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(54) RAPIDLY CRYSTALLISING POLYESTER COMPOSITIONS

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of the Federal Republic of Germany, of 509 Leverkusen, Germany do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to highly crystalline, rapidly crystallizing thermoplastic compositions comprising a high molecular weight polyalkylene terephthalate and a phthalic acid ester.

Polyalkylene terephthalates are used for manufacturing fibres, films and moulded articles. They have excellent physical properties such as high wear resistance, durability, and high dimensional accuracy, i.e. due to their partly crystalline structure and they are, therefore, particularly suitable for the manufacture of heavy duty moulded articles. The mechanical properties can be further improved by incorporating reinforcing materials such as glass-fibres (British Patent No. 1,111,012, US-Patent No. 3,368,995, and German Auslegeschrift No. 2,042,447).

Polyethylene terephthalate (PET) is particularly suitable for the manufacture of fibres, filaments, and sheets, but it is hardly suitable for injection moulding because of high moulding temperatures (approximately 140°C) and relatively long moulding times required. These stringent processing conditions prevent the use of polyethylene terephthalate for injection moulding in spite of its high rigidity and heat distortion temperature.

Although polypropylene terephthalate (PPT) and polybutylene terephthalate (PBT) require shorter moulding times and lower moulding temperatures (approximately 80°C) owing to their higher rate of crystallisation, they are inferior to polyethylene terephthalate in their physical properties, particularly in their heat distortion temperature.

High crystallinity ensures hardness, dimensional stability and resistance to distortion even at elevated temperatures. For optimum properties high crystallinity must be arrived at as rapidly as possible. Thus, in polyethylene terephthalate crystallisation can be improved and accelerated by nucleation with finely divided inorganic solids (Netherlands Patent Application No. 65.11744). The injection moulding cycle time which governs the economics of the process depends on the time interval for which the cast must stay in the mould. These cycles are too long even at high moulding temperature and, therefore, prevent the wide use of polyethylene terephthalate in the manufacture of injection moulded articles.

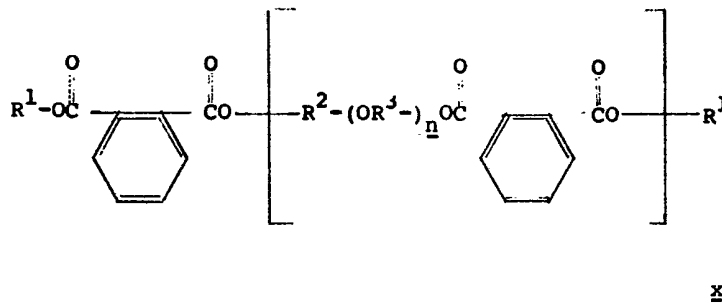
Developing of other polyalkylene terephthalates which have a higher crystallisation velocity and higher crystallinity is, therefore, necessary. We have sought to provide polyalkylene terephthalates which contain from 0.5 to 30% by weight of a phthalic acid ester. Such mixtures have improved crystallisation velocity.

In these polyester compositions the degree of crystallinity required for high dimensional stability is achieved more rapidly so that the injection moulding cycles are substantially shortened. Also, the moulding temperature can be lower without impairing the crystallisation behaviour. The injection moulded casts, therefore, cool more rapidly, and the residence time in the mould is, therefore, also reduced.

The present invention provides a highly crystalline, rapidly crystallising thermoplastic composition comprising

(1) from 70 to 99.5% by weight of a high molecular weight polyalkylene terephthalate having an intrinsic viscosity of at least 0.6 dl/g (determined on a 0.5% by weight solution in a mixture of phenol and tetrachloroethane in proportions by weight of 1:1 at 25°C), and

(2) from 0.5 to 30% by weight of a phthalic acid ester having an average molecular weight of from 200 to 2000, represented by the following formula:



wherein

R¹ represents a branched chain aliphatic group having from 3 to 12 C-atoms, R² and R³ each independently represents a linear or branched chain aliphatic group having from 1 to 12 C-atoms,

n represents 0 or an integer of from 1 to 4, and

x represents 0 or an integer of from 1 to 15, with the proviso that, when the phthalic acid ester is di-2-ethylhexyl phthalate, the proportion of the phthalic acid ester is not substantially 0.5% by weight, and with the further proviso that the composition does not contain a polyolefin or vinyl type polymer when component (2) is dibutyl phthalate or dioctyl phthalate.

