

STYRENE BUTADIENE BLOCK COPOLYMERS WITH LOW CROSSLINKING

Description

- 5 The invention relates to a thermoplastic polymer composition comprising vinylaromatic diene block copolymers, a process for its preparation, and the use thereof for the preparation of shrink films.

10 Vinyl aromatic diene block copolymers and in particular styrene butadiene block copolymers (SBC) have the tendency to crosslink under energy (i.e. heat and shear) exposure during processing (e.g. extrusion, heat exchangers and melt pumps). Specifically the diene monomer units are sensitive for crosslinking, more specifically the pendant double bonds of the 1,2-coupled diene units. Typically, the higher the amount of diene in the block copolymer, the higher the energy induced crosslinking. When still in polymer solution, the crosslinked block copolymer is typically not soluble anymore in the organic solvent due to the increased molar mass resulting from crosslinking.

20 Crosslinked block copolymers can cause fouling of the production (e.g. fouling of reactor, heat exchangers, static mixers, etc.) and processing (e.g. injection molding machines, extruders, melt filters, etc.) equipment by slow deposition over time and ultimately can lead to blocking of production and processing installations. When fragments of these cross-linked deposits are released from the production or processing installations via the polymer melt into molded (shaped) articles (e.g. pellets, films, sheets, or injection molded parts etc.) produced from the vinyl aromatic diene block copolymers, these crosslinked deposits appear as dimensional and optical defects - also known as 'fish eyes' or 'gels' - in the final material. This happens as the crosslinking creates a three dimensional structure that cannot be reshaped as a thermoplast. These said dimensional and optical defects are disliked by end customers in final transparent products (such as bottles, trays, boxes, films) and technical issues like the non-printability are also caused and thus the value of the material decreases.

Thus, low or no fish-eyes from crosslinked diene in the obtained block copolymers are a key quality requirement especially in the SBC shrink sleeve market.

- 35 EP 0636 654 A1 describes a color stable and heat resistant block copolymer composition for a hot melt adhesive comprising (a) a linear styrene-isoprene-styrene triblock copolymer and (b) 0.1 to 5 pbw of a stabilizer set comprising specific UV-stabilizers (I), and

specific phosphite oxidants (II). Exemplified combinations (b) are commercial stabilizers Irgafos® 168 (0.4 wt.-%) and Irganox® 565 (0.09 wt.-%), and Irgafos® 168 (0.4 wt.-%) and Sumilizer GM (0.09 wt.-%).

- 5 WO 2018/153808 discloses a polymer composition comprising a mixture of specific star shaped block copolymers A1 and A2 for the production of shrink films. The use of a stabilizer in amounts of 0.01 to 0.7 wt.-% is preferred. As stabilizers oxygen radical scavengers such as Irganox® 1010, Songnox® 1010, Irganox® 1076, Irganox® 565 and blends thereof, carbon radical scavengers such as Sumilizer® GS, Sumilizer® GM and blends thereof, and/or secondary stabilizers such as Irgafos® 168 are mentioned. In the exam-
10 ples Irganox® 1010 alone, or 0.2 wt.-% Sumilizer® GS and 0.2 wt.-% Irganox® 1010 are used.

- The block copolymers comprised in said prior art compositions often have the afore-
15 mentioned disadvantages in respect to crosslinking and the formation of fish-eyes.

- One objective of the present invention is to provide block copolymers having low or preferably nearly no fish-eyes from crosslinked conjugated diene. A further objective is to provide a process for the preparation of block copolymers wherein crosslinking during
20 production and post-production processing is reduced.

One aspect of the present invention is a thermoplastic polymer composition (I) comprising (or consisting of) components (A), (B), and optionally (C), (D) and/or (E):

- (A) at least one block copolymer A comprising (consisting of):
25 A1: 60 to 95 wt.-% - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, preferably styrene, and
A2: 5 to 40 wt.-% - based on block copolymer A - polymerized units of at least one conjugated diene, preferably butadiene or isoprene;
(B) a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):
30 B1: 200 to 2500 ppm (0.020 to 0.250 wt.-%), often 500 to 2500 ppm (0.05 to 0.250 wt.-%), preferably 200 to 2250 ppm (0.020 to 0.225 wt.-%), more preferably 250 to 2100 ppm (0.025 to 0.210 wt.-%), – based on thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS number: 991-84-4),
35 B2: 500 to 2500 ppm (0.050 to 0.250 wt.-%), preferably 750 to 1750 ppm (0.075 to 0.175 wt.-%), more preferably 1000 to 1600 ppm (0.100 to

