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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
23 June 2011 (23.06.2011)

PCT

(10) International Publication Number
WO 2011/073308 A1

(51) International Patent Classification:
C08G 69/44 (2006.01) *B32B 27/36* (2006.01)
C08G 69/34 (2006.01) *C08L 77/12* (2006.01)
F16L 11/04 (2006.01) *C08L 77/08* (2006.01)
B32B 1/08 (2006.01) *C08L 53/02* (2006.01)
B32B 27/34 (2006.01)

(21) International Application Number:
PCT/EP2010/069872

(22) International Filing Date:
16 December 2010 (16.12.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09179385.1 16 December 2009 (16.12.2009) EP

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(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, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, 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, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, 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, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2011/073308 A1

(54) **Title**: THERMOPLASTIC POLYMER FOR PLASTIC COMPONENTS FOR PUMPS

(57) **Abstract**: The invention relates to a block copolymer comprising hard segments and soft segments, wherein the copolymer comprises 20-42 wt.% of hard segments consisting of repeat units of a semi-crystalline semi-aromatic polyester, and 58-80 wt.% of soft segments consisting of repeat units of an amorphous polyamide, and wherein the weight percentages (wt.%) are relative to the total weight of the copolymer, the soft segments have a number average molecular weight (Mn) of 1750-3000, and the soft segments contain polymerization residues of a dimerised fatty acid and/or a dimerised fatty diamine and optionally other aliphatic dicarboxylic acids or other aliphatic diamines.

THERMOPLASTIC POLYMER FOR PLASTIC COMPONENTS FOR PUMPS

The invention relates to a thermoplastic polymer for use in plastic components for pumps, more particular for tubes in peristaltic pumps.

Plastics components are widely used in pump systems. Such components include diaphragms, gaskets, seals, o-rings, belts, tubes and bellows. General requirements for the materials from which such components are made include the combination of strength and toughness, the materials much be flexible, durable, and chemical resistant, and preferably also usable at elevated temperature. A particular problem is posed by tubings for peristaltic pumps, which require repeated flexing. For example, peristaltic pumps are used to transport liquids and pastes through elastomeric tubes in which the tube is repeatedly squeezed between a series of rotating rollers and a fixed pump housing.

Silicone elastomers are frequently used for peristaltic pump tubing. Other materials that are used are, for example, natural rubbers and fluoro elastomers. Such materials and pump components made thereof are described for example in US patent US-6,673,455-B2. Silicone and fluoro-elastomers are generally quite expensive. Natural rubbers have the advantage that these are less expensive and can be made from renewable raw materials. But the performance is not as good as for example silicone and fluoroelastomers; specific problems are indicated in US-6,673,455-B2. There are also other plastic materials used in plastic components for pumps, but these generally suffer in one or more properties making these materials less suited for flexible tubings. As also indicated in US-6,673,455-B2, there is need for other materials that can be used in tubings in peristaltic pumps.

Object of the present invention is to provide new materials that can be used in plastic components for pumps, which combine a good balance in properties and can be made at least partly from renewable materials. Another aim is to provide plastic components for pumps made of such new materials.

Surprisingly, this object has been achieved with the block copolymer according to the invention, comprising

a. 20-42 wt.% of hard segments consisting of repeat units of a semi-crystalline semi-aromatic polyester, and
b. 58-80 wt.% of soft segments consisting of repeat units of an amorphous or essentially amorphous polyamide

wherein the weight percentages (wt.%) are relative to the total weight of the copolymer, the soft segments have a number average molecular weight (Mn) of 1750-3500, and the soft segments contain polymerization residues of a dimerised fatty acid and/or a dimerised fatty diamine and optionally other aliphatic dicarboxylic acids or other aliphatic diamines.

It is noted that for the term “segment” as appearing in the form of soft segments and hard segments in the block copolymers also the term “block” is used. In this respect it is noted that the term “soft block” has the same meaning as “soft segment”; analogously the term “hard block” has the same meaning as “hard segment”.

With the term “soft” in the soft segments is herein understood that the material from which these segments are composed is an amorphous material or essentially so, showing a low glass transition temperature (Tg). This Tg, when measured on the block copolymer, generally is at most about room temperature.

With the term “hard” in the hard segments is herein understood that the material from which these segments are composed is a semicrystalline material or essentially so, showing a high melting temperature (Tg). This Tm, when measured on the block copolymer, generally is at least about 150 °C.

With the term melting temperature (Tm) is herein understood the temperature, measured according to ASTM D3418-97 by DSC under nitrogen gas with a heating rate of 20°C/min, falling in the melting range and showing the highest melting rate. With the term glass transition temperature (Tg) is herein understood the temperature, measured according to ASTM E 1356-91 by DSC under nitrogen gas with a heating rate of 20°C/minute and determined as the temperature at the peak of the first derivative (with respect of time) of the parent thermal curve corresponding with the inflection point of the parent thermal curve. The shore A hardness is the hardness measured by the method according to IS0 868.

The block copolymer according to the invention has elastomeric properties, combines strength and toughness over a wide temperature range, has a high softening or melting temperature and a low glass transition temperature, and is very soft and flexible.