The composition preferably comprises from 85—99.5% by weight of the polyalkylene terephthalate and from 0.5—15% by weight of the phthalic acid ester. The intrinsic viscosity of the polyalkylene terephthalate is preferably at least 0.8 dl/g.

The average molecular weight of the phthalic acid ester (2), even if it is a mixture of oligomers, can be determined by vapour pressure osmosis in acetone.

The present invention also provides a process for the production of highly crystalline, rapidly crystallising thermoplastic compositions, wherein from 70 to 99.5% by weight, preferably from 85 to 99.5% by weight, of a high molecular weight polyalkylene terephthalate having an intrinsic viscosity of at least 0.6 dl/g, preferably at least 0.8 dl/g (determined on a 0.5% by weight solution in a mixture of phenol and tetrachloroethane in proportions by weight of 1:1 at 25°C) and from 0.5 to 30% by weight, preferably from 0.5 to 15% by weight, of a phthalic acid ester of formula I above are mixed together and homogenised in the melt. The operation can be carried out in a mixing screw extruder, for example; the solidified melt can, subsequently, be granulated.

The dicarboxylic acid component of the polyalkylene terephthalate (1) consists of terephthalic acid which may contain up to 10 mol%, based on the acid component of other aromatic dicarboxylic acids having from 6 to 14 C-atoms, of aliphatic dicarboxylic acids having from 4 to 8 C-atoms, or of cycloaliphatic dicarboxylic acids having from 8 to 12 C-atoms. Examples of such dicarboxylic acids are phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, diphenyl-4,4'-dicarboxylic acid, adipic acid, sebacic acid, and cyclohexanediadicetic acid.

The diol component of the polyalkylene terephthalate is, for example, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol or cyclohexane-1,4-dimethanol and, preferably, ethylene glycol; it may contain up to 10 mol% of other aliphatic diols having from 3 to 8 C-atoms, cycloaliphatic diols having from 6 to 15 C-atoms or aromatic diols having from 6 to 21 C-atoms. Examples of such additional diols ("Codiols") include 3 - methylpentanediol - (2,4), 2 - methylpentanediol - (1,4), 2,2,4 - trimethylpentanediol - (1,3), 2 - ethylhexanediol - (1,3), 2,2 - diethylpropanediol - (1,3), hexanediol - (1,3), 1,4 - di - (β - hydroxyethoxy) - benzene, 2,2 - bis - (4 - hydroxycyclohexyl) - propane, 2,4 - dihydroxy - 1,1,3,3 - tetramethyl - cyclobutane, 2,2 - bis - (3 - β -

hydroxyethoxyphenyl) - propane and 2,2 - bis - (4 - hydroxypropoxyphenyl) - propane.

The polyalkylene terephthalates (1) can be branched by incorporating trihydric or tetrahydric alcohols or tribasic or tetrabasic acids as described in German Offenlegungsschrift No. 1,900,270 and in US Patent No. 3,692,744. Examples of suitable branching agents include trimesic acid, pyromellitic acid, trimethylolpropane and ethane, and pentaerythritol. It is advisable not to use more than 1 mol% of branching agent, based on the quantity of acid component.

The polyalkylene terephthalates can be prepared in known manner by a) esterification or transesterification of terephthalic acid and/or of the corresponding dialkylterephthalates, preferably the dimethyl ester, with from 1.05 to 5.0 mol, preferably from 1.4 to 3.6 mol of the diol, based on 1 mol of the dicarboxylic acid component, and optionally the branching agent, in the presence of esterification and/or transesterification catalysts (first stage), and

b) polycondensation of the resulting reaction products in the presence of polycondensation catalysts at temperatures between 200 and 320°C at reduced pressure (preferably below 1 Torr) (second stage).

Both the first step (a) and the second step (b) of condensation are usually carried out in the presence of catalysts, e.g., those described by R. E. Wilfong in J. Polym. Sci. 54, 385 (1961). Some of these catalysts (A) are more powerful accelerators of the esterification reaction, (a) others (B) for the polycondensation reaction (b), still others (C) are fairly active for both (a) and (b).

