyl carbodiimide, p-phenylene-bis-di-p-chlorophenyl carbodiimide or ethylene-bis-diphenyl carbodiimide; and a polycarbodiimide compound such as poly(4,4'-diphenylmethane carbodiimide), poly(3,5'-dimethyl-4,4'-biphenylmethane carbodiimide), poly(p-phenylene carbodiimide), poly(m-phenylene carbodiimide), poly(3,5'-dimethyl-4,4'-diphenylmethane carbodiimide), poly(naphthylene carbodiimide), poly(1,3-

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diisopropylphenylene carbodiimide), poly(1-methyl-3,5-diisopropylphenylene carbodiimide), poly(1,3,5-triethylphenylene carbodiimide), and poly(triisopropylphenylene carbodiimide). These compounds can be used in combination of two or more of them. Among these, specifically preferred ones to be used are di-2,6-dimethylphenyl carbodiimide, poly(4,4'-diphenylmethane carbodiimide), poly(phenylene carbodiimide), and poly(triisopropylphenylene carbodiimide).

A preferred (B) carbodiimide compound to be used is the one having 2000 or larger molecular weight. The one having a molecular weight of less than 2000 may generate gas and odor when the retention time is long during melt-kneading and during molding.

The blending amount of (B) carbodiimide compound corresponds to the amount of carbodiimide functional group within the range of 0.3 to 1.5 equivalents when the amount of the terminal carboxyl groups in the (A) polybutylene terephthalate resin is set as 1.

If the amount of (B) component is excessively small, the effect of improving the resistance to heat shock, which is an object of the present invention, cannot be attained. If the amount thereof is excessively large, there likely appears the lowering of flowability and the generation of gel component and carbide at the time of compounding and molding processing, and appear the deterioration of mechanical characteristics such as tensile strength and flexural strength, and the rapid decrease in strength in a moist heat environment. This is because of the deterioration of adhesion between the polybutylene terephthalate resin and the glass fiber caused by the (B) component. A preferred blending amount of the (B) component corresponds to the amount of carbodiimide functional group within the range of 0.5 to 1.5 equivalents, and more preferably 0.8 to 1.2 equivalents.

Examples of the (C) fibrous filler used in the present invention include glass fiber, carbon fiber, potassium titanate fiber, silica-alumina fiber, zirconia fiber, metal fiber, organic fiber, or the like. Among these, glass fiber is preferred.

For the glass fiber, any of known glass fibers is preferably used irrespective of the fiber diameter, the shape such as cylinder, cocoon, or elliptical cross section of the glass fiber, and the length of and the cutting method in manufacturing chopped strand, roving, or the like. Although the present invention is independent of the kind of glass, preferred ones are E-glass and corrosion-resistant glass containing zirconium element in the composition in view of the quality.

According to the present invention, in order to improve the characteristic of interface between the fibrous filler and the resin matrix, a fibrous filler surface-treated by using an organic treatment agent such as amino-silane compound and epoxy compound is specifically preferred, and a glass fiber containing 1% by weight or more of organic treatment agent, expressed by the loss on heating, is specifically preferred. Preferable amino-silane compound and epoxy compound used in those fibrous fillers are any of known ones, irrespective of the kind of amino-silane and epoxy compound used for the surface treatment of the fibrous filler according to the present invention.

The amount of (C) fibrous filler to be used is 20 to 100 parts by weight relative to 100 parts by weight of the (A) polybutylene terephthalate resin. If the amount of (C) fibrous filler is smaller than the above range, the variations in linear expansion accompanied with the cold cycle become large, which is not preferable in view of resistance to heat shock. If the amount of (C) fibrous filler to be used exceeds the above range, the allowable strain of the material decreases, which is unfavorable from the point of resistance

