

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

23 May 2019 (23.05.2019)



(10) International Publication Number

WO 2019/096652 A1

(51) International Patent Classification:

C08J 9/12 (2006.01) *C08G 63/183* (2006.01)

C08J 9/14 (2006.01) *C08G 63/20* (2006.01)

C08G 63/127 (2006.01) *C08G 63/80* (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(21) International Application Number:

PCT/EP2018/080462

(22) International Filing Date:

07 November 2018 (07.11.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

IN201741041178 17 November 2017 (17.11.2017) IN

18160093.3 06 March 2018 (06.03.2018) EP

(71) Applicant: **SABIC GLOBAL TECHNOLOGIES B.V.**

[NL/NL]; Plasticslaan 1, 4612 PX Bergen op Zoom (NL).

(72) Inventors: **AL-FARHOOD, Bander**; P.O. Box 3008,

6160 GA Geleen (NL). **JHA, Roshan, Kumar**; P.O. Box

3008, 6160 GA Geleen (NL). **GADIGONE, Nitin**; c/o

SABIC Intellectual Property Group, P.O. Box 3008, 6160

GA Geleen (NL). **RAHA, Sumanta**; c/o SABIC Intellect-

ual Property Group, P.O. Box 3008, 6160 GA GELEEN

(NL).

(74) Agent: **SABIC INTELLECTUAL PROPERTY**

GROUP; P.O. Box 3008, 6160 GA GELEEN (NL).

(81) Designated States (*unless otherwise indicated, for every*

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every*

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: POLYESTER COPOLYMER FOR THE PRODUCTION OF FOAMED ARTICLES

(57) Abstract: The present invention relates to a thermoplastic polyester copolymer comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester. Such thermoplastic polyester copolymer allows for the production of high-quality foamed articles, whilst reducing the need for additives that are to be incorporated into the copolymer. Such thermoplastic polyester copolymer is understood to have a desirably high degree of long-chain branching.



WO 2019/096652 A1

Polyester copolymer for the production of foamed articles

[0001] The present invention relates to a thermoplastic polyester copolymer having improved
5 foamability properties. The invention further relates to a process for the production of such
thermoplastic polyester copolymer. The invention also relates to foamed objects comprising
such thermoplastic polyester copolymer.

[0002] Thermoplastic foamed articles are increasingly finding their application in a wide array of
10 outlets. To produce such foamed articles, various thermoplastics are available and are being
developed.

[0003] A particular family of thermoplastic materials that are widely acknowledged for their
advantageous material properties are thermoplastic polyesters. Amongst others, one of the
15 particular advantages of thermoplastic polyesters is their recyclability. In many countries,
collection of waste thermoplastic polyesters is well established, and waste thermoplastic
polyesters may be processed by various processes including depolymerisation processes to
obtain materials that can further be converted to a useable application. Further advantageous
properties of thermoplastic polyesters include their high temperature resistance, fatigue
20 resistance and thermoformability.

[0004] For example for these reasons, there is a desire to be able to produce foamed objects
from thermoplastic polyesters. Foamed objects are advantageous for many reasons, amongst
others that they demonstrate an excellent balance of weight to mechanical properties, allowing
25 to produce for example objects that provide a mechanical structural function at a very light
weight. Typical densities of suitable thermoplastic foams are below 100 kg/m³.

[0005] A disadvantage of thermoplastic polyesters is that in homopolymer form, they are not
intrinsically foamable, which requires further measures to be taken to ensure that a foamed
30 article can be manufactured using thermoplastic polyesters. The rheological properties of
thermoplastic polyesters, in particular poly(ethylene terephthalates), are insufficient; melt
viscosity and melt elasticity are not sufficiently high, and crystallisation rates tend to be too low.
For example, the thermoplastic polyester materials may be melt compounded with chain
extenders. This however requires a substantial quantity of such chain extenders to be

incorporated, like up to 5 wt%, which negatively influences the material properties and the costs of the thermoplastic polyester material.

[0006] For amongst others that reason, there is a desire to have access to thermoplastic polyester materials suitable for producing foamed objects, wherein the quantity of additives incorporated in the thermoplastic polyester is reduced.

[0007] This has now been achieved according to the present invention by a thermoplastic polyester copolymer comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester

[0008] Such thermoplastic polyester copolymer allows for the production of high-quality foamed articles, whilst reducing the need for additives that are to be incorporated into the copolymer. In particular, it reduces the need for incorporation of chain extenders into the copolymer. Such thermoplastic polyester copolymer is understood to have a desirably high degree of long-chain branching, which is believed to contribute to achieving the desired melt strength for foamability.

[0009] In the context of the present invention, the presence of long-chain branching in the polyester molecules is presented as determined by the tangens delta ($\tan \delta$), which is the ratio of the loss modulus G'' to the storage modulus G' of the material, determined at low frequency of 0.1 rad/s via Dynamic Mechanical Analysis (DMA). Further also G' and G'' , determined at 0.1 rad/s, are considered to present indicators of desired foamability of the polyester materials. High $\tan \delta$ at 0.1 rad/s and high G' at given G'' , such as at $G''=10$ kPa, are considered to indicate good foamability.

[0010] The thermoplastic polyester copolymer of the present invention presents a significantly increase in $\tan \delta$ and G' at given G'' , thus demonstrating improved melt strength and hence foamability properties.

[0011] It is particularly preferred that the thermoplastic polyester copolymer is a polymer selected from a poly(ethylene terephthalate) copolymer, a poly(trimethylene terephthalate) copolymer, a poly(butylene terephthalate) copolymer, a poly(ethylene naphthalate) copolymer, or a poly(ethylene furanoate) copolymer. For example, the thermoplastic polyester copolymer

may be a poly(ethylene terephthalate) copolymer. Alternatively, the thermoplastic polyester copolymer may be a poly(ethylene furanoate) copolymer.

[0012] In the context of the present invention, a poly(ethylene terephthalate) copolymer is also referred to as a PET copolymer; a poly(trimethylene terephthalate) copolymer is also referred to as a PTT copolymer; a poly(butylene terephthalate) copolymer is also referred to as a PBT copolymer; a poly(ethylene naphthanoate) copolymer is also referred to as a PEN copolymer; and a poly(ethylene furanoate) copolymer is also referred to as a PEF copolymer.