The high softening or melting temperature is due to the hard segments being semi-crystalline or essentially so. The low glass transition temperature is due to the soft segments being amorphous or essentially so.

The softness is illustrated with low hardness values, in the medium upper Shore A range. Next to that, the block copolymer is thermoplastically processable. Moreover, in view of the block copolymer being thermoplastically processable and very soft and flexible, it has very good chemical resistance. Therefore this block copolymer may be used for many applications, but is particular suitable for making plastic components for pumps. The block copolymer may for example be processed by extrusion for making tubings for peristaltic pumps. Furthermore, the block copolymer according to the present invention can be made in large part from renewable raw materials. Alternatively, tubing segments can be obtained by injection moulding or any other suitable processing technique. The block copolymer according to may also be processed by extrusion techniques for producing, for example, films.

The block copolymer according to the invention consisting of hard polyester segments and soft polyamide segments can be represented by the general formula

$$X\text{-}\left[\ \{\ [\text{-CO-D-CO-O-E-O}]_x\ \}\ \text{-}\ \{\ [\text{CO-F-CO-NH-G-NH}]_y\text{-}\}\ \right]_z\text{-}Y \qquad (I)$$

$$X\text{-}\left[\ \{\text{-O-E-O - }[\text{-CO-D-CO-O-E-O}]_x\ \}\ \text{-}\ \{\ [\text{CO-F-CO-NH-G-NH}]_y\text{ - CO-F-CO -}\}\ \right]_z\text{-}Y \qquad (II)$$

or

$$X\text{-}\left[\ \{\ [\text{-CO-D-CO-O-E-O}]_x\text{ - CO-D-CO }\}\ \text{-}\{\text{NH-G-NH - }[\text{CO-F-CO-NH-G-NH}]_y\text{ -}\}\ \right]_z\text{ -}Y \qquad (III)$$

or a combination thereof,

wherein

$\{[\text{-CO-D-CO-O-E-O}]_x\}$, $\{\text{-O-E-O - }[\text{-CO-D-CO-O-E-O}]_x\ \}$ - respectively $\text{–}\{\ [\text{-CO-D-CO-O-E-O}]_x\text{ - CO-D-CO -}\}$ represent polyester hard segments with either a terminal residue of a carboxylic acid and a terminal residue of an hydroxyl group, 2 terminal residues of hydroxyl groups or 2 terminal residues of dicarboxylic acid groups,

$\{\ [\text{CO-F-CO-NH-G-NH}]_y\text{-}\}$, - $\{\ [\text{CO-F-CO-NH-G-NH}]_y\text{ - CO-F-CO -}\}$ respectively $\{\text{NH-G-NH - }[\text{CO-F-CO-NH-G-NH}]_y\text{ -}\}$ represent polyamide soft segments with respectively a terminal residue of a carboxylic acid and a terminal residue of a hydroxyl group, 2 terminal residues of carboxyl groups or 2 terminal residues of amino groups,

-CO-D-CO- represents the polymerization residue of an aromatic dicarboxylic acid, -O-E-O- represents the polymerization residue of an aliphatic diol, -CO-F-CO- represents the polymerization residue of a dicarboxylic acid and –NH-G-NH- represents the polymerization residue of a diamine, and wherein either –CO-F-CO- or –NH-G-NH- or both are polymerization residues of dimerised fatty acid derivatives, X

and Y are terminal groups which each can be a polymerization residue of either a dicarboxylic acid, an aliphatic diol or a diamine, and of **x** and **y** are integers and indicate the number of repeat units in respectively a polyester hard segment and a polyamide soft segment, and **z** is an integer indicating the number of recurring alternations of the soft segments and hard segments in the polymer.

It will be clear for the person skilled in the art of polymers, in particular condensation polymers like polyesters and polyamides, that within a polymer chain not all hard segments will have the same number **x** of repeat units and also that not all the soft segments will have the same number **y** of repeat units. In practice there will be a distribution in number of repeat units, and most practically one can use average values, $\mathbf{x}_{avg}$, $\mathbf{y}_{avg}$ and $\mathbf{z}_{avg}$, which averages will not necessarily be integers anymore. The same holds for the molecular weight of the soft and hard segments. In practice there will be a distribution in molecular weight, and most practically one can deal with average values.

Polyesters and polyamides are both considered polycondensation polymers. Condensation polymers are any kind of polymers formed through a condensation reaction, releasing small molecules as by-products such as water or low molecular weight alcohols. Polyesters are formed by condensation reactions between compounds bearing carboxylic acids, or ester or anhydride derivatives thereof, and compounds bearing hydroxyl groups. Polyamides can be formed by condensation reactions between compounds bearing carboxylic acids, or ester or anhydride derivatives thereof, and compounds bearing amine groups. Compounds used for creating the building blocks in thermoplastic polymers are generally bi-functional. These can be either dicarboxylic acids or ester derivatives thereof, diols and diamines, and/or hydroxyl functional and or amine functional carboxylic acids or ester derivatives thereof. Next to the bi-functional compounds, small amounts of mono-functional and / or tri- and higher functional compounds may be used. Polymerization residues are herein understood to be the residues of the compounds used for forming the buildings blocks of the polymer chain and remaining as such in the polymer chain after the condensation reaction.