The following are examples: catalysts (A) which are suitable for accelerating reaction (a):

1. Lithium, sodium, potassium, calcium, strontium and boron in the form of the metals or their oxides, hydrides, formates, acetates, alcoholates or glycollates;
2. Calcium and strontium chlorides and bromides;
3. tertiary amines;
4. Calcium and strontium malonates, adipates, benzoates, etc.;
5. Lithium salts of dithiocarbamic acids.

The following are examples of catalysts (B) suitable for the polycondensation reaction (b):

1. Molybdenum, germanium, lead, tin, and antimony in the form of the metals or their oxides, hydrides, formates, alcoholates or glycollates;
2. Zinc and lead perborates and borates;
3. Zinc, manganese(II), cobalt, magnesium, chromium, iron and cadmium succinates, butyrates, adipates or enolates of a diketone;
4. Zinc chloride and bromide;
5. Lanthanum dioxide and titanate;
6. Neodymium chloride;
7. Mixed salts of antimony, e.g. potassium antimony tartrate, and salts of antimoninic acids, such as potassium pyroantimonate;
8. Zinc or manganese salts of dithiocarbamic acids;
9. Cobalt naphthenate;
10. Titanium tetrafluoride or tetrachloride;
11. Alkyl ortho-titanates;
12. Titanium tetrachloride ether complexes;
13. Quaternary ammonium salts carrying a titanium hexaalkoxy group; titanium tetraalkoxides, alkali metal or alkaline earth metal compounds of aluminium, zirconium or titanium alkoxides;
14. Organic quaternary ammonium, sulphonium, phosphonium and oxonium hydroxides and salts;
15. Barium malonate, adipate, benzoate, etc;
16. Lead, zinc, cadmium or manganese salts of the monoalkyl ester of a phenylene dicarboxylic acid;
17. Antimony catechuic complexes with an amino alcohol or with an amine and an alcohol;
18. Uranium trioxide, tetrahalide, nitrate, sulphate or acetate.

The following are examples of catalysts (C) which are suitable for accelerating both steps (a) & (b) of the reaction:

1. Barium, magnesium, zinc, cadmium, aluminium, manganese and cobalt as the metals or their oxides, hydrides, formates, alcoholates, glycolates or, preferably, as acetates;
2. Aluminium chloride and bromide;

3. Zinc, manganese(II), cobalt, magnesium, chromium, iron and cadmium succinates, butyrates, adipates or enolates of a diketone.

The most suitable compounds for use as catalysts (A) are calcium, zinc and manganese salts, particularly the acetates.

The most suitable catalysts (B) are the compounds of zinc, manganese, cobalt, antimony, germanium, titanium and tin, e.g. zinc and manganese acetate, antimony trioxide, trichloride and triacetate, and germanium dioxide and tetrachloride.

The most suitable catalysts (C) are particularly the titanium compounds, e.g. tetraalkyltitanium acid esters having alkyl groups with from 1 to 10 C-atoms, such as tetraisopropyltitanate and tetrabutyltitanate.

The catalysts are used in quantities of from 0.001 to 0.2% by weight, based on the dicarboxylic acid components.

Inhibitors may be added in the process to inhibit the catalysts (A) after completion of the first reaction step (a) and to increase the stability of the end product.

(cf. "Polyesterfasern" by H. Ludewig, 2nd Edition, publishers Akademie-Verlag, Berlin 1974). The following are examples of such inhibitors: phosphoric acid, phosphorous acid and aliphatic, aromatic and araliphatic esters thereof, e.g. the alkyl esters having from 6 to 18 C-atoms in the alcohol component, phenyl esters in which the phenyl groups can carry 1 to 3 substituents having 6 to 18 C-atoms, such as trinonylphenyl phosphate, dodecyl phenyl phosphate or triphenyl phosphate. These inhibitors are usually added in quantities of from 0.01 to 0.6% by weight, based on the dicarboxylic acid component.

In order to obtain an even higher molecular weight, the polyalkylene terephthalates may be subjected to a solid phase polycondensation. This is generally carried out by subjecting the granulated product to a temperature which is from 60 to 6°C below the melting point of the polymer, either in a steam of nitrogen or under a vacuum of less than 1 Torr.

The phthalic acid esters (2) can be prepared by esterification or transesterification of phthalic acid, its anhydride and/or its dialkyl esters, preferably its methyl esters, with monohydric alcohols or with monohydric and dihydric alcohols. A detailed description of the various methods of preparation is in E. Müller, "Methoden der Organischen Chemie" (Houben-Weyl), Vol. 14/2, page 1 et seq., Georg Thieme Verlag, Stuttgart 1963, and in V. V. Korshak and S. V. Vinogradova, "Polyesters", Pergamon Press, Oxford 1965, pages 34—63.