[0013] The thermoplastic polyester copolymer may for example comprise ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from a dicarboxylic acid or a diester thereof and an alkanediol, with regard to the total weight of the thermoplastic polyester copolymer. The dicarboxylic acid or diester thereof may for example comprise 4-20 carbon atoms. The dicarboxylic acid or diester thereof may for example be an aromatic dicarboxylic acid or diester thereof, preferably an aromatic dicarboxylic acid or diester thereof comprising 4-20 carbon atoms. The dicarboxylic acid or diester thereof may for example be selected from terephthalic acid, dimethyl terephthalate, isophthalic acid, 2,6-naphthalenedicarboxylic acid, dimethyl-2,6-naphthalenedicarboxylate, 2,5-furandicarboxylic acid, dimethyl-2,5-furandicarboxylate, or succinic acid. Preferably, the dicarboxylic acid or diester thereof is terephthalic acid.

[0014] The alkanediol may for example be an alkanediol comprising 2-10 carbon atoms. The alkanediol may for example be an aliphatic alkanediol, preferably an aliphatic alkanediol comprising 2-10 carbon atoms. The alkanediol may for example be selected from ethylene glycol, propanediol, 1,4-butanediol, or cyclohexanedimethanol. Preferably, the alkanediol is ethylene glycol.

[0015] For example, the thermoplastic polyester copolymer may comprise ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from a dicarboxylic acid or a diester thereof and an alkanediol, with regard to the total weight of the thermoplastic polyester copolymer, wherein the dicarboxylic acid or diester thereof may for example be selected from terephthalic acid, dimethyl terephthalate, isophthalic acid, 2,6-naphthalenedicarboxylic acid, dimethyl-2,6-naphthalenedicarboxylate, 2,5-furandicarboxylic

acid, or succinic acid, and wherein the alkanediol may for example be selected from ethylene glycol, propanediol, 1,4-butanediol, or cyclohexanedimethanol.

[0016] The PET copolymer may for example be a copolymer comprising ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from a terephthalic acid or dimethyl terephthalate and ethylene glycol, with regard to the total weight of the PET copolymer.

[0017] The PTT copolymer may for example be a copolymer comprising ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from a terephthalic acid or dimethyl terephthalate and 1,3-propanediol, with regard to the total weight of the PTT copolymer.

[0018] The PBT copolymer may for example be a copolymer comprising ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from a terephthalic acid or dimethyl terephthalate and 1,4-butanediol, with regard to the total weight of the PBT copolymer.

[0019] The PEN copolymer may for example be a copolymer comprising ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from a 2,6-naphthalenedicarboxylic acid or dimethyl-2,6-naphthalenedicarboxylate and ethylene glycol, with regard to the total weight of the PEN copolymer.

[0020] The PEF copolymer may for example be a copolymer comprising ≥ 95.0 wt%, preferably ≥ 97.0 wt%, more preferably ≥ 98.5 wt% of moieties derived from 2,5-furandicarboxylic acid or dimethyl-2,5-furandicarboxylate and ethylene glycol, with regard to the total weight of the PEF copolymer.

[0021] It is particularly preferred that the thermoplastic polyester copolymer comprises $\geq 95\%$ of moieties derived from ethylene glycol and terephthalic acid or a diester thereof, with regard to the total weight of the thermoplastic polyester copolymer.

[0022] In certain particular embodiments of the present invention, the thermoplastic polyester copolymer has an intrinsic viscosity of ≥ 0.60 dl/g and ≤ 3.00 dl/g as determined in accordance with ASTM D2857-95 (2007). More preferably, the thermoplastic polyester copolymer has an intrinsic viscosity of ≥ 0.80 and ≤ 2.50 dl/g, even more preferably ≥ 1.00 and ≤ 2.00 dl/g, further even more preferably ≥ 1.00 and ≤ 1.50 dl/g.

[0023] The thermoplastic polyester copolymer according to the present invention may for example comprise ≤ 5.00 wt% with regard to the total weight of the thermoplastic polyester copolymer of polymeric units derived from the polyfunctional compound, preferably ≤ 4.00 wt%,
5 more preferably ≤ 3.00 wt%, even more preferably ≤ 2.00 wt%, even more preferably ≤ 1.50 wt%. The thermoplastic polyester copolymer may for example comprise ≤ 1.30 wt% of polymeric units derived from the polyfunctional compound, preferably ≤ 1.20 wt%, more preferably ≤ 1.10 wt%.

10 [0024] The thermoplastic polyester copolymer according to the present invention may for example comprise ≥ 0.10 wt% with regard to the total weight of the thermoplastic polyester copolymer of polymeric units derived the polyfunctional compound, preferably ≥ 0.25 wt%, more preferably ≥ 0.50 wt%.

15 [0025] The thermoplastic polyester copolymer according to the present invention may for example comprise ≥ 0.10 wt% and ≤ 5.00 wt% with regard to the total weight of the thermoplastic polyester copolymer of polymeric units derived from the polyfunctional compound, preferably ≥ 0.25 wt% and ≤ 3.00 wt%, more preferably ≥ 0.50 wt% and ≤ 2.00 wt%.

20 [0026] The presence of moieties derived from such polyfunctional compound leads to branching of the polymeric chains of the thermoplastic polyester copolymer. It is believed that a certain degree of branching present in the thermoplastic polyester copolymer may contribute to the improvement of the melt strength of the polymer. This is in particular relevant in the formation of foamed materials. In the process of foaming, a foaming agent is supplied to the polyester at
25 certain stage, preferably in a situation where the polyester is in molten condition. The foaming agent executes its expanding function commonly upon exiting a melt processing device, such as a melt extruder or an injection moulding machine. The polyester comprising the foaming agent is in such situation formed into a desired shape for example by entering a portion of the molten material in a mould or by shaping the material into a desired profile by forcing it through an
30 extruder die. The foaming agent then provides its expanding function by generation of gaseous material, resulting in the formation of foam cells. The thermoplastic polyester material is during formation of these foam cells still in molten condition, and needs to solidify under the right circumstances when the foam cells have been formed, thus freezing the foam shape.

[0027] In this foaming process, it is required that the polyester has a certain high melt strength, to ensure that the foam cells retain their form during the solidification process to result in a foamed article having the desired structure. The presence of moieties derived from the polyfunctional compound of the present invention is understood as supportive of the branching of the polyester and thus of the melt strength.