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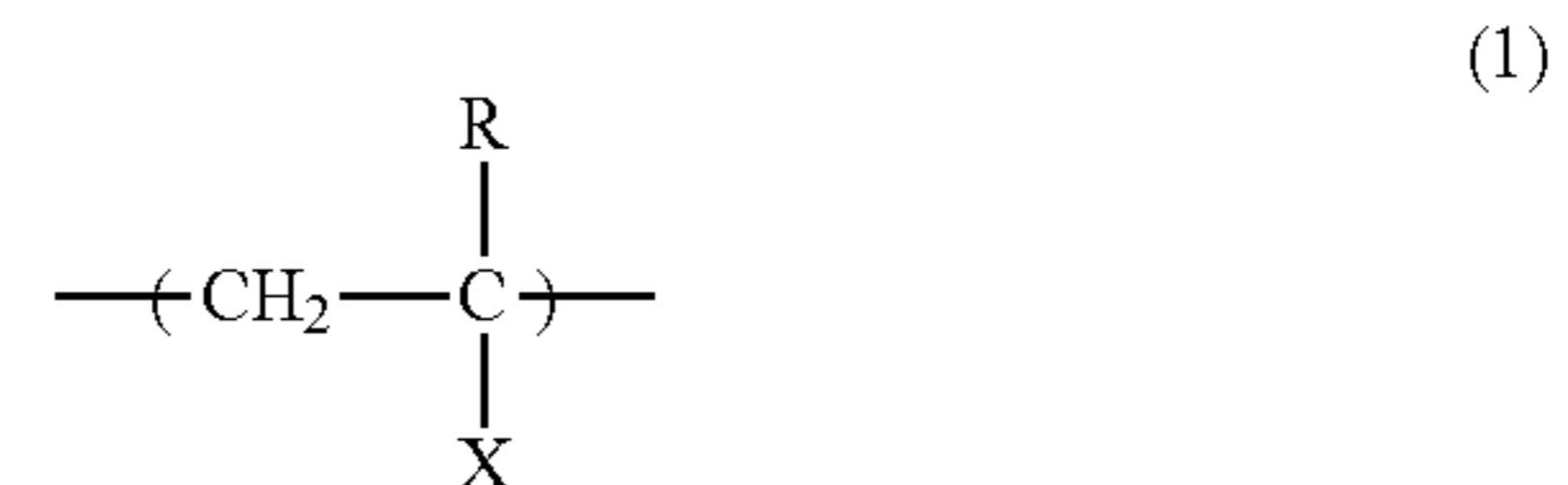
to heat shock. The amount of (C) fibrous filler is preferably within the range of 20 to 80 parts by weight, and more preferably 30 to 60 parts by weight.

Meanwhile, the present invention allows the combined blending of a non-fibrous filler which has no fibrous shape as in the case of the (C) component, that is to say, an inorganic filler in plate shape or granular shape, or a mixture thereof. Such non-fibrous filler includes glass flake, glass bead, mica, talc, carbon black, calcium carbonate, or the like.

The (D) elastomer used in the present invention is preferably a thermoplastic elastomer or a core-shell elastomer. The thermoplastic elastomer includes a grafted olefin-based elastomer, a grafted styrene-based elastomer, and a grafted polyester-based elastomer.

The addition amount of the (D) elastomer is within the range of 5 to 15 parts by weight relative to 100 parts by weight of the (A) polybutylene terephthalate resin, and preferably 5 to 10 parts by weight. If the addition amount of the (D) elastomer is less than 5 parts by weight, the effect of improving the resistance to heat shock cannot be attained. If the addition amount thereof exceeds 15 parts by weight, the strength decreases.