0.160 wt.-%) – based on thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate (CAS number: 123968-25-2) or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (CAS number: 61167-58-6) or mixtures thereof, and

B3: 500 to 2000 ppm (0.050 to 0.200 wt.-%), preferably 750 to 1750 ppm (0.075 to 0.175 wt.-%), more preferably 1000 to 1600 ppm (0.100 to 0.160 wt.-%) — based on thermoplastic polymer composition (I) - tris(2,4-di-tert-butylphenyl)-phosphite (CAS number: 31570-04-4);

(C) 0 to 5000 ppm (0 to 0.500 wt.-%) – based on thermoplastic polymer composition (I) - of one or more stabilizers different from (B1), (B2) and (B3);

(D) optionally one or more additives and/or processing aids other than (B) and (C):

(E) optionally at least one, preferably 1, 2 or 3, more preferably one, thermoplastic polymer TP other than block copolymer A.

‘ppm’ means ‘parts per million (mg/kg)’ based on the entire thermoplastic polymer composition (I).

‘Butadiene’ means 1,3-butadiene.

If optional component (D) is present, its minimum amount used is 0.01 wt.-%, based on the entire thermoplastic polymer composition (I). Generally component (D) can be used in amounts of from 0 to 6% by weight, based on the entire thermoplastic polymer composition (I), preferably 0.01 wt% to 3 wt% and more preferably 0.01 wt% to 1 wt%.

Component (C) can be used in a total amount of 0 to 5000 ppm (0 to 0.5 wt.-%), often 0 to 2000 ppm (0 to 0.20 wt.-%), or, 0 to 1750 ppm (0 to 0.175 wt.-%), or, 0 to 1500 ppm (0 to 0.15 wt.-%), more often 0 to 1100 ppm (0 to 0.11 wt.-%), based on the entire thermoplastic polymer composition (I). Preferably optional component (C) is not present.

Often optional component (C) is present - based on the entire thermoplastic polymer composition (I) - in a total amount of 500 to 2000 ppm (0.05 to 0.20 wt.-%), or, 500 to 1750 ppm (0.05 to 0.175 wt.-%), or, 500 to 1100 ppm (0.05 to 0.11 wt.-%), more often 750 to 2000 ppm (0.075 to 0.20 wt.-%), or, 750 to 1750 ppm (0.075 to 0.175 wt.-%), or, 750 to 1100 ppm (0.075 to 0.11 wt.-%), mostly 950 to 2000 ppm (0.095 to 0.20 wt.-%), or, 950 to 1750 ppm (0.095 to 0.175 wt.-%), or, 950 to 1050 ppm (0.095 to 0.105 wt.-%),

in particular 950 to 1050 ppm (0.095 to 0.105 wt.-%). Often component (C) is only one stabilizer.

If optional component (E) is present, it is preferably used in a total amount of 0.5 to 85 wt.-%, preferably 1 to 75 wt.-% more preferably 1 to 55 wt.-%, based on the entire thermoplastic polymer composition (I).

Often the thermoplastic polymer composition (I) according to the invention comprises (or consists of) components (A), (B), and optionally (C), (D) and/or (E):