[0028] The moieties of the polyfunctional compound that are able to react with the polyester-forming monomers during the polymerisation of the polyester may for example be hydroxyl moieties or carboxylic acid moieties. Preferably, the moieties of the polyfunctional compound that are able to react with the polyester-forming monomers during the polymerisation of the polyester are hydroxyl moieties.

[0029] The polyfunctional compound may for example be a compound having 1-10 carbon atoms. Preferably, the polyfunctional compound is a compound having 1-10 carbon atoms and three hydroxyl moieties. The polyfunctional compound may for example be a compound selected from a trihydroxymethane, a trihydroxyethane, a trihydroxypropane, a trihydroxybutane, a methanetricarboxylic acid, an ethanetricarboxylic acid, a propanetricarboxylic acid, or a butanetricarboxylic acid. Preferably, the polyfunctional compound is glycerol.

[0030] The thermoplastic polyester copolymer may for example comprise ≥ 0.1 wt% of polymeric units derived from the polyfunctional compound, with regard to the total weight of the copolymer, preferably, ≥ 0.2 wt%, more preferably ≥ 0.5 wt%. The thermoplastic polyester copolymer may for example comprise ≤ 5.0 wt% of polymeric units derived from the polyfunctional compound, preferably ≤ 4.0 wt%, more preferably ≤ 3.0 wt%, with regard to the total weight of the copolymer. For example, the thermoplastic polyester copolymer may comprise ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from the polyfunctional compound, preferably ≥ 0.2 and ≤ 4.0 wt%, more preferably ≥ 0.5 and ≤ 3.0 wt%, with regard to the total weight of the copolymer.

[0031] For example, the thermoplastic polyester copolymer may comprise ≥ 0.1 and ≤ 1.5 wt% of polymeric units derived from the polyfunctional compound, with regard to the total weight of the copolymer, preferably ≥ 0.1 and < 1.5 wt%, more preferably ≥ 0.1 and ≤ 1.3 wt%, even more preferably ≥ 0.3 and ≤ 1.3 wt%. Particularly, the thermoplastic polyester copolymer may

comprise ≥ 0.1 and ≤ 1.5 wt% of polymeric units derived from the polyfunctional compound, with regard to the total weight of the copolymer, preferably ≥ 0.3 and ≤ 1.3 wt%, wherein the polyfunctional compound is glycerol. More particularly, the thermoplastic polyester copolymer may comprise ≥ 0.1 and ≤ 1.5 wt% of polymeric units derived from the polyfunctional compound, with regard to the total weight of the copolymer, preferably ≥ 0.3 and ≤ 1.3 wt%, wherein the polyfunctional compound is glycerol, and wherein thermoplastic polyester copolymer comprises ≥ 95.0 wt% of polymeric units derived from a dicarboxylic acid or a diester thereof and an alkanediol. Even more particularly, the thermoplastic polyester copolymer may comprise ≥ 0.1 and ≤ 1.5 wt% of polymeric units derived from the polyfunctional compound, with regard to the total weight of the copolymer, preferably ≥ 0.3 and ≤ 1.3 wt%, wherein the polyfunctional compound is glycerol, and wherein thermoplastic polyester copolymer comprises ≥ 95.0 wt% of polymeric units derived from a dicarboxylic acid or a diester thereof, being terephthalic acid or dimethyl terephthalate, and an alkanediol, being ethylene glycol.

[0032] Such thermoplastic polyester copolymer does not contain long-chain branching in the situation prior to processing into a foam structure, but does contain a degree of long-chain branching upon being subjected to a certain dwell period, such as 15 minutes, as a certain temperature, such as 260°C , reflecting typical conditions to which the copolymer is subject during foam article production.

[0033] The presence of long-chain branching may be performed via Dynamic Mechanical Analysis using a rheometer, wherein the degree of long-chain branching is expressed by the value for G_0 . G_0 is the value for G' on extrapolation of G'' to 0, fitting data for G'' to G' using a quadratic fit model. G_0 represents the extent of long-chain branching in the polyesters; high G_0 indicates higher degree of long-chain branching. G' is the storage modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C , in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa. G'' is the loss modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C , in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa.

[0034] The determination of G_0 in a rheometer serves to determine the presence of long-chain branching at the start of the rheometer measurement (G_0 , $t=0$), and after intervals of 15 minutes (G_0 , $t=15$), 30 minutes (G_0 , $t=30$) and 45 minutes (G_0 , $t=45$). This dwell time emulates the duration of the processing of the material during the production of a foam based on the material.

[0035] As G_0 indicates the degree of long-chain branching, it can be observed that at $t=0$, none of the samples demonstrated any long-chain branching. This means that the material as produced from the polyester polymerisation process was free from long-chain branching.

5 However, for the examples 1-3, it can be observed that at 15, 30 and 45 minutes, a certain high G_0 is achieved, indicating the desired presence of long-chain branching, which is required for the foaming process to provide foam of desired quality. It thus can be observed that the polyester compositions of the present invention provide both the melt processability that is desired, as demonstrated by G_0 at $t=0$ being 0, and the foam stability upon melt processing that
10 is desired, as demonstrated by G_0 at $t=15, 30$ and 45 to be of certain desired value.

[0036] The polyester-forming monomers may for example be selected from mixtures of a dicarboxylic acid or a diester thereof with an alkanediol. The thermoplastic polyester copolymer may for example comprise ≥ 95.0 wt% of polymeric units derived from a dicarboxylic acid or a
15 diester thereof and an alkanediol.

[0037] The dicarboxylic acid or diester thereof may for example be selected from terephthalic acid, dimethyl terephthalate, isophthalic acid, 2,6-naphthalenedicarboxylic acid, dimethyl-2,6-naphthalenedicarboxylate, 2,5-furandicarboxylic acid, dimethyl-2,5-furandicarboxylate, or
20 succinic acid. Preferably, the dicarboxylic acid or diester thereof is selected from terephthalic acid, dimethyl terephthalate or 2,5-furandicarboxylic acid. More preferably, the dicarboxylic acid or diester thereof is terephthalic acid.

[0038] The alkanediol may for example be selected from ethylene glycol, propanediol, 1,4-butanediol, or cyclohexanedimethanol. Preferably, the alkanediol is selected from ethylene
25 glycol or 1,4-butanediol. More preferably, the alkanediol is ethylene glycol.