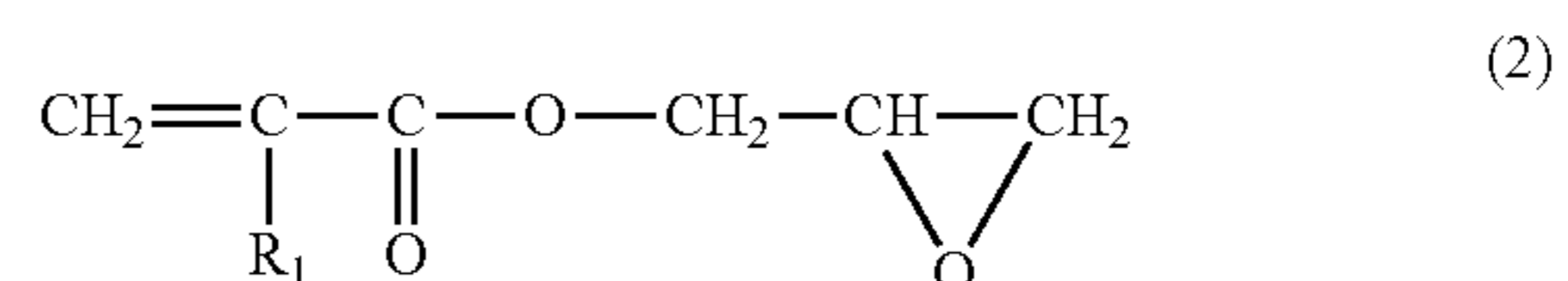
A preferable grafted olefin-based elastomer is a copolymer composed mainly of ethylene and/or propylene, and there is preferably applicable a graft-copolymer chemically bonded by branching or cross-linking one or more of: (a-1) a copolymer of ethylene-unsaturated carboxylic acid alkyl ester or (a-2) an olefin-based copolymer composed of  $\alpha$ -olefin and glycidyl ester of  $\alpha,\beta$ -unsaturated acid; and (b) a polymer or copolymer constituted mainly by repeated units represented by the formula (1).



where, R is hydrogen or a lower alkyl group, and X is one, two or more group selected from  $\text{---COOCH}_3$ ,  $\text{---COOC}_2\text{H}_5$ ,  $\text{---COOC}_4\text{H}_9$ ,  $\text{---COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$ ,  $\text{---C}_6\text{H}_5$ , and  $\text{---CN}$ .

Such graft-copolymer specifically produces the improvement effect of resistance to heat shock.

Examples of the (a-1) ethylene-unsaturated carboxylic acid alkyl ester copolymer include random copolymers such as ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, ethylene-acrylic acid-ethyl acrylate copolymer, ethylene-acrylic acid-ethyl acrylate copolymer, ethylene-vinyl acrylate copolymer, and ethylene-vinyl acetate-ethyl acrylate copolymer. These copolymers can be mixed for use. Furthermore, the  $\alpha$ -olefin as one of the monomers structuring the olefin-based copolymer of (a-2) includes ethylene, propylene, and butene-1, and ethylene is preferably used. Moreover, the glycidyl ester of  $\alpha,\beta$ -unsaturated acid as another monomer structuring (a-2) is a compound represented by the general formula (2), including acrylic acid glycidyl ester, methacrylic acid glycidyl ester, and ethacrylic acid glycidyl ester. Specifically, methacrylic acid glycidyl ester is preferably used.



where,  $\text{R}_1$  is hydrogen atom or lower alkyl group.

The olefin-based copolymer composed of  $\alpha$ -olefin (such as ethylene) and glycidyl ester of  $\alpha,\beta$ -unsaturated acid can be obtained by copolymerization through a known radical polymerization reaction. The ratio of the  $\alpha$ -olefin to the glycidyl ester of  $\alpha,\beta$ -unsaturated acid is preferably 70 to 99% by weight of the  $\alpha$ -olefin to 1 to 30% by weight of the glycidyl ester of  $\alpha,\beta$ -unsaturated acid.

The polymer or copolymer (b) which is graft-polymerized with the olefin-based copolymer (a-1) or (a-2) is a copolymer composed of a single polymer or two or more polymers constituted by a repeated single unit represented by the general formula (I), such as polymethylmethacrylate, polyethylacrylate, polybutylacrylate, poly(2-ethylhexylacrylate), polystyrene, polyacrylonitrile, acrylonitrile-styrene copolymer, butylacrylate-methylmethacrylate copolymer or butylacrylate-styrene copolymer. Specifically preferred one is butylacrylate-methylmethacrylate copolymer. Also these polymers and copolymers (b) are prepared by radical polymerization of corresponding vinyl-based monomers.