It has been found by the inventors of the present invention that the molecular weight of the soft segments, and more particular the number average molecular weight of the soft segments is one of the critical parameters, next to the composition and amount thereof, for the properties of the block copolymer according to the invention.

To obtain a block copolymer with good properties the number average molecular weight (Mn) of the soft segments has to be in the range of 1750-3500.

The number average molecular weight (Mn) of the soft blocks is calculated by the formula:

$$Mn = 1000*2*56/Z,$$

wherein Z is the number of end groups, expressed in milliequivalents (meq) KOH / g soft block.

The end groups, either OH groups and/or NH2 groups, or carboxylic groups, can be determined by standard methods, e.g. by titration methods.

The number average molecular weight of the polyester hard blocks (Mp) than simply results from the following formula:

$Mp = Mn * W_{polyester} / W_{polyamide,}$

wherein $W_{polyester}$ is the weight % of the polyester hard blocks in the block copolymer and $W_{polyamide}$ is the weight % of the polyamide soft blocks in the block copolymer.

Preferably this Mn is in the range of 1800 – 3000, more preferably 1900 – 2800, and still more preferably 2000 – 2750. The advantage of a higher Mn is that the block copolymer becomes even softer and more flexible, while retaining a high melting temperature, making it even more suited for tubings for peristaltic pumps. On the other hand, though the preparation of the block copolymer can be done with soft segments having an Mn in the high range, this becomes easier and less critical with soft segments having a lower Mn. In certain modifications one could get softer block copolymers also with soft segments having an Mn in the lower range, but this generally goes hand in hand with a lowering in melting temperature of the block copolymers. These polymers are still of interest for less critical applications.

In relation with the number average molecular weight of the soft segments the weight percentages (wt.%) of the soft segments and hard segments in the block copolymer constitute another critical parameter. In the block copolymer the hard segments constitute 20-42 wt.% and the soft segments constitute 58-80 wt.% of the total weight of the copolymer.

The weight % of the soft blocks (SB) and the hard blocks (HB) is calculated as follows

$$wt.\%\ SB = W_{SB}/W_{polymer} * 100\%,$$

and

wt.% HB = 100 – wt.% SB

It is noted that for the calculations of the weight percentages of the soft segments, the terminal groups are included therein, such that the polymerization residues of aliphatic carboxylic acids and amines in the terminal groups are also included in the soft segments.

It has been found advantageous to further limit the higher amount of soft blocks with low Mn on one hand and also to further increase the lower amount of soft blocks with high Mn. Preferably, the soft segment in the block copolymer according to the invention is present in an amount of at most (61+Mn*0.008) wt.%, more preferably at most (59+Mn*0.008) wt.%, more preferably at most (57+Mn*0.008) relative to the total weight of the copolymer. Limiting the amount of soft block in this way has the advantage that block copolymer has a higher melting point. While simultaneous increasing the Mn of the soft block thereby increasing the absolute amount thereof has the advantage that the block copolymer has an further increased softness.

Also preferably, the soft segment in the block copolymer according to the invention is present in an amount of at least (15 + Mn*0.02) wt.%, more preferably at least (18 + Mn*0.02) wt.%, and still more preferably at least (20 + Mn*0.02) wt.%, relative to the total weight of the copolymer. Increasing the minimum amount of the soft block in this way not only has the advantage that the block copolymer becomes softer, but also that the preparation of the block copolymers becomes less critical. In particular cases depending on the composition of the soft blocks, but in particular in case of soft blocks consisting of polymerization residues of dimerised fatty acid and dimerised fatty amines , the preparation of the copolymer tends to macro-phase separate, forming a dispersion of two different block copolymers rather than resulting in the homogeneous target block copolymer. This tendency can be overcome by either lowering the Mn and/or increasing the amount of soft blocks in the indicated direction. Phase separation is a general characteristic in the production of block-copolymers. The extend is generally determined by the compatibility of the different constituents. Some extend of phase separation is generally acceptable, although low to no phase separation is preferred in case transparent products are required.

With the dimerised fatty acid / dimerised fatty diamine combinations very good results are obtained with Mn of the soft blocks in the range of 2000-2750 and the amounts of the soft blocks in the range between (20 + Mn*0.02) wt.% and

(57+Mn*0.008) wt.%. These combinations result in block-copolymers with an optimal balance in terms of high melting point, low Tg, very low softness and ease of preparation.

The soft segments in the block copolymer according to the invention contain polymerization residues of a dimerised fatty acid and/or a dimerised fatty diamine and optionally other aliphatic dicarboxylic acids and/or other aliphatic diamines.

The dimerised fatty acids and the dimerised fatty diamine s that can be used in the present invention can be obtained from biorenewable sources.

The dimerised fatty acids may be obtained from monomeric unsaturated fatty acids by an oligomerisation reaction. The oligomer mixture is further processed, for example by distillation, to yield a mixture having a high content of the dimerised fatty acid. For example C12 to C24 monomeric unsaturated fatty acids result in C24 – C48 dimerised fatty acids. C18 fatty acids are especially useful and advantageously employed for preparing dimerised fatty acids that can be used in the present invention. Processes for the production of dimerised fatty acids are well known in the art and by way of illustration, as described for example in US patents US-2,793,219 and US-2,955,121. The dimerised fatty acids may also be hydrogenated, thereby converting the double bonds and producing saturated dimerised fatty acids. The term dimerised fatty acid as it is used herein relates to both types of dimerised fatty acid, the saturated and the unsaturated. Suitable dimerised fatty acids are available commercially under the trade name “Empol“ from Cognis Corporation and the trade name “Pripol” from Croda International.