[0039] For example, the dicarboxylic acid or diester thereof may be selected from terephthalic acid, dimethyl terephthalate, isophthalic acid, 2,6-naphthalenedicarboxylic acid, dimethyl-2,6-naphthalenedicarboxylate, 2,5-furandicarboxylic acid, dimethyl-2,5-furandicarboxylate, or
30 succinic acid, and the alkanediol may for example be selected from ethylene glycol, propanediol, 1,4-butanediol, or cyclohexanedimethanol. Preferably, the dicarboxylic acid or diester thereof is selected from terephthalic acid, dimethyl terephthalate or 2,5-furandicarboxylic

acid and the alkanediol is selected from ethylene glycol or 1,4-butanediol. More preferably, the dicarboxylic acid or diester thereof is terephthalic acid and the alkanediol is ethylene glycol.

[0040] The thermoplastic polyester copolymer preferably is a poly(ethylene terephthalate)-co-glycerol.

[0041] The thermoplastic polyester copolymer according to the present invention may for example be produced in a process comprising the steps of esterification and melt polycondensation, in this order. Preferably, the thermoplastic polyester copolymer according to the present invention is produced in a process comprising the steps of esterification, melt polycondensation and solid state polymerisation, in this order. It is preferred that a feed stream comprising a dicarboxylic acid or diester thereof, an alkanediol and a polyfunctional compound that has three moieties that can react with the dicarboxylic acid or diester thereof and/or the alkanediol during the polymerisation of the polyester is supplied to the esterification step of the process.

[0042] The esterification step typically comprises a paste mixing vessel and one or more esterification reactor(s). For example, a composition comprising the alkanediol, the dicarboxylic acid or diester thereof, the polyfunctional compound, a catalyst such as antimony triacetate and optionally further compounds such as further comonomers may be pre-mixed in the paste mixing vessel, from which the composition is introduced into the one or more esterification reactor(s). In a particular embodiment, a composition comprising ethylene glycol, terephthalic acid, glycerol and antimony triacetate may be pre-mixed in the paste mixing vessel. The molar ratio of the alkanediol to the dicarboxylic acid or diester thereof may for example be ≥ 1.1 , such as ≥ 1.1 and ≤ 3.0 , preferably ≥ 1.1 and ≤ 2.0 .

[0043] In the esterification reactor, the composition may be subjected to a temperature of 220-270°C, preferably 240-260°C. The pressure during the esterification step in the esterification reactor is preferably atmospheric or superatmospheric, for example ≥ 1.0 bar, such as ≥ 1.0 and ≤ 10.0 bar, during the esterification reaction. The esterification reaction may be conducted during a period of for example 2.0-5.0 hours. During the reaction, a pressure profile may be applied to the reactor. For example, the reaction may be initiated at a pressure of ≥ 2.0 bar, such as ≥ 2.0 and ≤ 6.0 bar, and reduced during the reaction to a pressure of ≥ 1.0 and ≤ 2.0 bar, such as ≥ 1.0 and ≤ 1.5 bar. In a particular embodiment, the esterification reaction may be

conducted during a period of 2.0-5.0 hours using a pressure profile of ≥ 2.0 and ≤ 6.0 bar at the initiation of the reaction and reduction to ≥ 1.0 and ≤ 1.5 bar at the end of the reaction. During the reaction, byproducts such as water may be formed. Preferably, such byproducts are removed from the reaction vessel.

5

[0044] The esterification step results in a polyester oligomer. The polyester oligomer product may be subjected to a polycondensation step in a polycondensation reactor. The polyester oligomer may for example be subjected to the polycondensation for a period of 20 to 100 minutes. The pressure during the polycondensation preferably is subatmospheric, such as for example ≤ 10 mbar, more preferably ≤ 5 mbar. The application of such pressure results in reduction of volatile byproducts as a result of which the reaction shifts towards higher degrees of polymerisation. The polycondensation may be performed at a temperature of 275-300°C. The product obtained from the polycondensation may be solidified and shaped into granules.

10

15 [0045] The product from the polycondensation is a thermoplastic polyester copolymer. The thermoplastic polyester copolymer obtained from the polycondensation may for example have an intrinsic viscosity of ≥ 0.20 and ≤ 0.90 dl/g, such as ≥ 0.40 and ≤ 0.80 dl/g.

[0046] In certain embodiments, the granules obtained from the polycondensation may be further subjected to solid state polymerisation (SSP). SSP may for example be performed in a vessel such as a tumble drier. To conduct the SSP, the contents of the tumble drier may be subjected to a temperature of for example 120-200°C, preferably 150-180°C, for a period of 1-5 hrs, preferably 1-3 hrs, to remove moisture and crystallise the granules, under continuous agitation and under continuous nitrogen flow. Subsequently the SSP reaction may be performed by increasing the temperature to 200-220°C. Preferably, the SSP is performed under a vacuum of ≤ 20 mbar, more preferably ≤ 10 mbar, even more preferably ≤ 5 mbar, under continuous agitation. SSP may for example be performed for a period of 5-50 hours, preferably 10-40 hours, to obtain a thermoplastic polyester copolymer according to the invention.

20

25

30 [0047] In a particular embodiment, the invention relates to a process of a thermoplastic polyester copolymer wherein the process comprises the steps of an esterification step in which a composition comprising an alkanediol, a dicarboxylic acid or diester thereof and the polyfunctional compound react to form a polyester oligomer, which is subsequently subjected to

polycondensation at a pressure of ≤ 5 mbar at a temperature of 275-300°C to obtain a polycondensation product, which upon solidification and drying is subjected to solid-state polymerisation at a temperature of 200-220°C for a period of 5-50 hours.

5 [0048] The thermoplastic polyester copolymer according to the present invention may further in certain embodiments comprise ≥ 0.5 and ≤ 8.0 wt% of moieties derived from a chain extender, with regard to the total weight of the thermoplastic polyester copolymer, preferably ≥ 0.5 and ≤ 4.0 wt%, even more preferably ≥ 1.0 and ≤ 2.5 wt%. The chain extender may for example be selected from diepoxides, dianhydrides, diisocyanates, bisoxazines, bisoxazolines, or
10 bislactams.