The graft copolymer preferably used in the present invention is not a single use of the olefin-based copolymer of (a-1) or (a-2) or of the (co)polymer of (b), but has the features as a graft copolymer having a branched or cross-linked structure in which the copolymer of (a-1) or (a-2) and the (co)polymer of (b) are chemically bonded at least at one position of the molecular structure. With such a graft structure, there can be attained a significant effect which cannot be obtained by a sole composition of (a-1), (a-2), or (b). The ratio of (a-1) or (a-2) to (b) to constitute the graft copolymer is within the range of 95:5 to 5:95 (weight ratio), preferably 80:20 to 20:80.

The styrene-based elastomer includes a block or graft copolymer (or hydrogenated compound thereof) composed of: the hard segment constituted by a polymer or copolymer of aromatic vinyl monomer such as styrene,  $\alpha$ -methylstyrene, or vinyltoluene; and the soft segment constituted by a polymer or copolymer of at least one monomer selected from  $\alpha$ -olefin (including  $\alpha$ -C<sub>2</sub>-C<sub>12</sub> olefin such as ethylene, propylene, 1-butene, 1-hexene, or 1-octene), and diene-based monomer (such as butadiene or isoprene).

The styrene-based elastomer may be an acid-modified elastomer obtained by being modified with acid or acid anhydride such as (meth)acrylic acid or maleic anhydride, a copolymerizable monomer having glycidyl group or epoxy group, (such as glycidyl(meth)acrylate), and an elastomer having reactive functional group, such as epoxy-modified elastomer obtained by epoxidizing the unsaturated bond of the elastomer.

Examples of typical styrene-based elastomers can include: a styrene-diene-styrene block copolymer (styrene-butadiene-styrene block copolymer (SBBS), and styrene-isoprene-styrene block copolymer (SIS)); a hydrogenated block copolymer (styrene-ethylene butylene-styrene block copolymer (or hydrogenated (styrene-butadiene-styrene block copolymer)) (SEBS), styrene-ethylene propylene-styrene block copolymer (or hydrogenated (styrene-isoprene-styrene block copolymer)) (SEPS), styrene-ethylene ethylene propylene-styrene block copolymer (SEEPS), and hydrogenated polymer of random styrene-butadiene copolymer); and a modified copolymer prepared by introducing a functional group (such as epoxy group, carboxyl groups or acid anhydride group) to these copolymers (epoxylated styrene-diene copolymer in which the unsaturated bond of diene is epoxylated, (such as epoxylated styrene-diene-styrene block copolymer and a hydrogenated polymer thereof)).

Next, the core-shell elastomer is a polymer having multi-layer structure composed of a core layer (core part) and a shell layer which covers a portion or all of the core layer (surface of the core layer). The core-shell elastomer preferably has the core layer made of a rubber component (soft component), specifically made of an acrylic-based rubber. The glass transition temperature of the rubber component is, for example, less than 0° C. (-10° C. or less, for example), preferably -20° C. or less (about -180° C. to -25° C., for example), and more preferably may be -30° C. or less (about -150° C. to -40° C., for example).

The acrylic-based rubber as the rubber component is a polymer composed mainly of an acrylic monomer (specifically acrylic acid ester such as alkylacrylate (acrylic acid C<sub>1</sub>-C<sub>12</sub> alkyl ester such as butyl acrylate, preferably acrylic acid C<sub>1</sub>-C<sub>8</sub> alkyl ester, more preferably acrylic acid C<sub>2</sub>-C<sub>6</sub> alkyl ester)). The acrylic-based rubber may be a polymer or copolymer of acrylic-based monomer, (copolymer of acrylic-based monomers, copolymer of acrylic-based monomer with another monomer containing unsaturated bond, and the like), and may be a copolymer of acrylic-based monomer (and another monomer containing unsaturated bond) with cross-linking monomer.

The shell layer of the core-shell elastomer adopts a vinyl-based polymer. The vinyl-based polymer is obtained by polymerization or copolymerization of at least one monomer selected from aromatic vinyl monomer, cyanated vinyl monomer, methacrylic acid ester-based monomer, and acrylic acid ester monomer. The rubber layer and the shell layer of such a core-shell type copolymer are normally bonded together by graft copolymerization. The graft copolymerization is attained, as needed, by adding a graft-crossing agent which reacts with the shell layer at the time of polymerization of the rubber layer, thus providing the rubber layer with the reactive group, followed by forming the shell layer.