- 10 (A) at least one block copolymer A comprising (consisting of):
A1: 60 to 95 wt.-% - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, preferably styrene, and
A2: 5 to 40 wt.-% - based on block copolymer A - polymerized units of at least one conjugated diene, preferably butadiene or isoprene;
- 15 (B) a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):
B1: 500 to 2500 ppm (0.05 to 0.250 wt.-%), preferably 1000 to 2250 ppm (0.100 to 0.225 wt.-%), more preferably 1500 to 2100 ppm (0.150 to 0.210 wt.-%) – based on thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS number: 991-84-4),
20 B2: 500 to 2500 ppm (0.050 to 0.250 wt.-%), preferably 750 to 1750 ppm (0.075 to 0.175 wt.-%), more preferably 1000 to 1600 ppm (0.100 to 0.160 wt.-%) – based on thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate (CAS number: 123968-25-2) or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (CAS number: 61167-58-6) or mixtures thereof,
25 and
B3: 500 to 2000 ppm (0.050 to 0.200 wt.-%), preferably 750 to 1750 ppm (0.075 to 0.175 wt.-%), more preferably 1000 to 1600 ppm (0.100 to 0.160 wt.-%) — based on thermoplastic polymer composition (I) - tris(2,4-di-tert.-butylphenyl)-phosphite (CAS number: 31570-04-4);
30 (C) 0 to 5000 ppm (0 to 0.500 wt.-%) – based on thermoplastic polymer composition (I) - of one or more stabilizers different from (B1), (B2) and (B3);
(D) optionally one or more additives and/or processing aids other than (B) and (C):
(E) optionally at least one, preferably 1, 2 or 3, more preferably one, thermoplastic
35 polymer TP other than block copolymer A.

Preferably the thermoplastic polymer composition (I) consists of components (A), (B), and optionally (C), (D) and/or (E).

5 More preferably, the thermoplastic polymer composition (I) consists of components (A), (B), and optionally (D) and/or (E).

More preferably the thermoplastic polymer composition (I) consists of components (A) and (B).

10 Block copolymer A

Block copolymer A comprises (or consists of):

A1: 60 to 95 wt.-% - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, in particular styrene, and

15 A2: 5 to 40 wt.-%, based on block copolymer A - polymerized units, of at least one conjugated diene, in particular butadiene or isoprene.

Preferably block copolymer A comprises (consists of):

A1: 60 to 80 wt.-% - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, in particular styrene, and

20 A2: 20 to 40 wt.-% - based on block copolymer A - polymerized units of at least one conjugated diene, in particular butadiene or isoprene.

More preferably block copolymer A comprises (consists of):

A1: 60 to 76 wt.-% - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, in particular styrene, and

25 A2: 24 to 40 wt.-% - based on block copolymer A - polymerized units of at least one conjugated diene, in particular butadiene or isoprene.

More preferred block copolymer A comprises (consists of):

A1: 65 to 76 wt.-%, - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, in particular styrene, and

A2: 24 to 35 wt.-%, - based on block copolymer A - polymerized units of at least one conjugated diene, in particular butadiene or isoprene.

Generally block copolymer A is obtained by an anionic polymerization process. Preferably block copolymer A is obtained by an anionic polymerization process with 1, 2 or 3
5 initiation steps and sequential monomer addition and polymerization.

Block copolymer A can be a linear or star shaped block copolymer. The preparation of such block copolymers by sequential anionic polymerization is commonly known (cp. e.g. US 6,593,430, col. 3, l. 1 to col. 4, l. 45).

Generally suitable block copolymer A comprise at least one hard polymer block S composed of from 95 to 100 wt.-% of vinylaromatic monomers and of from 0 to 5 wt.-% of conjugated dienes, optionally one or more hard copolymer blocks (B/S) each composed of conjugated dienes and vinylaromatic monomers having a B/S-ratio (= diene/vinylaromatic monomer-ratio) < 0.25, preferably 0.1 to 0.2, more preferably 0.1 to 0.15, and a glass transition temperature $T_g > 37^\circ\text{C}$, and one or more soft blocks B composed of
10 100 wt.-% conjugated diene and/or one or more soft copolymer blocks (S/B) each composed of vinylaromatic monomers and of conjugated dienes having a S/B-ratio (= vinylaromatic monomer/diene-ratio) < 0.5, preferably 0.15 to 0.45, more preferably 0.2 to 0.4, and a glass transition temperature $T_g < 37^\circ\text{C}$.
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The hard and soft copolymer blocks (B/S) and (S/B) can be random or tapered copolymer blocks, preferably the copolymer blocks (B/S) and (S/B) are random copolymer blocks.
20

The copolymer blocks (B/S), (S/B), S or B can be a block $[(B/S)]_n$, $[(S/B)]_n$, S_n or B_n respectively, consisting of n, respectively one or more, preferably 1 to 10, different or identical copolymer blocks (B/S), (S/B), S or B, where the blocks (B/S) or (S/B) can differ in their molar masses and/or in their vinylaromatic/diene ratio.