[0049] The chain extender may for example be selected from 2,2'-methylene-bis(4,1-phenyleneoxy)bisoxirane, 2,2'-ethylidene-bis(4,1-phenyleneoxy)bisoxirane, 2,2'-(1-methylethylidene)-bis(4,1-phenyleneoxy)bisoxirane, 2,2'-ethylidene-bis(4,1-phenyleneoxy)bisoxirane, 2,2'-(1-methylethylidene)-bis(4,1-phenyleneoxy)bis(3-methyl-oxirane),
15 4,4'-bis(1,2-epoxypropoxy)biphenyl, 2,2'-((1,1'-biphenyl))-4,4'-diylbis(oxy))bisoxirane, 1,4-bis(1,2-epoxypropoxy)benzene, 2,2'-(1,4-phenylenebis(oxy))bisoxirane, 2,2'-((1,1'-binaphthalene)-2,2'-diylbis(oxy))bisoxirane, ((6'-oxiranylmethoxy(2,2'-binaphthalene)-6-yl)oxy)oxirane, 2,2'-(1,6-naphthalenediylbis(oxy))bisoxirane, 2,2'-((1,1'-biphenyl)-4,4'-
20 diylbis(oxy))bis(2-methyl-oxirane), 2,2'-(2,6-naphthalenediylbis(oxy))bis(2-methyl-oxirane), 2,2'-(methylenebis(4,1-phenyleneoxy))bis(2-methyl-oxirane), 2,2'-(1,4-phenylenebis(oxy))bis(2-methyl-oxirane), (2-methyl-4-((oxiranyloxy)methyl)phenoxy)oxirane, or (2,6-dimethyl-4-((oxiranyloxy)methyl)phenoxy)oxirane. In a preferred embodiment, the chain extender is 2,2'-(1-methylethylidene)-bis(4,1-phenyleneoxy)bisoxirane.

25 [0050] It is preferred that the chain extending compound is added in a quantity of ≥ 0.5 and ≤ 8.0 wt% with regard to the total weight of the polyester to the reaction of the polyester and the chain extending compound, more preferably ≥ 0.5 and ≤ 5.0 wt%, even more preferably ≥ 0.5 and ≤ 1.0 wt%, even more preferably ≥ 0.6 and ≤ 1.0 wt%.

30 [0051] The invention also relates to a foam comprising the thermoplastic polyester copolymer. In the context of the present invention, a foam of the polyester may be understood to be a shaped object produced using the polyester wherein the density of the object is reduced to a density lower than the density of the polyester itself by the presence of numerous small cavities,

also referred to as cells, which may or may not be interconnected, and which are dispersed throughout the mass of the polyester.

[0052] The conversion of the polyester material into a foam may occur via any process known in the art to produce foams from thermoplastic materials. Typical processes for the production of foams from thermoplastic materials that are applicable for the production of foams from the thermoplastic polyester copolymer of the present invention include extrusion moulding processes and injection moulding processes.

[0053] For example, such process may be an extrusion moulding process. Suitable extrusion moulding processes involve one single melt extruder equipped with a die suitable for foam production, or it may involve multiple melt extruders positioned in series, for example a first twin-screw extruder and a second single-screw extruder, also referred to as a tandem layout. In such tandem layout, a feed comprising the thermoplastic materials, in the case of the present invention the thermoplastic polyester copolymer, is introduced to the feed inlet of the first twin-screw extruder. The feed may comprise further components, such as for example fillers, reinforcing agents, stabilisers and further thermoplastic materials other than the thermoplastic polyester copolymer. In the twin-screw extruder, the feed material is processed to a molten, mixed composition under the influence of heat and shear.

[0054] Upon exiting the twin-screw extruder, the molten composition is introduced to the feed inlet of the second single-screw melt extruder. In this single-screw extruder, the molten material is homogenised and pressurised, and transported to a die outlet. The die outlet of the single-screw extruder is designed for production of foamed structures.

[0055] A foaming agent, also referred to as blowing agent, may be introduced into the extrusion process. Such blowing agent may be understood to be compounds that cause the expansion in the production of the foamed object. Where the extrusion process is of a tandem layout, the blowing agent may be introduced in either the first twin-screw extruder or in the second single-screw extruder. For example, the blowing agent may be introduced in the first twin-screw extruder.

[0056] The blowing agent may for example be a physical blowing agent. Physical blowing agents are to be understood to be compounds that cause an expansion thus forming a gaseous cell in the thermoplastic polyester copolymer as a result of a physical state change, such as the

change from liquid state to gaseous state of a certain quantity of the blowing agent. To produce a foam of the thermoplastic polyester copolymer having a desired homogeneous cell structure in the foam, the blowing agent is to be homogeneously distributed in the molten composition.

Introduction of the blowing agent in the first twin-screw extruder of the tandem extrusion layout
5 is believed to contribute to such homogeneous distribution.

[0057] The blowing agent may for example be selected from n-pentane, cyclopentane, carbon dioxides, nitrogen, or mixtures thereof.

10 [0058] The blowing agent may for example be introduced in a quantity of 1.0-10.0 wt% with regard to the total weight of the thermoplastic polyester copolymer. Preferably, the blowing agent is introduced in a quantity of 1.5-5.0 wt%, more preferably 2.0-4.0 wt%.

[0059] The use of such blowing agent in such quantities is believed to contribute to obtaining a
15 foam with a desired cell structure. The cell structure of a foam may be expressed in terms of the quantity of open cells and closed cells. It is preferred that the foam that may be produced using the thermoplastic polyester copolymer according to the present invention has an open cell fraction of $\leq 20.0\%$, more preferably $\leq 10.0\%$. The open cell fraction may be determined in accordance with ASTM D6226 (2010).

20 [0060] The use of such blowing agent in such quantities is also believed to contribute to obtaining a foam with a desired low density. It is preferred that the foam that may be produced using the thermoplastic polyester copolymer according to the present invention has a density of $\leq 100 \text{ kg/m}^3$, more preferably $\leq 75 \text{ kg/m}^3$, even more preferably ≥ 50 and $\leq 75 \text{ kg/m}^3$. The foam
25 density may be determined in accordance with ASTM D6226 (2010).