Dimerised fatty amines are similar in composition and structure to the dimerised fatty acids, but contain primary amine groups instead of carboxylic acid groups. These compounds may be obtained for example by conversion of the carboxylic acid groups in dimerised fatty acids by reaction with ammonia into amide groups, converting these amide groups into nitril groups, and subsequent hydrogenation. Suitable dimerised fatty amines are available commercially under the trade name “Versamine“ from Cognis Corporation and the trade name “Priamine” from Croda International, e.g. Priamine 1074.

It is noted that the dimerised fatty acids and the dimerised fatty amines contain small amounts of mono- and trifuctional components or even higher functional components next to the difunctional components as the main components. Such mixtures can also be used for making the block copolymers according to the

invention, and unless specifically noted otherwise the terms dimerised fatty acids and dimerised fatty amines include mixtures comprising small amounts of such lower and higher functional components.

For the preparation of the soft blocks that can be used in the block copolymers according to the invention, the dimerised fatty acids can be mixed with a diamine selected from dimerised fatty amines and aliphatic diamines, or a combination thereof, and subjected to a condensation reaction at elevated temperature. Alternatively, the dimerised fatty diamine can be mixed with a dicarboxylic acid selected from dimerised fatty acid and an aliphatic dicarboxylic acid, or a mixture thereof, and subsequently subjected to a condensation reaction at elevated temperature.

Mixtures of different dicarboxylic acids and diamines can also be used, provided at least 50 mole % of the diacids and diamines is based on dimerised fatty acids and/or amino derivatives thereof.

The aliphatic diamine, if used at all, preferably has at least 4 C-atoms, more preferably at least 6, still more preferably at least 10 C-atoms. Most suitably the number of C-atoms in the aliphatic diamine is in the range of 12-18 C-atoms. This is in particular the case when the diamine, used in combination with the dimerised fatty acids, is only selected from aliphatic diamines.

The advantage of using aliphatic diamines with more C atoms is that the resulting block-copolymer is softer and more flexible at or around room temperature.

Analogously, the aliphatic dicarboxylic acid, if used at all, preferably has at least 6 C-atoms, more preferably at least 10 C-atoms. Most preferably the number of C-atoms in the aliphatic dicarboxylic acid is in the range of 12-18 C-atoms. This is in particular the case when the dicarboxylic acid, used in combination with the dimerised fatty amines, is only selected from aliphatic dicarboxylic acids. The advantage of using aliphatic dicarboxylic acid with more C atoms is that the resulting block-copolymer is softer and more flexible at or around room temperature.

Preferebly, the amount of aliphatic dicarboxylic acid in the soft block to at most 50 mole %, more preferably at most 25 mole %, and most preferably in the range of 0-10 mole %, relative to the total molar amount of aliphatic dicarboxylic acid and dimerised fatty acids.

Analogously, preferably, the amount of aliphatic diamine in the soft block is at most 50 mole %, more preferably at most 25 mole %, and most preferably in

the range of 0-10 mole %, relative to the total molar amount of aliphatic diamine and dimerised fatty diamine. The advantage of these lower amounts is that the resulting block-copolymer is softer and more flexible at or around room temperature.

The block copolymer according to the invention contains hard blocks consisting of repeat units of a semi-crystalline semi-aromatic polyester. Such repeat units can be obtained from alkylene diols and aromatic dicarboxylic acids or esters thereof. Suitable alkylene diols are short chain linear and cycloaliphatic alkylene diols. These diols generally contain 2-8 C-atoms, preferably 2-4 C-atoms. Examples thereof include ethylene glycol, 1,3-propylene glycol and butylene glycol. Preferably butylene glycol or ethylene glycol are used, more preferably 1,4-butylene glycol. Examples of suitable aromatic dicarboxylic acids include terephthalic acid, 2,6-naphthalene dicarboxylic acid, 4,4'-biphenyldicarboxylic acid or combinations thereof. These aromatic dicarboxylic acids may be combined with isophthalic acid, the amount of which suitably is less than 50 mole %, more preferably less than 25 mole % and most preferably less than 10 mole %, relative to the total molar amount of aromatic dicarboxylic acid. Preferably terephthalic acid and/or naphthalene dicarboxylic acid are used as the aromatic dicarboxylic acid.

The advantage of the combination of aromatic dicarboxylic acids and alkylene diols with 2-4 C-atoms is that the resulting polyester hard blocks in the block-copolymer according to the invention are semi-crystalline with a melting point of around 150 ºC or higher. Higher melting temperatures of preferably above 165 ºC, or even better above 175 ºC can be obtained by using soft blocks in an amount in the lower range of the invention, or by using soft blocks with higher average molecular weight. Products with even higher melting temperature are further possible using hard blocks made of ethylene terephthalate, ethylene naphthanate or butylene naphthanate, which can give block copolymers with melting temperatures above 200 ºC, without compromising or only in limited extend on softness and flexibility. In case of hard blocks made of semi-crystalline polyesters with a low crystallization speed, such as with ethylene terephthalate, it can be advantageous to use nucleating agents in combination with the block-copolymer.