The polyester-based elastomer can be grouped into polyether type and polyester type. Any of them can be used if only the flexural modulus is 1000 MPa or less, preferably 700 MPa or less. If the flexural modulus exceeds 1000 MPa, sufficient flexibility cannot be attained. The polyether type polyester-based elastomer is a polyester elastomer composed of an aromatic polyester as the hard segment, and a polyester as the soft segment made of an oxy-alkylene glycol polymer and dicarboxylic acid. The aromatic polyester unit in the hard segment is a polycondensate of dicarboxylic acid compound with dihydroxy compound, a polycondensate of oxycarboxylic acid compound, or a polycondensate of these three components. For example, polybutylene terephthalate and the like are used as the hard segment. The soft segment to be used includes a compound obtained by polycondensation of polyalkylene ether with dicarboxylic acid. For example, an esterified compound of polyoxy tetramethylene glycol, derived from tetrahydrofuran is used. The above polyether elastomer is commercially available as: PELPRENE P-30B, P-70B, P-90B, and P-280B, manufactured by Toyobo Co., Ltd.; Hytrel 4057, 4767, 6347, and 7247, manufactured by Du Pont-Toray Co., Ltd.; Riteflex 655 manufactured by Ticona LLC; or the like.

The polyester type elastomer is a polyester elastomer composed of an aromatic polyester as the hard segment and an amorphous polyester as the soft segment. The aromatic polyester unit in the hard segment is the same to that of the above polyether type elastomer. The soft segment is a ring-opening polymer of lactone, that is to say, a polylactone, or an aliphatic polyester derived from aliphatic dicarboxylic acid and aliphatic diol. The polyester type elastomer

is commercially available as PELPRENE S-1002 and S-2002, manufactured by Toyobo Co., Ltd., or the like.

In order to further impart a desired characteristic depending on the object, the composition of the present invention can contain known substances which are commonly added to thermoplastic resins and thermosetting resins, such as stabilizer including antioxidant, heat-stabilizer, or UV absorber, antistatic agent, coloring agent such as dye or pigment, lubricant, plasticizer, crystallization accelerator, crystal nucleating agent, and epoxy compound within the range not deteriorating the effect of the present invention.

In particular, although antistatic agent, coloring agent, lubricant, and plasticizer often contain carboxyl groups, hydroxyl group, and amino group, these functional groups are preferably not contained because they likely react with carbodiimide group.

In the present invention, in order to improve the moldability, a mold releasing agent can be added. Any type of mold releasing agent can be preferably applied, including olefin-based polymer, aliphatic amide compound, and aliphatic ester compound. Specifically preferred mold releasing agent is an olefin-based polymer presumed to have low reactivity with carbodiimide compound, or an aliphatic ester compound having 100 or less of hydroxyl group value determined by the Japan Oil Chemists' Society Method 2, 4, 9, 2-71 (Pyridine-acetic anhydride method).

Additive containing carboxyl groups, hydroxyl group, or amino group is preferably not used.

The resin composition to be used in the present invention can be easily prepared by facilities and method commonly used as the conventional resin composition preparation method. Examples are: (1) the method in which the respective components are mixed together, and the mixture is kneaded in and extruded from a single screw or twin screw extruder to form pellets, followed by molding; (2) the method in which pellets having different compositions from each other are prepared, and specified amounts of the respective pellets are mixed together to be subjected to molding, and then the molded article having a desired composition is obtained; and (3) the method in which one or more components are directly supplied to the molding machine. Any of above-given methods can be applied. The method in which a portion of a resin component is prepared in fine powder form, which is then mixed with other components, is a preferred one to attain homogeneous blending of the components.

In preparing pellets kneaded by using an extruder, the temperature of cylinder of the extruder is preferably set so that the temperature of resin in the extruder is within the range of 240° C. to 300° C., and more preferably 250° C. to 270° C. If the temperature thereof is below 240° C., the reaction between polybutylene terephthalate and carbodiimide becomes insufficient, and thus, resistance to hydrolysis and resistance to heat-shock may be insufficient, or excessively high viscosity of molten material may result in breaking fibrous filler, which may finally lead to failing to attain necessary mechanical properties. When the temperature of the resin exceeds 300° C., the resin decomposition likely occurs, and the resistance to hydrolysis and the resistance to heat shock may become insufficient.