Preferably block copolymers A comprise at least one hard polymer block S composed of from 95 to 100 wt.-% of vinylaromatic monomers and of from 0 to 5 wt.-% of conjugated dienes, and comprises one or more copolymer blocks $(B/S)_A$ each composed of from 65 to 95% by weight of vinylaromatic monomers and of from 35 to 5% by weight of conjugated dienes and of a glass transition temperature T_{gA} in the range from 40° to 90°C , and comprises one or more copolymer blocks $(B/S)_B$ each composed of from 1 to 60 wt.-%, preferably 1 to 30 wt.-%, of vinylaromatic monomers and of from 99 to 40 wt.-%, preferably 99 to 70 wt.-%, of conjugated dienes and of a glass transition temperature T_{gB} in the range from -90° to -40°C , preferably -80° to -65°C .
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The glass transition temperature is affected by the nature, constitution, and distribution of the monomers, and can be determined by differential scanning calorimetry (DSC) or differential mechanical thermal analysis (DMTA), or, if the distribution of the monomers is random, from the Fox equation. Precise DSC determination is usually based on ISO 11357-2, with evaluation of the 2nd cycle with a heating rate of 20 K/min.

The afore-mentioned preferred block copolymer A used in the thermoplastic polymer composition (I) of the invention has at least one polymer block S and copolymer block $(B/S)_A$ acting as hard blocks, and at least one block $(B/S)_B$ acting as soft block. Generally block copolymers A are tough materials which can preferably be used in the production of shrink films.

Preferably the vinylaromatic monomer used for the preparation of the blocks S, $(B/S)_B$ and $(B/S)_A$ is styrene, and the conjugated diene used for the preparation of blocks $(B/S)_B$ and $(B/S)_A$ is preferably isoprene or butadiene, more preferably butadiene.

More preferably block copolymers A are star-shaped.

The polymer blocks S can occur terminally (= outer block, first block after first initiation) - designated as block (S_e) - and also between the blocks $(B/S)_A$ and $(B/S)_B$ - designated as block (S_i) (= inner block). The number-average molar mass M_n of the hard polymer blocks S, in particular blocks S_e and S_i , of the block copolymer A is generally in the range from 2000 to 30000 g/mol.

The S_i block maximizes incompatibility of the hard block $(B/S)_A$ with the homo- or copolymer soft block $(B/S)_B$ acting as soft phase. This means that the intermediate phase that forms between the hard phase and the soft phase in the polymer matrix can be kept small.

The proportion by weight of phases, that soften in the range of room temperature. i.e. from 10 to 40°C, can thus be kept small which is beneficial for a low natural shrinkage at temperatures below 40°C.

Further short polymer blocks S can occur as a final polymer block - designated as block (S_f) - at the end of the polymerization (before chain termination or coupling) and/or as a short first polymer block (S_e) formed at the start of the polymerization (after the first initiation).

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The number-average molar mass M_n of the short polymer blocks S, in particular S_f and S_e , is – independently from each other – less than 4000 g/mol.

10 The number-average molar mass M_n of the copolymer block $(B/S)_A$ is generally in the range from 30000 to 300000 g/mol, preferably in the range of from 35000 to 150000 g/mol, more preferably in the range from 40000 to 100000 g/mol.

15 The molecular weights are usually determined by means of gel permeation chromatography (GPC) in THF as solvent, using polystyrene as standard. In the case of anionic polymerization, weight-average molecular weight is approximately identical with number-average molecular weight and peak molecular weight or peak molecular weight increase in case of polymer growth. The molecular weights of polybutadiene segments are generally overestimated by factor 1.7, compared to the theoretical values derived from the amount of monomer to initiator ratio, when measured in gel permeation chromatography
20 calibrated using polystyrene standard.

The block copolymers A used according to the invention are prepared anionically, thus the molecular weight can be controlled by way of the ratio of amount of monomer to amount of initiator. The initiator can also be added repeatedly after monomer feed has taken place, the result then being a bi- or multimodal distribution.