The following are examples of suitable phthalic acid esters (2):

diisopropylphthalate,

ditert.-butylphthalate,

di-2-ethylhexylphthalate,

diisononylphthalate, and

di-isononyl-poly-triethylene glycol phthalate.

The mixtures of polyalkylene terephthalate (1) and phthalic acid ester (2) can be obtained in usual commercial mixing apparatus such as kneaders and one-shaft or two-shaft screw-extruders. The solidified melt of the mixtures can be granulated for further processing, and this can be followed by a post-condensation in the solid phase.

The usual quantities of stabilizers, preferably from 0.01 to 0.5% by wt. based on the weight of the polyalkylene terephthalates (exclusive fillers or reinforcements) can be added to protect against thermooxidative degradation. Suitable stabilizers include phenols and phenol derivatives, particularly sterically hindered phenols which have alkyl substituents with 1 to 6 C-atoms in both ortho-positions to the phenolic hydroxyl group, amines, preferably secondary arylamines and their derivatives, phosphates and phosphites, preferably their aryl derivatives, quinones, copper salts of organic acids, addition compounds of copper (I) halides with phosphites, e.g. 4,4' - bis - (2,6 - di - tert. - butylphenol); 1,3,5 - trimethyl - 2,4,6 - tris - (3,5 - di - tert. - butyl - 4 - hydroxy - benzyl) - benzene; 4,4' - butylidene - bis - (6 - tert. - butyl - *m* - cresol); 3,5 - di - tert. - butyl - 4 - hydroxy - benzyl - phosphonic acid diethyl ester; N,N' - bis - (β - naphthyl) - *p* - phenylenediamine; N,N' - bis - (1 - methylheptyl) - *p* - phenylenediamine; phenyl - β - naphthylamine; 4,4' - bis - (α,α - dimethylbenzyl) - diphenylamine; 1,3,5 - tris - (3,5 - di - tert. - butyl - 4 - hydroxy - hydrocinnamoyl) - hexahydro - *s* - triazine; hydroquinone; *p* - benzoquinone; toluhydroquinone; *p* - tert.-butyl-pyrocatechol; chloranil; naphthoquinone; copper naphthenate; copper octoate; Cu(I)Cl/triphenylphosphate; Cu(I)Cl/trimethylphosphite; Cu(I)Cl/tris-chloroethylphosphite; Cu(I)Cl/tripropylphosphite; and *p*-nitrosodimethylaniline.

The thermoplastic compositions of the invention can be reinforced, e.g., with metals, silicates, carbon and glass, primarily, in the form of fibres and woven or non-woven webs. Glass fibres are preferred.

Inorganic or organic pigments, dyes, lubricants and mould release agents such as zinc stearate, montan wax, and UV absorbers can also be added in the usual quantities.

Flame-retardant compositions are obtained by the addition of from 2 to 20% by weight, based on the composition of known flame-retarding agents such as halogen-containing compounds, elementary phosphorus or phosphorus compounds, phosphorus-nitrogen compounds, antimony trioxide or mixtures of these, preferably antimony trioxide, decarbromobiphenyl ether and tetrabromobisphenol-A-polycarbonate.

The crystallisation velocity of the thermoplastic polyester moulding compositions can be further increased by adding nucleating agents in quantities of from 0.01 to 1% by weight, based on the quantity of polyester without filler or reinforcing material. Compounds of this kind are known in the art (cf. *Kunststoff-Handbuch*, Volume VIII, "Polyester", Carl Hanser Verlag, Munich, 1973, page 701).

The thermoplastic compositions of this invention are suitable for the manufacture of all kinds of moulded articles by injection moulding.

Examples

An injection mould designed for the production of a gear wheel (diameter 40 mm) was used for determining the length of processing cycle required. The moulded product was ejected from the mould by four ejector pins. The minimum injection cycle at which the ejector pins just failed to penetrate the moulded product and the product dropped from the mould without difficulty was determined.