The content of renewable components in the polymer might be further increased by using diols from renewable sources, for instance, 1,3-propane diol and 1,4 butane diol produced from renewable sources.

The block copolymer according to the invention preferably has a melting temperature (Tm) of at least 160 °C, preferably at least 170 °C, and more preferably in the range of 180-220 °C.

The block copolymer generally has a glass transition temperature (Tg) of at most about 20 °C. Preferably, the Tg is at most 0 °C, more preferably at most -10 °C, and still more preferably the Tg is in the range of -20°C - - 40°C (i.e. from and including minus 20°C up to and including minus 40°C). Such low Tg can be obtained with soft blocks having an Mn in the higher range of the present invention and with soft blocks comprising a higher amount of dimerised fatty acid and dimerised fatty amine and less, if any, aliphatic diamine or aliphatic dicarboxylic acid. The advantage of the block copolymer having a higher Tm and or a lower Tg is that plastic parts made of the block copolymer can be used over a wider temperature range.

The block copolymer according to the invention generally has a Shore A hardness of at most 90. Preferebly, the shore A hardness is at most 80, more preferably at 70. In particular cases the Shore A hardness can even be as low as 60 or even lower. Such low values in Shore A hardness are obtained, for example with soft blocks based on dimerised fatty acid / dimerised fatty diamine combinations and with an Mn of the in the range of 2250-2600 and the amounts of the soft blocks in the range between (20 + Mn*0.02) wt.% and (57+Mn*0.008) wt.%. These block copolymers offer an optimal balance in properties including Shore A hardness and melting temperature, mechanical properties, processing and phase separation, and also offer good chemical resistance. This makes these products very suitable, e.g. for tubings for peristaltic pumps.

The block copolymer according to the invention may be prepared for example by first preparing a polyamide prepolymer for the soft segments, and than adding the aromatic dicarboxylic acid, or ester derivative thereof, and the aliphatic diol and polymerizing these until a polymer of sufficiently high molecular weight is obtained. No indication of significant amide / ester interchange between the polyamide components and the polyester components has been obtained.

The number average molecular weight (Mn) of the polyamide soft block is determined in the prepolymerization step. The Mn can be controlled by using a molar excess of dicarboxylic acid components to obtain a predominantly carboxyl functional prepolymer, or alternatively by using a molar excess of diamine components to obtain a predominantly amine functional prepolymer. The block-copolymer with polyester hard blocks is produced by adding the aromatic dicarboxylic acid, or ester

derivative thereof, and the aliphatic diol, and polycondensing these components under normal conditions for polyester synthesis.

The invention also relates to a polymer composition comprising a block copolymer according to the present invention and at least one additive. The block copolymer according to the invention may be compounded in all kind of polymer compositions replacing known thermoplastic elastomers. Such compositions may further contain the usual additives, for example heat stabilizers, UV stabilizers, antistatic agents, flame retardants, lubricants and mould release agents. The polymer composition suitably contains stabilizers for the stabilization of nylons, for instance Bruggeman additives, stabilizers for polyesters, and/or stabilizers used typically in polyolefines.

The invention also relates to polymer blends and to a polymer composition comprising a blend of a block copolymer according to the invention, or any preferred embodiment thereof, and at least one other polymer. Suitably, the other polymer comprises or is a styrene block copolymer, and preferably comprises or is SEBS. The advantage of such a blend with SEBS is that the chemical resistance of the polymer composition is increased while the composition retains its flexibility in large extent.

The invention also relates to molded articles containing the block copolymer according to the invention. The invention in particular relates to plastic components for pumps made from the block copolymer according to the invention or from a polymer composition comprising said block copolymer, as well as to plastic components for pumps comprising a layer or a part consisting of the block copolymer according to the invention or from a polymer composition comprising said block copolymer.

Compared to molded articles made from polyetherester block copolymers, the molded articles made of the block copolymers according to the invention show a much better thermal and oxidative stability. Suitably, the molded articles according to the present invention are heated to a temperature in the range of 130 – 160ºC for a time period of 12 - 164 hours, for example for about 144 hours at about 135 ºC, or 48 hours at 150 ºC . Moreover, the molded articles according to the present invention show an improved solvent resistance after such heat treatment at elevated temperature.

In a preferred embodiment of the invention the block copolymer the molded article is cross-linked. Cross-linking can simply be accomplished by subjecting the molded article to a temperature and for a time period as indicated hereabove.

The good resistance of the block copolymers against high temperatures makes these very suitable for use in applications that require sterilization, in particular heat sterilization, or other type of sterilization in combination with heat sterilization.

The molded article suitable is a diaphragm, a gasket, a seal, an o-ring, a belt, a tube or a bellow.

The invention also relates to a pump comprising a diaphragm, a gasket, a seal, an o-ring, a belt, a tube, a hose or a bellow made from or comprising a block copolymer according to the invention. Suitably the pump is a peristaltic pump comprising a tube made from the block copolymer or from a composition comprising the block copolymer according to the present invention.