In the same way as in molding, it is preferable to set the temperature of cylinder of the extruder so that the resin temperature in the molding machine is within the range of 240° C. to 300° C., and more preferably 250° C. to 270° C. Outside that temperature range, insufficient properties may result in the same way as in the above case. The mold temperature at the time of injection molding is preferably

within the range of 40° C. to 100° C., more preferably 60° C. to 90° C. If the mold temperature is below 40° C., the post-shrinkage occurs and strain is generated to thereby fail in attaining a desired shape or to fail in attaining sufficient resistance to heat shock. If the mold temperature exceeds 100° C., the molding cycle takes a long time, which deteriorates the mass-production performance.

Furthermore, the (B) carbodiimide compound can be blended as the master batch made up of a resin as the matrix, and the use of master batch is often easy in terms of practical handling. A master batch of polybutylene terephthalate resin is preferably used. However, a master batch prepared by other resins may also be applicable. In the case of master batch of polybutylene terephthalate resin, the amount of the master batch may be adjusted so as to assure the range of specified blending amount of the (B) carbodiimide compound. The master batch may be preliminarily added at the time of melting and kneading to form homogeneous pellets. Alternatively, components other than the carbodiimide compound are preliminarily formed as homogeneous pellets by melt-kneading and the like, and the pellet-blend, in which the master batch pellets of the carbodiimide compound are dry-blended at the time of molding, may be used for molding.

The resin composition of the present invention can be set as 300 Pa•s or less of the melt viscosity at a temperature of 260° C. and a shear rate of 1000 sec<sup>-1</sup> in accordance with ISO 11443. Furthermore, the melt viscosity can also be set as 250 Pa•s or less. Unless the melt viscosity secures 300 Pa•s or less, the flowability becomes insufficient, and the resin may not be filled in the mold in some cases.

The resin composition of the present invention can achieve the tensile strength of 120 MPa or more, specifically 130 MPa or more in accordance with ISO 527.

The polybutylene terephthalate resin composition according to the present invention is particularly useful for varieties of insert-injection molded articles.

## EXAMPLES

The present invention is described below in more detail referring to the following Examples. However, the present invention is not limited to these examples.

### Examples 1 to 5, Comparative Examples 1 to 4

The respective components given in Table 1 were weighed and were dry-blended together. The blend was then melt-kneaded in a 30 mm dia. twin screw extruder (TEX-30, manufactured by The Japan Steel Works, Ltd.) at a cylinder temperature of 260° C., an extrusion rate of 15 kg/h, and a screw rotational speed of 150 rpm, to form pellets. By using the pellets prepared, respective test pieces were formed to measure various physical properties. The results are summarized in Table 1.

The detail of the components used and the measurement method for evaluating the physical properties are given below.

#### (A) Polybutylene Terephthalate Resin

(A-1) Manufactured by WinTech Polymer Ltd.; intrinsic viscosity of 0.69, and amount of terminal carboxyl groups of 24 meq/kg

(A-2) Manufactured by WinTech Polymer Ltd.; intrinsic viscosity of 0.70, and amount of terminal carboxyl groups of 44 meq/kg

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(B) Carbodiimide Compound

(B-1) Aromatic carbodiimide compound: Stabaxol P, manufactured by Rhein Chemie Japan Ltd.

(B-2) Aromatic carbodiimide compound: Stabaxol P400, manufactured by Rhein Chemie Japan Ltd.

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527. After that, by using the pressure cooker tester, the tensile test piece was exposed to an environment of 121° C. and 100% RH for 50 hours. From the tensile strength before and after the exposure, the tensile strength retention rate was calculated.