25 The copolymer blocks $(B/S)_A$ and $(B/S)_B$ can be a block $[(B/S)_A]_n$ or $[(B/S)_B]_n$, respectively, consisting of n, respectively one or more, preferably 1 to 10, different or identical copolymer blocks $(B/S)_A$ or $(B/S)_B$, where the blocks $(B/S)_A$ or $(B/S)_B$ can differ in their molar masses and/or in their vinylaromatic/diene ratio. Preferably, the block $(B/S)_A$ or $(B/S)_B$ is a single block.

30 It is preferable that the copolymer block $(B/S)_A$ is made from 85 to 93 wt.-% of a vinylaromatic monomer, in particular styrene, and from 7 to 15 wt.-% of a diene, in particular isoprene or butadiene. Particular preference is given to butadiene. The glass transition temperature of the copolymer block $(B/S)_A$ is preferably in the range from 50 to 80°C, particularly preferably from 60 to 75°C.

The distribution of the polymerized units of vinylaromatic monomers and dienes in the copolymer blocks $(B/S)_B$ and $(B/S)_A$ of the block copolymer A is preferably random. These can by way of example be obtained by anionic polymerization using alkylolithium compounds in presence of randomizers, such as tetrahydrofuran, or potassium salts. Preference is given to use of potassium salts where the molar ratio of anionic initiator to potassium salt is in the range from 25:1 to 60:1, particularly preferably from 30:1 to 40:1. This method can at the same time achieve a low proportion of 1,2 linkages of the butadiene units. Suitable potassium salts are K alcoholates, in particular those soluble in the polymerization solvent, e.g. tert-amyl alcoholate or triethylcarbinolate, or other C-rich tertiary alcoholates.

The proportion of 1,2 linkages of the butadiene units is preferably in the range from 8 to 15%, based on the entirety of the 1,2, 1,4-cis, and 1,4-trans linkages.

The number-average molar mass M_n of the copolymer blocks $(B/S)_B$ is generally in the range of from 5000 to 50000 g/mol, preferably from 10000 to 40000 g/mol, more preferably 12000 to 35000 g/mol.

It is preferable that the block $(B/S)_B$ is a copolymer block made from 1 to 30 wt.-%, more preferably 5 to 28 wt.-%, most preferred 10 to 28 wt.-% vinylaromatic monomers, in particular styrene, and 99 to 70 wt.-%, more preferably 95 to 72 wt.-%, most preferred 90 to 72 wt.-% dienes, preferably isoprene or butadiene, in particular butadiene.

The glass transition temperature T_{gB} of the homo- or copolymer block $(B/S)_B$ is preferably in the range from -80 to -65 °C.

Preferably block copolymer A is a star shaped block copolymer. The preparation of star-shaped block copolymers by sequential anionic polymerization is commonly known (e.g. US 6,593,430, col. 3, l. 1 to col. 4, l. 45).

Usually coupling with a coupling agent takes place after the last addition and complete polymerization of the finally added monomer(s), and the plurality of living anionic polymer chain ends are thus bonded to one another, and block copolymers A having star-shaped molecular architecture are formed.

It is generally possible to use any polyfunctional compound as coupling agent. It is preferable that the coupling agent has been selected from epoxidized vegetable oils, such as epoxidized linseed oil or epoxidized soybean oil, silanes, such as alkoxy silanes, e.g. $\text{Si}(\text{OMe})_4$, chlorosilanes, such as SiCl_4 , $\text{Si}(\text{Alkyl})_2\text{Cl}_2$, $\text{Si}(\text{alkyl})\text{Cl}_3$, where alkyl is a C_1 - C_4 -alkyl moiety, preferably methyl, halides of aliphatic hydrocarbons, such as dibromomethane or bischloromethylbenzene, tin tetrachloride, polyfunctional aldehydes, such as terephthalaldehyde, polyfunctional ketones, polyfunctional esters, such as carboxylic esters, e.g. ethyl acetate, diethyl succinate, dimethyl or diethyl adipate, polyfunctional anhydrides, oligo-epoxides, such as 1,4-butanediol glycidyl ether, activated diolefins, such as diisopropenylbenzene, divinylbenzene, or distyrylbenzene; preferred coupling agents are epoxidized vegetable oils, such as epoxidized linseed oil or epoxidized soy oil, e.g. Efka® PL 5382 (old Dehysol® D82) from BASF AG or Vikoflex® 7170 from Arkema.