Suitably, the block copolymer according to the invention or the polymer composition comprising the block copolymer according to the invention is used in a multilayer tube or a reinforced hose. The multilayered tube advantageously comprises a first layer comprising the block copolymer according to the invention, and a second layer comprising a polyester or a polyester block copolymer different from the block copolymer according to the invention, wherein the first layer and the second layer are in direct contact with each other. The advantage of such a multilayered tube is that there is a reduced risk in delamination compared to multilayered tubes wherein the second layer is combined with a first layer comprising another soft and flexible polymer. The multilayered tube is suitably made by co-extrusion.

Suitable processing techniques for the block copolymer according to the invention and polymer compositions comprising this block copolymer include extrusion, injection molding, compression molding, blow molding etc.

The invention is further explained by the examples, without being restricted thereto.

Experimental part

Methods

Determination of number average molecular weight (Mn) of the soft blocks

The soft blocks were prepared which excess dicarboxylic acid components, such that the resulting soft blocks had carboxylic acids end-groups. The number of residual carboxylic groups end groups of these prepolymers has been determined by titration and has been expressed in meqKOH/g. The number average molecular weight (Mn) of the soft blocks has been calculated as follows. For a soft block possessing Z meqKOH/g number of -COOH end group, the Mn is calculated as 1000*2*56/Z g/mol.

Melting temperature and Glass transition temperature

A differential scanning calorimeter (DSC), model Mettler Toledo DSC 821e auto sampler was utilised to measure the glass transition and the melting temperature. The melting temperature (Tm) has been measured according to ASTM D3418-97 by DSC under nitrogen gas with a heating rate of 20°C/min, falling in the melting range and showing the highest melting rate.

The glass transition temperature (Tg) has been measured by the method according to ASTM E 1356-91 by DSC under nitrogen gas with a heating rate of 20°C/minute and determined as the temperature at the peak of the first derivative (with respect of time) of the parent thermal curve corresponding with the inflection point of the parent thermal curve.

Shore A hardness

The shore A hardness has been measured by the method according to IS0 868.

Relative viscosity

The relative viscosity (ηrel) was measured for the polymers obtained by processes described below. The measurement of ηrel was performed according to ISO 307, fourth edition. For the measurement a pre-dried polymer sample was used, the drying of which was performed under high vacuum (i.e. less than 50 mbar) at 80°C during 24 hrs. Determination of the relative viscosity was done at a concentration of 1 gram of polymer in 100 ml of meta-cresol at 25,00 ± 0,05 °C. The flow time of the

solution (t) and the solvent (to) were measured using a DIN-Ubbelohde from Schott (ref. no. 53020) at 25°C. The relative viscosity is defined as t/t0.

Materials used

BDO: Butanediol, delivered by BASF Germany

DMT: dimethylterephthalate, delivered by Oxxynova in Germany

$Mg(OAc)_2.4H_2O$, and ammonia, delivered by Sigma-Aldrich in Belgium

DFA: Pripol 1009: dimerised fatty acid, delivered by Croda in Germany

DFDA: Priamine 1074 dimer fatty diamine, delivered by Croda in Germany

HMDA: Hexamethylendiamine

C12DA: dodecane diamine

Preparation of the prepolymerised soft segments:

Soft segment 1 (DFA/DFDA, Mn ≈ 2000) Used for Example 1

To a 2000ml 3-neck flask equipped with stirrer, nitrogen inlet, PT100, Dean-Stark receiver filled with xylene, heating mantle and temperature control unit, 796.8g (1.4 mol) Pripol 1009 and 35g xylene were added and heated to about 130°C while stirring and padding with nitrogen. 432.4g (0.81 mol) of the dimerised fatty amine was added and the resulting mixture was heated until no more water was distilled of. The Dean-Stark receiver was replaced by a distillation setup and the mixture was heated to 180°C. When 180°C was reached, vacuum was applied to the reactor. The reaction mixture was maintained at 180°C until the amine value was below the detection limit. The resulting acid value was 56mg KOH/g.

Example 1: preparation of thermoplastic elastomer 1: Soft segment 1 (DFA/DFDA, Mn ≈ 2000) 70wt.%: Hard segment 1 (TPA/BD, Mn 857) 30 wt.%.

Preparation of the block copolymer from soft segment 1 was started by adding 1,4-BDO (21.47 g), DMT (26.24 g) soft segment 1 (70 g), Irganox 1330 (0.25 g), TBT (40.0713 mg/g BDO) stock solution (2.0688 g), $Mg(OAc)_24H_2O$ (0.052 g) into a stirred reaction flask and degassing the reaction mixture 3 times at 20 mbar followed by a nitrogen purge. During a first heating step the temperature was raised to 225°C and kept at that temperature till all the formed methanol is removed from the medium in ~70 minutes under nitrogen at 1 atm. Last traces of methanol are removed by keeping the pressure (step wise) at 100 mBar for 20 min. At the second step the temperature is increased to 240°C beginning of the polycondensation reaction and toward the end,

finally the reaction is continued under high vacuum. At the second step, polycondensation occurs via transesterfication reaction and excess of BDO is distilled of during the second step. Usually the reaction is decided to stop while the torque reaches 70 N/cm for 25 rpm. When the polyesterification reaction is complete, thermoplastic elastomer 1 is removed while it is warm and it is quenched in water.