[0061] The invention particularly relates to a process for the production of a foam via an extrusion moulding process comprising a first twin-screw melt extruder and a second single-screw melt extruder positioned in series, wherein a feed composition comprising the
30 thermoplastic polyester copolymer is introduced to the feed inlet of the first twin-screw melt extruder, wherein a quantity of a blowing agent is introduced to the first twin-screw melt extruder, and wherein the molten composition comprising the thermoplastic polyester copolymer and the blowing agent upon exiting the twin-screw melt extruder is fed to the feed inlet of the

single-screw melt extruder and extruder from the single-screw melt extruder through a die to form a foam.

[0062] In a particular embodiment, the present invention relates to a thermoplastic polyester copolymer for production of foamed articles, comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester.

[0063] Further particularly, the invention relates to a thermoplastic polyester copolymer for production of foamed articles, comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester, wherein the polyester-forming monomers are a mixture of terephthalic acid and ethylene glycol.

[0064] Even further particularly, the invention relates to a thermoplastic polyester copolymer for production of foamed articles, comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester, wherein the polyester-forming monomers are a mixture of terephthalic acid and ethylene glycol, wherein the polyfunctional compound is glycerol.

[0065] Yet even further particularly, the invention relates to a thermoplastic polyester copolymer for production of foamed articles, comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester, wherein the polyester-forming monomers are a mixture of terephthalic acid and ethylene glycol in a molar ratio of ethylene glycol to terephthalic acid of ≥ 1.1 and ≤ 2.0 .

[0066] Yet another embodiment of the invention relates to a thermoplastic polyester copolymer comprising ≥ 95.0 wt% of polymeric units derived from terephthalic acid and ethylene glycol, and ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from glycerol, with regard to the total weight of the thermoplastic polyester copolymer, wherein the copolymer has a polydispersity index

M_w/M_n of ≥ 3 and ≤ 10 as determined in accordance with ASTM D5296-11, using polystyrene standards.

[0067] Another particular further embodiment of the invention relates to a thermoplastic polyester copolymer comprising ≥ 95.0 wt% of polymeric units derived from terephthalic acid and ethylene glycol, and ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from glycerol, with regard to the total weight of the thermoplastic polyester copolymer, wherein the copolymer has a polydispersity index M_w/M_n of ≥ 3 and ≤ 10 as determined in accordance with ASTM D5296-11, using polystyrene standards, and wherein the copolymer has an intrinsic viscosity of ≥ 0.60 dl/g and ≤ 3.00 dl/g as determined in accordance with ASTM D2857-95 (2007). In particular, the invention relates to a thermoplastic polyester copolymer for production of foamed articles comprising ≥ 95.0 wt% of polymeric units derived from terephthalic acid and ethylene glycol, and ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from glycerol, with regard to the total weight of the thermoplastic polyester copolymer, wherein the copolymer has a polydispersity index M_w/M_n of ≥ 3 and ≤ 10 as determined in accordance with ASTM D5296-11, using polystyrene standards, and wherein the copolymer has an intrinsic viscosity of ≥ 0.60 dl/g and ≤ 3.00 dl/g as determined in accordance with ASTM D2857-95 (2007).

[0068] A further embodiment of the invention relates to a foam from a thermoplastic polyester copolymer comprising ≥ 95.0 wt% of polymeric units derived from terephthalic acid and ethylene glycol, and ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from glycerol, with regard to the total weight of the thermoplastic polyester copolymer.

[0069] In a further particular embodiment, the invention relates to a foam from a thermoplastic polyester copolymer comprising ≥ 95.0 wt% of polymeric units derived from terephthalic acid and ethylene glycol, and ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from glycerol, with regard to the total weight of the thermoplastic polyester copolymer, wherein the foam has a density of ≥ 50 and ≤ 100 kg/m³ as determined in accordance with ASTM D6226 (2010).

[0070] The invention also relates to a process for manufacturing of a foamed article using the thermoplastic polyester copolymer of the invention, wherein the thermoplastic polyester copolymer has a G_0 at $t=0$ of 0 Pa and a G_0 at $t=15$ of > 0 Pa, wherein G_0 is determined as the value for G' on extrapolation of G'' to 0, fitting data for G'' to G' using a quadratic fit model, wherein G' is the storage modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1

rad/s determined at 260°C, in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa, and wherein G'' is the loss modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C, in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa, wherein $t=0$ indicates a dwell time in DMA of 0 minutes and $t=15$ indicates a dwell time of 15 minutes. It is preferable that G_0 at $t=15$ is > 500 Pa, more preferably > 1000 Pa.

[0071] The invention also relates to the use of a thermoplastic polyester copolymer according to the invention for improving the melt stability of a polyester foam.

[0072] The invention will now be illustrated by the following non-limiting examples.

[0073] Poly(ethylene terephthalate) copolymers according to the invention were produced via a process involving a first melt polymerisation stage, involving esterification and polycondensation, and a subsequent solid state polymerisation stage. The melt polymerisation was performed as a batch reaction in a 25 l reaction vessel. Batches of each ca. 8 kg of PET copolymer were produced. Table I below presents the raw material formulations used in the production of the inventive PET copolymers. In each experimental example 1-3, the raw materials composition according to table I was introduced to the reaction vessel.

Table I: raw material formulation

Compound	CAS reg. nr.	Ex. 1	Ex. 2	Ex. 3
Terephthalic acid	100-21-0	6917 g	6917 g	6917 g
Monoethylene glycol	107-21-1	3358 g	3358 g	3358 g
Antimony triacetate	6923-52-0	5.37 g	5.37 g	5.37 g
Glycerol	56-81-5	40 g	80 g	120 g
Cobalt acetate tetrahydrate	6147-53-1	0.5 g	0.5 g	0.5 g

[0074] The temperature inside the reaction vessel was increased to 250°C such that esterification occurred. The contents of the vessel were continuously stirred at 100 rpm. Pressure during esterification was set at 4.0 bar, with gradual reduction to 1.0 bar during the course of the reaction, which was allowed to proceed for between 2 and 3 hours. The water
5 formed during esterification was removed. A quantity of 0.6 g of phosphoric acid was added to the reactor and allowed to mix with the PET oligomer for 3-4 min.

[0075] Upon completion of the esterification, the oligomers were subjected to polycondensation in the same reactor. Agitation was set at 60 rpm. Pressure was gradually reduced to 2 mbar
10 over a period of 25 min and maintained during the polycondensation. The temperature during polycondensation was 275°C. During polycondensation, MEG was liberated from the polymerisation reaction and evacuated from the reaction vessel. The polycondensation was allowed to proceed until the torque reading of the agitator reached 30 Nm. The reactor was flushed with nitrogen and the produced PET copolymer was extruded from the vessel in the
15 form of molten strands which were quenched in cooling water and cut into granules having a diameter of 2-5 mm.