TABLE 1

	Examples					Comparative Examples			
	1	2	3	4	5	1	2	3	4
(A) A-1 (parts by weight)	100	100	100	100	100		100	100	100
A-2 (parts by weight)						100			
(B) B-1 (parts by weight)	0.4	0.4	0.4	0.4		1.4			
B-2 (parts by weight)					0.7				
(C) C-1 (parts by weight)	47	47	47	47	47	46	50	50	50
(D) D-1 (parts by weight)	8				8	8	17		
D-2 (parts by weight)		8							
D-3 (parts by weight)			8					17	
D-4 (parts by weight)				8					17
【Carbodiimide equivalent/Amount of carboxyl group】	[1-0]	[1-0]	[1-0]	[1-0]	[1.0]	[1.0]	—	—	—
Evaluation Melt viscosity (Pa · s)	205	280	280	270	280	240	200	300	280
Resistance to heat shock	360<	300<	300<	300<	300<	240	200	240	120
Tensile strength (MPa)	130	132	135	132	130	130	115	118	122
Tensile strength retention rate after 50 hr (%)	92	92	90	85	90	70	90	81	58

(C) Glass Fiber

(C-1) ECS03-T127, manufactured by Nippon Electric Glass Co., Ltd.

(D) Elastomer

(D-1) MODIPER A5300 (ethylene ethyl acrylate-graft-butylacrylate/methylmethacrylate), manufactured by NOF Corporation

(D-2) SEPTON 4055 (polystyrene-poly(ethylene-ethylene-propylene) block polystyrene copolymer), manufactured by Kuraray Co., Ltd.

(D-3) EXL 5136, acrylic-based core-shell polymer, manufactured by Rohm and Haas Company

(D-4) PERPREN P90BD (polyester-based elastomer), manufactured by Toyobo Co., Ltd.

[Melt Viscosity Characteristic]

The melt viscosity was measured in accordance with ISO 11443 under the condition of a cylinder temperature of 260° C. and a shear rate of 1000 sec<sup>-1</sup>.

[Resistance to Heat Shock]

Pellets to be used were molded into an insert-molded article by insert-injection molding under the condition of a resin temperature of 260° C., a mold temperature of 65° C., an injection time of 25 sec, and a cooling time of 10 sec by using a mold for forming test piece (a mold inserting an iron core of 18 mm in length, 18 mm in width, and 30 mm in height into a rectangular cylinder of 22 mm in length, 22 mm in width, and 51 mm in height) so that the minimum thickness of a portion of resin section becomes 1 mm. The insert molded article obtained was subjected to heat shock resistance testing in which one cycle includes heating at 140° C. for one hour and 30 minutes by using a cold impact tester, and then lowering the temperature to -40° C. to cool for one hour and 30 minutes, and then further raising the temperature to 140° C., and the number of cycles until the molded article generated cracks was measured to evaluate the resistance to heat shock.

[Pressure Cooker Test]

Pellets to be used were injection-molded to prepare ISO 3167 tensile test piece under the condition of a resin temperature of 260° C., a mold temperature of 80° C., an injection time of 15 sec, and a cooling time of 15 sec, and the tensile strength was measured in accordance with ISO

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The invention claimed is:

1. A method of manufacturing an insert injection-molded article wherein the injected portion thereof is a polybutylene [terephthalate] *terephthalate* composition formed by blending a composition in the absence of an aromatic polyvalent carboxylic acid esters, the composition comprising:

100 parts by weight of a polybutylene terephthalate resin (A) having 30 meq/kg or less of terminal carboxyl groups with

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a carbodiimide compound (B) in an amount of 0.8 to 1.2 equivalents of the carbodiimide functional group when the amount of terminal carboxyl groups in the polybutylene terephthalate resin (A) is set as 1, wherein the carbodiimide is selected from the group consisting of di-2,6-dimethylphenyl carbodiimide, poly(4,4'-diphenylmethane carbodiimide), poly(phenylene carbodiimide), and poly(triisopropylphenylene carbodiimide);

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20 to 100 parts by weight of a fibrous filler (C); and 5 to 15 parts by weight of an elastomer (D) selected from the group consisting of styrene-based thermoplastic elastomer, a grafted olefin-based thermoplastic elastomer, a core-shell elastomer composed mainly of an acrylic-based rubber, a polyester-based thermoplastic elastomer, and mixtures thereof;