Soft segment 2 (DFA/DFDA, Mn ≈ 2500) Used for Ex 2

To a 2000ml 3-neck flask equipped with stirrer, nitrogen inlet, PT100, distillation set up, heating mantle and temperature control unit, 636.9 g Pripol 1009 and 389.4 g of the dimerised fatty amine are added and slowly heated to 180°C while stirring and padding with nitrogen. When 180°C is reached, vacuum is applied to the reactor. The reaction mixture is maintained at 180°C until acid value 45mg KOH/g.

Example 1: preparation of thermoplastic elastomer 1: Soft segment 1 (DFA/DFDA, Mn ≈ 2000) 70wt.%: Hard segment 1 (TPA/BD, Mn 857) 30 wt.%.

Preparation of the block copolymer from soft segment 1 was started by adding 1,4-BDO (21.47 g), DMT (26.24 g) soft segment 1 (70 g), Irganox 1330 (0.25 g), TBT (40.0713 mg/g BDO) stock solution (2.0688 g), $Mg(OAc)_2 4H_2O$ (0.052 g) into a stirred reaction flask and degassing the reaction mixture 3 times at 20 mbar followed by a nitrogen purge. The polymerization was carried out under nitrogen at atmospheric pressure. During a first heating step the temperature was raised to 225ºC in about in ~70 minutes and kept at that temperature till all the formed methanol was removed from the medium. Last traces of methanol were removed by lowering the pressure step wise to 100 mBar and keeping it for 20 min. Then the reaction mixture was brought again under nitrogen at atmospheric pressure. During a second step the temperature is increased to 240ºC, as a result of which the polycondensation reaction proceeded. During the second step, polycondensation occurs via transesterfication reaction and excess of BDO was distilled of. Finally the reaction was continued under high vacuum. The reaction was decided to stop when no BDO was distilled anymore and the torque of the stirrer reached a constant level. Than the thermoplastic elastomer was removed while it is warm and it is quenched in water.

Example 2: preparation of thermoplastic elastomer 2: Soft segment 2 (DFA/DFDA, Mn ≈ 2500) 77.5 wt.%: Hard segment (TPA/BD, Mn ≈ 726) 22.5 wt.%

Preparation of the block copolymer from soft segment 2 was started by adding 1,4-BDO (15.52 g), DMT (18.33 g), soft segment 2 (77.5 g), Irganox 1330 (0.25 g), TBT (40.0713 mg/g BDO) stock solution (2.0688 g), and $Mg(OAc)_2 4H_2O$ (0.052 g) into a stirred reaction flask and degassing the reaction mixture 3 times at 20 mbar followed by a nitrogen purge. The polymerization was carried out under nitrogen at atmospheric pressure. During the first heating step the temperature was raised to 225°C in about in ~70 minutes and kept at that temperature till all the methanol that was formed was removed from the medium. Last traces of methanol were removed by lowering the pressure step wise to 100 mBar and keeping it for 20 min. Then the reaction mixture was brought again under nitrogen at atmospheric pressure. During a second step the temperature is increased to 240°C, as a result of which the polycondensation reaction proceeded. Finally the reaction was continued under high vacuum. During the second step, polycondensation occurs via transesterfication reaction and excess of BDO was distilled ofThe reaction was decided to stop when no BDO was distilled anymore and the torque of the stirrer reached a constant level. The resulting thermoplastic elastomer was removed while it is warm and it is quenched in water.

Table 1. Composition and test results for block copolymers according to the invention: Examples 1 and 2.

EX	wt.% Soft	wt.% Hard	Mn-S	Mn-H	Tg (°C)	Tm (°C)	Shore A (D)	Shore D	Hrel
1	70	30	2000	857	-22	182	80	26.5	1.82
2	77.5	22.5	2500	726	-26	170	69	20	

Chemical resistance of the block copolymer of Example 1 was tested against polar solvents including distilled water, acetone, acetic acid, ethanol 15wt.% and 50wt.% in water, and salad oil. The test results were expressed in reduction of the modulus and elongation at break after exposure for fixed time. The test results were compared with those for another thermoplastic elastomer block copolymer used in tubings. The elastomer block copolymer, based on polyester hard blocks and polyether soft blocks, Arnitel EB 464, a Tm of 210 °C and a hardness of Shore D 42. The block copolymer of Example 1 showed results as good as that of the polyetherpolyester block

copolymer, despite the much softer character of the block copolymer according to the invention.