The coupling agent forms the coupling center X, which is formed by reaction of the living anionic chain ends with one of the abovementioned coupling agents.

Preferred are star-shaped block copolymers A in which the stars have short branches of structure $\text{S}_e\text{-(B/S)}_B\sim$ and long branches of structure $(\text{B/S})_A\text{-S}_i\text{-(B/S)}_B\sim$, linked to one another via a coupling agent by way of the soft blocks $(\text{B/S})_B$.

Further preferred are star-shaped block copolymers A in which the stars have short branches of structure $\text{S}_e\text{-(B/S)}_B\sim$ and long branches of structure $\text{S}_e\text{-(B/S)}_A\text{-S}_i\text{-(B/S)}_B\sim$, linked to one another via a coupling agent by way of the soft blocks $(\text{B/S})_B$.

Prior to linkage, a short polystyrene block S_f can optionally be incorporated into the living polymer chains to improve the coupling efficiency. Further preferred star-shaped block copolymers A of this type are:

star-shaped block copolymers A in which the stars have short branches of structure $\text{S}_e\text{-(B/S)}_B\text{-S}_f\sim$ and long branches of structure $(\text{B/S})_A\text{-S}_i\text{-(B/S)}_B\text{-S}_f\sim$, linked to one another via a coupling agent by way of the blocks S_f ; and

star-shaped block copolymers A in which the stars have short branches of structure $\text{S}_e\text{-(B/S)}_B\text{-S}_f\sim$ and long branches of structure $\text{S}_e\text{-(B/S)}_A\text{-S}_i\text{-(B/S)}_B\text{-S}_f\sim$, linked to one another via a coupling agent by way of the blocks S_f .

The afore-mentioned preferred star-shaped block copolymers A are prepared by sequential anionic polymerization method using double initiation. The polymer blocks S_e and S_i of said preferred star-shaped block copolymers A have the same constitution and number-average molar masses M_n .

- 5 In said afore-mentioned preferred star-shaped block copolymers A, the proportion of the entirety of the blocks $(B/S)_B$ is preferably from 26 to 37 wt.-%, based on the entire block copolymer A.

In particular preferred are star-shaped block copolymers A where the proportion of the entirety of all of the blocks $(B/S)_B$ is from 30 to 37 wt.-%, preferably 31 to 35 wt.-%, more
10 preferably 32 to 33 wt.-%, based on the entire star-shaped block copolymer A.

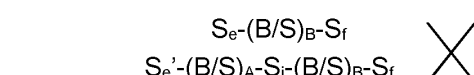
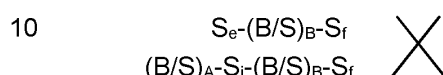
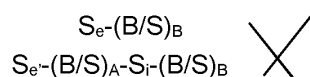
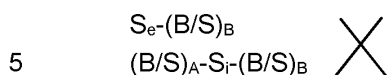
More preferred are star-shaped block copolymers A as hereinbefore described, wherein the (hard) polymer blocks S_e , S_i , and, if present, S_r and/or S_e' are made from 95 to 100 wt.-% of vinylaromatic monomers, and 0 to 5 wt.-% of dienes, the blocks S_e and S_i have
15 number-average molar masses M_n in the range from 5000 to 30000 g/mol, if present, the blocks S_r and/or S_e' have number-average molar masses M_n of less than 4000 g/mol; the (hard) copolymer block $(B/S)_A$ is made from 65 to 95 wt.-% vinylaromatic monomers and 35 to 5 wt.-% dienes and has a glass transition temperature T_{gA} in the range from 40 to 90°C and a number-average molar mass M_n in the range of from 30000 to 100000 g/mol,
20 and the (soft) homo- or copolymer blocks $(B/S)_B$ are each made from 1 to 30 wt.-%, preferably 5 to 28 wt.-%, vinylaromatic monomers and 99 to 70 wt.-%, preferably 95 to 72 wt.-%, dienes and have a glass transition temperature T_{gB} in the range from -90 to -60°C, preferably -80 to -65°C, and a number-average molar mass M_n in the range of from 5000 to 50000 g/mol.

25 In particular preferred are the afore-mentioned star-shaped block copolymers A where the proportion of the entirety of all of the blocks $(B/S)_B$ is from 30 to 37 wt.-%, preferably 31 to 35 wt.-%, more preferably 32 to 33 wt.-%, based on the entire star-shaped block copolymer.