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wherein said composition displays good flowability as evidenced by a melt viscosity of 300 Pa·s or less at a temperature of 260° C. and a shear rate of 1000 sec<sup>-1</sup> in accordance with ISO 11443, and

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injecting said polybutylene terephthalate composition while molten into a mold including a metal insert to form an insert injection-molded article exhibiting improved resistance to heat shock and wherein (A) and (B) are selected and provided in said composition in concentrations so that 0.5 to 1.5 equivalents of carbodiimide functional groups are present per each carboxyl functional group of (A) and wherein (A), (B), (C) and (D) are provided in said composition within the specified ranges so as to facilitate the expression of said improved resistance to heat shock of said insert injection-molded article when subjected to 300 cycles of heating at 140° C. for 1.5 hr, and cooling to -40° C. for 1.5 hr., and a tensile strength retention after 50 hours of

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85% to 92% pursuant to ISO 527 at 121° C. and 100% relative humidity after 50 hours.

2. A method of manufacturing an insert injection-molded article wherein the injected portion thereof is a polybutylene terephthalate composition formed by blending a composition comprising:

100 parts by weight of a polybutylene terephthalate resin (A) having 30 meq/kg or less of terminal carboxyl groups with

a carbodiimide compound (B) having a molecular weight of 2000 or more in an amount of 0.8 to 1.2 equivalents of the carbodiimide functional group when the amount of terminal carboxyl groups in the polybutylene terephthalate resin (A) is set as 1, wherein the carbodiimide is selected from the group consisting of di-2, 6-dimethylphenyl carbodiimide, poly(4,4'-diphenylmethane carbodiimide), poly(phenylene carbodiimide), and poly(triisopropylphenylene carbodiimide);

20 to 100 parts by weight of a fibrous filler (C); and

5 to 15 parts by weight of an elastomer (D), selected from the group consisting of styrene-based thermoplastic elastomer, a grafted olefin-based thermoplastic elastomer, a core-shell elastomer composed mainly of an acrylic-based rubber, a polyester-based thermoplastic elastomer, and mixtures thereof;

wherein said composition displays good fluidity as evidenced by a melt viscosity of 300 Pa•s or less at a temperature of 260° C. and a shear rate of 1000 sec<sup>-1</sup> in accordance with ISO 11443, and

injecting said polybutylene terephthalate composition while molten into a mold including a metal insert to form an insert injection-molded article exhibiting improved resistance to heat shock and wherein (A) and (B) are selected and provided in said composition in concentrations so that 0.5 to 1.5 equivalents of carbodiimide functional groups are present per each carboxyl

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functional group of (A) and wherein (A), (B), (C) and (D) are provided in said composition within the specified ranges so as to facilitate the expression of said improved resistance to heat shock of said insert injection-molded article when subjected to 300 cycles of heating at 140° C. for 1.5 hr, and cooling to -40° C. for 1.5 hr., and a tensile strength retention after 50 hours of 85% to 92% pursuant to ISO 527 at 121° C. and 100% relative humidity for 50 hours.

3. The method of manufacturing an insert injection-molded article according to claim 1, wherein the intrinsic viscosity of the polybutylene terephthalate resin (A) of the polybutylene terephthalate resin composition is within the range of 0.67 to 0.90 dL/g.

4. The method of manufacturing an insert injection-molded article according to claim 2, wherein the intrinsic viscosity of the polybutylene terephthalate resin (A) of the polybutylene terephthalate resin composition is within the range of 0.67 to 0.90 dL/g.

5. The method of manufacturing an insert injection-molded article according to claim 1, wherein the tensile strength of the resulting article in accordance with ISO 527 is 120 MPa or more.

6. The method of manufacturing an insert injection-molded article according to claim 2, wherein the tensile strength of the resulting article in accordance with ISO 527 is 120 MPa or more.

7. The method of manufacturing an insert injection-molded article according to claim 1, wherein the tensile strength of the resulting article in accordance with ISO 527 is 130 MPa or more.

8. The method of manufacturing an insert injection-molded article according to claim 2, wherein the tensile strength of the resulting article in accordance with ISO 527 is 130 MPa or more.

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