CLAIMS

1. Block copolymer comprising hard segments and soft segments, wherein the copolymer comprises
   a. 20-42 wt.% of hard segments consisting of repeat units of a semi-crystalline semi-aromatic polyester, and
   b. 58-80 wt.% of soft segments consisting of repeat units of an amorphous polyamide

   wherein the weight percentages (wt.%) are relative to the total weight of the copolymer,
   the soft segments have a number average molecular weight (Mn) of 1750-3500, and
   the soft segments contain polymerization residues of a dimerised fatty acid and/or a dimerised fatty diamine and optionally other aliphatic dicarboxylic acids or other aliphatic diamines.
2. Block copolymer according to claim 1, wherein the number average molecular weight (Mn) of the soft segments is in the range of 2000 – 2750.
3. Block copolymer according to claim 1 or 2, wherein the soft segment is present in an amount of at least (15 + Mn*0.02) wt.% and/or at most (64+Mn*0.0075) wt.%, relative to the total weight of the copolymer, wherein Mn is the number average molecular weight of the soft segments.
4. Block copolymer according to any of claims 1-3, wherein the repeat units of the amorphous polyamide consists of polymerization residues of
   - a dimerised fatty acid and an aliphatic diamine, and/or
   - a dimerised fatty diamine and an aliphatic dicarboxylic acid and/or
   - a dimerised fatty acid and a dimerised fatty diamine .
5. Block copolymer according to any of claims 1-4, wherein the dimerised fatty acid residue and/or the dimerised fatty diamine residue contain 24 – 48 C-atoms.
6. Block copolymer according to any of claims 1-5, wherein the aliphatic dicarboxylic acid residue and/or the aliphatic diamine residue contain at least 6 C-atoms, preferably at least 10, and better in the range of 12-18 C-atoms.
7. Block copolymer according to any of claims 1-6, wherein repeat units of the semi-crystalline polyester comprise repeat units derived from butylene glycol

and/or ethylene glycol, and from terephthalic acid and/or naphthalene dicarboxylic acid.

8. Block copolymer according to any of claims 1-7, wherein the block copolymer has
   a. a melting temperature of at least 160 °C, preferably at least 170 °C, and more preferably in the range of 180-220 °C and/or
   b. a Tg of at most 0 °C, preferably at most -10 °C, and preferably in the range of -20°C - - 40°C and/or
   c. a Shore A hardness of at most 90, preferably 80-60.

9. Polymer composition comprising a block copolymer according to any of claims 1-8 and at least one additive.

10. Polymer composition comprising a blend of a block copolymer according to any of claims 1-8 and at least one other polymer, preferably SEBS.

11. Molded article made from a block copolymer according to any of claims 1-8 or a polymer composition according to claim 9 or 10, or comprising a layer or a part consisting of a block copolymer according to any of claims 1-8 or a polymer composition according to claim 9 or 10.

12. Molded article according to claim 11, wherein the molded article is a plastic component for a pump.

13. Plastic component according to claim 12, being a diaphragm, a gasket, a seal, an o-ring, a belt, a tube, a hose or a bellow.

14. Plastic component according to claim 12, being multilayer tube or a reinforced hose.

15. Molded article according to claim 11, wherein the block copolymer is cross-linked.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/069872

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G69/44 C08G69/34 F16L11/04 B32B1/08 B32B27/34
B32B27/36 C08L77/12 C08L77/08 C08L53/02
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)
C08G F16L B32B C08L

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 practical, 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.
A	JP 10 296890 A (SEKISUI CHEMICAL CO LTD) 10 November 1998 (1998-11-10) claim 1 paragraph [0050]	1-15
A	US 4 343 743 A (COQUARD JEAN ET AL) 10 August 1982 (1982-08-10) claim 3 example 9	1-15
A	US 4 581 410 A (DONERMEYER DONALD D [US] ET AL) 8 April 1986 (1986-04-08) claim 1 example 1	1-15
A	US 4 542 047 A (DONERMEYER DONALD D [US] ET AL) 17 September 1985 (1985-09-17) example 1	1-15

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[X] Further documents are listed in the continuation of Box C.

[X] 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 document 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	Date of mailing of the international search report
11 April 2011	26/04/2011

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/069872

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 907 733 A (JACKSON JR WINSTON J ET AL) 23 September 1975 (1975-09-23) example 44	1-15
A	US 3 650 999 A (MARTINS JOSEPH G ET AL) 21 March 1972 (1972-03-21) example 1	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2010/069872

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10296890 A	10-11-1998	NONE	
US 4343743 A	10-08-1982	BR 8008041 A	23-06-1981
		CA 1147883 A1	07-06-1983
		DE 3070400 D1	02-05-1985
		DK 524580 A	11-06-1981
		EP 0030904 A1	24-06-1981
		ES 8203928 A1	16-07-1982
		FI 803824 A	11-06-1981
		FR 2471394 A1	19-06-1981
		GR 71621 A1	20-06-1983
		IE 50612 B1	28-05-1986
		JP 1429139 C	09-03-1988
		JP 61069831 A	10-04-1986
		JP 62038370 B	18-08-1987
		JP 1464317 C	28-10-1988
		JP 61069832 A	10-04-1986
		JP 63010168 B	04-03-1988
		JP 1369242 C	25-03-1987
		JP 56092920 A	28-07-1981
		JP 61036858 B	20-08-1986
US 4581410 A	08-04-1986	NONE	
US 4542047 A	17-09-1985	NONE	
US 3907733 A	23-09-1975	NONE	
US 3650999 A	21-03-1972	BE 768513 A1	14-12-1971
		CA 958143 A1	19-11-1974
		DE 2129476 A1	23-12-1971
		FR 2096287 A5	11-02-1972
		GB 1340214 A	12-12-1973