30 Particularly suitable star shaped block copolymers A are made from 60 to 80 wt.-%, preferably from 60 to 76 wt.-%, of vinylaromatic monomers, in particular styrene, and of from 20 to 40 wt.-%, preferably from 24 to 40 wt.-%, of diene, in particular butadiene or isoprene, based in each case on the entire block copolymer.

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According to one preferred embodiment the block copolymer A has one of the following star shaped structures:



where S_e , S_i , S_f , S_e' , $(B/S)_A$ and $(B/S)_B$ are as defined above and X is a coupling center, which is formed by reaction of the living anionic polymer chain ends (= linked by way of the blocks $(B/S)_B$ or S_f) with a polyfunctional coupling agent. Said polyfunctional coupling agent can generally be any suitable polyfunctional compound. Polyfunctional coupling agents can be e.g. polyfunctional aldehydes, ketones, esters, anhydrides or epoxides. It is preferably selected from epoxidized vegetable oils, in particular epoxidized linseed oil or epoxidized soybean oil.

The star shaped block copolymers of the general formula shown above can be of different compositions and can be symmetrical (e.g. having two long and 2 short branches) or asymmetrical (e.g. having one long and 3 short branches). The preparation of symmetrical star shaped block copolymers is described in detail in WO 2018/153808 (see page 15, line 28 through page 16, line 30).

30 Stabilizer Combination (B)

The stabilizer combination (B) is generally used in amounts of 1200 to 7000 ppm (0.120 to 0.700 wt.-%), often 1500 to 7000 ppm (0.150 to 0.700 wt.-%), preferably 1700 to 6000 ppm, often preferably 2500 to 6000 ppm (0.250 to 0.600 wt.-%), more preferably 2250 to 5500 ppm (0.225 to 0.550 wt.-%), often more preferably 3000 to 5500 ppm (0.300 to 0.550 wt.-%), most preferably 3200 to 5000 ppm (0.320 to 0.500 wt.-%), often most preferably 3500 to 5000 ppm (0.350 to 0.500 wt.-%), based on the entire thermoplastic polymer composition (I).

Preferably stabilizer combination (B) consists of:

B1: 200 to 2250 ppm (0.020 to 0.225 wt.-%) – based on the entire thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,

5 B2: 750 to 1750 ppm (0.075 to 0.175 wt.-%) – based on the entire thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and

10 B3: 750 to 1750 ppm (0.075 to 0.175 wt.-%) – based on the entire thermoplastic polymer composition (I) – tris(2,4-di-tert.-butylphenyl)phosphite.

Often preferably stabilizer combination (B) consists of:

15 B1: 1000 to 2250 ppm (0.100 to 0.225 wt.-%) – based on the entire thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,

B2: 750 to 1750 ppm (0.075 to 0.175 wt.-%) – based on the entire thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and

20 B3: 750 to 1750 ppm (0.075 to 0.175 wt.-%) – based on the entire thermoplastic polymer composition (I) – tris(2,4-di-tert.-butylphenyl)phosphite.

More preferably stabilizer combination (B) consists of:

25 B1: 250 to 2100 ppm (0.025 to 0.210 wt.-%) 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,

B2: 1000 to 1600 ppm (0.100 to 0.160 wt.-%) 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and

30 B3: 1000 to 1600 ppm (0.100 to 0.160 wt.-%) tris(2,4-di-tert.-butylphenyl)phosphite.

Often more preferably stabilizer combination (B) consists of:

35 B1: 1500 to 2100 ppm (0.150 to 0.210 wt.-%) 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,

- B2: 1000 to 1600 ppm (0.100 to 0.160 wt.-%) 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and
- 5 B3: 1000 to 1600 ppm (0.100 to 0.160 wt.-%) tris(2,4-di-tert.-butylphenyl)phosphite.

Often most preferably stabilizer combination (B) consists of:

- B1: 1900 to 2100 ppm (0.190 to 0.210 wt.-%), in particular 2000 ppm (0.200 wt.-%), 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,
- 10 B2: 1400 to 1600 ppm (0.140 to 0.160 wt.-%), in particular 1500 ppm (0.150 wt.-%), 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and
- 15 B3: 1400 to 1600 ppm (0.140 to 0.160 wt.-%), in particular 1500 ppm (0.150 wt.-%), tris(2,4-di-tert.-butylphenyl)phosphite.