Table 1 shows the length of time required in the mould as well as the total length of the injection moulding cycle of some polyester compositions according to the invention based on polyethylene terephthalate (intrinsic viscosity 0.94 dl/g) and phthalic acid esters (Examples 1 and 2), compared with the corresponding times required for unmodified polyethylene terephthalate. The comparison Examples 3—4 show the behaviour under processing conditions of polyethylene terephthalate mixtures containing phthalic acid esters which have linear aliphatic alcohols as end groups. Although these polyester compositions can be extruded to fully crystalline products at a lower mould temperature than pure polyethylene terephthalate, the residence time in the mould and the length of the whole operating cycle cannot be shortened.

TABLE 1

Example	Name	Phthalic acid ester Quantity (% by wt.)	Temperature of cylinder (°C)	Temperature of mould (°C)	Residence time in mould (sec.)	Total injection moulding cycle (sec.)
1	Di-isononyl- phthalate	5	260	107	17.5	19.5
2	Di-isononyl- poly-tri- ethylene- glycol- phthalate*	5	260	110	14.5	16.5
3	Di-ethyl- phthalate	5	260	111	47.5	49.5
4	Di-n-butyl- phthalate	5	260	112	42.5	44.5
5	—	—	270	140	37.5	39.5

*Average molecular weight about 700.

TABLE 2

Response under conditions of processing of polyester compositions based on copolyethylene terephthalate
(0.6 mol% of 2-ethylhexanediol-(1,3)) and phthalic acid esters

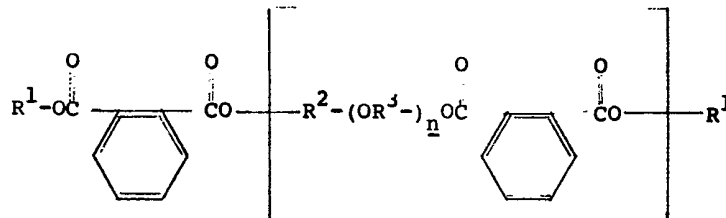
Example	Name	Phthalic acid ester Quantity (% by wt.)	Temperature of cylinder (°C)	Temperature of mould (°C)	Residence time in mould (sec.)	Total injection moulding cycle (sec.)
1	Di-isononyl- phthalate	5	260	110	12.5	14.5
2	Di-isononyl- poly-tri- ethylene glycol phthalate	5	260	108	10.5	12.5
3	—	—	270	130	17.5	19.5

WHAT WE CLAIM IS:—

1. A highly crystalline, rapidly crystallising thermoplastic composition comprising

(1) from 70 to 99.5% by weight of a high molecular weight polyalkylene terephthalate having an intrinsic viscosity of at least 0.6 dl/g (determined on a 0.5% by weight solution in a mixture of phenol and tetrachloroethane in proportions by weight of 1:1 at 25°C), and

(2) from 0.5 to 30% by weight of a phthalic acid ester having an average molecular weight of from 200 to 2000, represented by the following formula:



x

wherein

R¹ represents a branched chain aliphatic group having from 3 to 12 C-atoms,

R² and R³ each independently represents a linear or branched chain aliphatic group having from 1 to 12 C-atoms,

n represents 0 or an integer of from 1 to 4, and

x represents 0 or an integer of from 1 to 15, with the proviso that, when the phthalic acid ester is di-2-ethylhexyl phthalate, the proportion of the phthalic acid ester is not substantially 0.5% by weight, and with the further proviso that the composition does not contain a polyolefin or vinyl type polymer when component (2) is dibutyl phthalate or dioctyl phthalate.

2. A composition as claimed in Claim 1, comprising from 85 to 99.5% by weight of the polyalkylene terephthalate (1) and from 0.5 to 15% by weight of the phthalic acid ester (2).

3. A composition as claimed in Claim 1, substantially as hereinbefore described with reference to Example 1 or 2.

4. A process for the preparation of a composition according to Claim 1, which comprises mixing together and homogenising in the melt from 70 to 99.5% by weight of a high molecular weight polyalkylene terephthalate (1) as defined in Claim 1 and from 0.5 to 30% by weight of a phthalic acid ester (2) as defined in Claim 1.

5. A process as claimed in Claim 4, substantially as hereinbefore described with reference to Example 1 or 2.

6. A composition prepared by a process as claimed in Claim 4 or 5.

7. An injection moulding process wherein a composition as claimed in any one of Claims 1 to 3 and 6 is used.

8. Moulded products prepared by a process as claimed in Claim 7.

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