[0076] The granules were further subjected to solid state polymerisation (SSP). The granules were fed to a tumble drier acting as SSP reactor. The granules were first dried at 110°C for 30
20 min and subsequently subjected to a temperature of 170°C under nitrogen for 2 hrs for crystallisation, and further to a temperature of 210°C for 16 hrs under vacuum of 1 mbar to conduct the SSP. Experiment 1 resulted in a PET copolymer having an intrinsic viscosity (IV) of 0.81 dl/g; experiment 2 resulted in a PET copolymer having an IV of 0.87 dl/g; experiment 3 resulted in a PET copolymer having an IV of 2.34 dl/g. Intrinsic viscosity was determined in
25 accordance with ASTM D2857-95 (2007).

[0077] The content of units derived from glycerol in example 1 was 0.5 wt%, in example 2 1.0 wt%, and in example 3 1.5 wt%, with regard to the total weight of the copolymer.

[0078] The experimental PET copolymers 1-3 and a further commercial PET of grade BC112, obtainable from SABIC, IV 0.80 dl/g, referred to as experiment 4, presented here for comparative purposes, were all subjected to material analysis to identify the material characteristics, as presented below in table II.

Table II: Material characteristics.

Property	Ex. 1	Ex. 2	Ex. 3	Ex. 4
IV	0.87	0.81	2.34	0.80
M _w	228	344	168	125
M _n	59	59	41	55
PDI	3.9	5.8	4.0	2.3
Tan δ , t=0	3.00	2.90	2.48	158
Tan δ , t=30	1.32	1.36	1.46	18.8
G ₀ , t=0	0	0	0	0
G ₀ , t=15	860	2110	920	0
G ₀ , t=30	2970	5590	4700	0
G ₀ , t=45	4840	4700	8730	0
G' at t=2, at G''=10kPa	3400	5200	5800	800
G' at t=2, at G''=20kPa	8500	11900	14300	3400
G' at t=30, at G''=10kPa	9300	14700	15600	960

Wherein:

- 5
- IV is the intrinsic viscosity as determined in accordance with accordance with ASTM D2857-95 (2007), expressed in dl/g;
 - M_w is the weight average molecular weight as determined in accordance with ASTM D5296-11, using polystyrene standards, expressed in kg/mol;
 - M_n is the number average molecular weight as determined in accordance with
- 10
- ASATM D5296-11, using polystyrene standards, expressed in kg/mol;
 - PDI is the polydispersity index, calculated as the ratio M_w / M_n as determined above, dimensionless,
 - Tan δ is the ratio of G'' / G', each G'' and G' determined at 0.1 rad/sec, determined via Dynamic Mechanical Analysis (DMA) in accordance with ASTM D4065-12 in
- 15
- conjunction with ASTM D4440-15. Tan δ , t=0 was determined at time interval of

DMA testing 0 minutes, $\tan \delta$, $t=30$ was determined at time interval of DMA testing of 30 minutes. Measurements were performed at 260°C.

- G' is the storage modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C, in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa.
- G'' is the loss modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C, in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa.
- G_0 is the value for G' on extrapolation of G'' to 0, fitting data for G'' to G' using a quadratic fit model. G_0 represents the extent of long-chain branching in the polyesters; high G_0 indicates higher degree of long-chain branching.

[0079] The $\tan \delta$ is understood to reflect the level of branching, which in turn correlates to the melt strength of the copolymer. Melt strength is a critical parameter in qualification of a thermoplastic material for the production of foamed structures, as during the formation of the foam, a cell structure is formed by a gaseous material that forms cells that are at least partially surrounded by thermoplastic material in molten phase which upon solidification forms cell structures. When melt strength is not sufficiently high, the formed cells do not have sufficient strength to retain their shape during the phase before solidification, as a result of which the material is not converted to a desired foam structure.

[0080] The determination of G_0 in a rheometer serves to determine the presence of long-chain branching at the start of the rheometer measurement (G_0 , $t=0$), and after intervals of 15 minutes (G_0 , $t=15$), 30 minutes (G_0 , $t=30$) and 45 minutes (G_0 , $t=45$). This dwell time emulates the duration of the processing of the material during the production of a foam based on the material.

[0081] As G_0 indicates the degree of long-chain branching, it can be observed that at $t=0$, none of the samples demonstrated any long-chain branching. This means that the material as produced from the polyester polymerisation process was free from long-chain branching. However, for the examples 1-3, it can be observed that at 15, 30 and 45 minutes, a certain high G_0 is achieved, indicating the desired presence of long-chain branching, which is required for the foaming process to provide foam of desired quality. It thus can be observed that the polyester compositions of the present invention provide both the melt processability that is

desired, as demonstrated by G_0 at $t=0$ being 0, and the foam stability upon melt processing that is desired, as demonstrated by G_0 at $t=15, 30$ and 45 to be of certain desired value.

[0082] The polyester copolymers of examples 1 and 2 demonstrated a particularly desirable
5 intrinsic viscosity. This can be understood to reflect a desirably low quantity of short-chain
branching in the copolymers, which is understood to contribute to the desired crystallisation rate
during cooling of foam cells upon formation of a foam, which in turn contributes to improvement
of the mechanical properties of the foam.

Claims

1. Thermoplastic polyester copolymer comprising a quantity of polymeric units derived from a polyfunctional compound, wherein the polyfunctional compound has three moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester.
2. Thermoplastic polyester copolymer according to claim 1 wherein the moieties that are able to react with the polyester-forming monomers during the polymerisation of the polyester are hydroxyl moieties or carboxylic acid moieties.
3. Thermoplastic polyester copolymer according to any one of claims 1-2, wherein the copolymer comprises ≥ 0.1 and ≤ 5.0 wt% of polymeric units derived from the polyfunctional compound, preferably ≥ 0.1 and ≤ 1.5 wt%, more preferably ≥ 0.1 and ≤ 1.3 wt%, with regard to the total weight of the copolymer.
4. Thermoplastic polyester copolymer according to any one of claims 1-3, wherein the polyester-forming monomers are selected from mixtures of a dicarboxylic acid or a diester thereof with an alkanediol.
5. Thermoplastic polyester copolymer according to any one of claims 1-4, wherein the copolymer comprises ≥ 95.0 wt% of polymeric units derived from a dicarboxylic acid or a diester thereof and an alkanediol, with regard to the total weight of the copolymer.
6. Thermoplastic polyester copolymer according to claims 3-5 wherein
 - the dicarboxylic acid or diester thereof is selected from terephthalic acid, dimethyl terephthalate, isophthalic acid, 2,6-naphthalenedicarboxylic acid, dimethyl-2,6-naphthalenedicarboxylate, 2,5-furandicarboxylic acid, dimethyl-2,5-furandicarboxylate, or succinic acid; and/or
 - the alkanediol is selected from ethylene glycol, propanediol, 1,4-butanediol, or cyclohexanedimethanol.
7. Thermoplastic polyester copolymer according to any one of claims 1-7, wherein the polyfunctional compound is a compound having 1-10 carbon atoms.

8. Thermoplastic polyester copolymer according to any one of claims 1-8, wherein the polyfunctional compound is glycerol.
9. Thermoplastic polyester copolymer according to any one of claims 1-9, wherein the
5 copolymer is a poly(ethylene terephthalate)-co-glycerol.
10. Process for the production of a thermoplastic polyester copolymer according to any one of claims 1-10, wherein the process comprises the steps of esterification, melt
polycondensation and solid state polycondensation, in this order, wherein a feed stream
10 comprising a dicarboxylic acid or a diester thereof, an alkanediol and a polyfunctional compound that has three moieties that are able to react with the dicarboxylic acid or a diester thereof, and/or the alkanediol during the polymerisation of the polyester is supplied to the esterification step of the process.
- 15 11. Use of a thermoplastic polyester copolymer according to any one of claims 1-9 or produced according to the process of claim 10 in the production of foamed articles.
12. Process for manufacturing of a foamed article using the thermoplastic polyester copolymer of any one of claims 1-9, wherein the thermoplastic polyester copolymer has a G_0 at $t=0$ of 0 Pa and a G_0 at $t=15$ of > 0 Pa, wherein G_0 is determined as the value for G' on
20 extrapolation of G'' to 0, fitting data for G'' to G' using a quadratic fit model, wherein G' is the storage modulus, determined via Dynamic Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C, in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa, and wherein G'' is the loss modulus, determined via Dynamic
25 Mechanical Analysis (DMA) at 0.1 rad/s determined at 260°C, in accordance with ASTM D4065-12 in conjunction with ASTM D4440-15, expressed in Pa, wherein $t=0$ indicates a dwell time in DMA of 0 minutes and $t=15$ indicates a dwell time of 15 minutes.
13. Process according to claim 12 wherein G_0 at $t=15$ is > 500 Pa, preferably > 1000 Pa.
- 30 14. Foamed article produced using the thermoplastic polyester copolymer of any one of claims 1-11 or produced according to the process of any one of claims 12-13, preferably wherein the thermoplastic polyester copolymer has a polydispersity index PDI determined as the ration of M_w/M_n of ≥ 3 and ≤ 10 , wherein M_w and M_n are determined in accordance
35 with ASTM D5296-11, using polystyrene standards.

15. Use of a thermoplastic polyester copolymer according to any one of claims 1-9 for improving the melt stability of a polyester foam.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/080462

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J9/12 C08J9/14 C08G63/127 C08G63/183 C08G63/20
C08G63/80

ADD.

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)

C08J C08G C09J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/244584 A1 (KEPPELER UWE [DE]) 25 August 2016 (2016-08-25) paragraphs [0001] - [0012], [0053], [0138] - [0140] examples 1-9; table 2 claim 1	1-15
X	US 4 132 707 A (BORMAN WILLEM F H) 2 January 1979 (1979-01-02) column 2, lines 3-36 column 2, line 49 - column 3, line 6 column 3, lines 11-16, 28-54 column 4, lines 7-9 claims 1-3, 8, 9	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"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

"&" document member of the same patent family

Date of the actual completion of the international search

13 December 2018

Date of mailing of the international search report

21/12/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Mayer, Anne

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/080462

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 391 582 A (MUSCHIATTI LAWRENCE C [US] ET AL) 21 February 1995 (1995-02-21) column 2, line 35 - column 3, line 25 column 4, line 51 - column 5, line 30 claim 1 -----	1-15
X	US 2007/059465 A1 (THOMPSON DAVID E [US] ET AL) 15 March 2007 (2007-03-15) paragraphs [0192] - [0196], [0218] - [0219] -----	1,2,4-10
X	WO 2009/156457 A1 (DSM IP ASSETS BV [NL]; URMANOVA ANTONIA [NL]; MISEV TOSKO ALEXANDAR [N]) 30 December 2009 (2009-12-30) examples 2-4 -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/080462

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2016244584	A1	25-08-2016	BR 112016006949 A2 01-08-2017
		CN 105793337 A	20-07-2016
		CN 105814126 A	27-07-2016
		EP 3055351 A1	17-08-2016
		EP 3055352 A1	17-08-2016
		ES 2652157 T3	31-01-2018
		ES 2652344 T3	01-02-2018
		JP 6422957 B2	14-11-2018
		JP 2016537450 A	01-12-2016
		US 2016244583 A1	25-08-2016
		US 2016244584 A1	25-08-2016
		WO 2015052019 A1	16-04-2015
		WO 2015052020 A1	16-04-2015
US 4132707	A	02-01-1979	AU 516366 B2 28-05-1981
		CA 1107000 A	11-08-1981
		DE 2753998 A1	15-06-1978
		FR 2372854 A1	30-06-1978
		GB 1568756 A	04-06-1980
		JP S5394596 A	18-08-1978
		MX 146213 A	26-05-1982
		US 4132707 A	02-01-1979
US 5391582	A	21-02-1995	NONE
US 2007059465	A1	15-03-2007	US 2007059465 A1 15-03-2007
			US 2009176046 A1 09-07-2009
			US 2010221472 A1 02-09-2010
			US 2011212282 A1 01-09-2011
WO 2009156457	A1	30-12-2009	DK 2291433 T3 17-05-2016
			EP 2291433 A1 09-03-2011
			ES 2570972 T3 23-05-2016
			WO 2009156457 A1 30-12-2009