The afore-mentioned amounts of components B1, B2 and B3 are each based on the entire thermoplastic polymer composition (I).

20

Preferably component B2 is 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate.

- Component B1 - a free-radical scavenger for O-radicals - is commercially available as
- 25 e.g. Irganox[®] 565 obtainable from BASF SE, Germany.

Component B2 - a free-radical scavenger for C-radicals - is commercially available:

- 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate as e.g. Sumilizer[®] GS from BASF SE, Germany, or Chinox^(R) GS from DBC or Zikanox^(R) 549
- 30 from Ziko; and

2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate as e.g. Sumilizer[®] GM from BASF SE, Germany.

Component B3 - a secondary oxidation inhibitor - is commercially available as e.g. Irgafos[®] 168 obtainable from BASF SE, Germany, or Songnox[®] 168 FF from Songwon.

Component C

Suitable stabilizers which can be used as component C are other stabilizers than B1, B2 and B3. Examples are other free-radical scavengers e.g. other C-radical scavengers, such as α -tocopherol (vitamin E), other O-radical scavengers, such as pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate (CAS number: 6683-19-8 e.g. Irganox® 1010, Songnox® 1010), 2-hexadecan-2-yl-4,6-dimethylphenol (e.g. Irganox 1141), and/or octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (CAS number: 2082-79-3) (e.g. Irganox 1076), ethylene bis[3,3-bis[3-(1,1-dimethylethyl)-4-hydroxyphenyl]butanoate] (e.g. Hostanox® O3), and thio-ether based co-stabilizers such as dioctadecyl disulphide (e.g. Hostanox® SE10). Furthermore, as component C other secondary oxidation inhibitors based on phosphite such as triisobutylphenyl phosphite (TNPP) can be used.

15 In case component C is present, the use of pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate (e.g. Irganox® 1010, Songnox® 1010) is preferred.

In case component C, in particular pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate, is present, its amount is preferably 500 to 1900 ppm (0.050 to 0.190 wt.-%), more preferably 750 to 1800 ppm (0.075 to 0.180 wt.-%), in particular 950 to 1800 ppm (0.095 to 0.180 wt.-%), often 750 to 1100 ppm, or, often 1500 to 1800 ppm, more often 950 to 1050 ppm, or, more often 1650 to 1800 ppm, and the amount of component B1 is preferably 200 to 1500 ppm (0.020 to 0.015 wt.-%), more preferably 250 to 1100 ppm (0.025 to 0.110 wt.-%), in particular 250 to 1050 ppm (0.025 to 0.105 wt.-%), often 750 to 1100 ppm, or, often 200 to 500 ppm, more often 950 to 1050 ppm, or, more often 250 to 350 ppm, each based on the entire thermoplastic polymer composition (I).

Often in case component C, in particular pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate, is present, its amount is preferably 500 to 1500 ppm (0.050 to 0.150 wt.-%), more preferably 750 to 1100 ppm (0.075 to 0.110 wt.-%), in particular 950 to 1050 ppm (0.095 to 0.105 wt.-%), and the amount of component B1 is preferably 500 to 1500 ppm (0.050 to 0.015 wt.-%), more preferably 750 to 1100 ppm (0.075 to 0.110 wt.-%), in particular 950 to 1050 ppm (0.095 to 0.105 wt.-%), each based on the entire thermoplastic polymer composition (I).

35

According to one embodiment of the invention, in thermoplastic polymer composition (I) as described above component C, in particular pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate, is present in an amount of 750 to 1100 ppm, in particular 950 to 1050 ppm, and stabilizer combination (B) consists of:

- 5 B1: 500 to 1500 ppm, preferably 750 to 1100 ppm, more preferably 950 to 1050 ppm 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,
B2: 1000 to 1600 ppm, in particular 1400 to 1600 ppm, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-
10 3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and
B3: 1000 to 1600 ppm, in particular 1400 to 1600 ppm, tris(2,4-di-tert.-butylphenyl)phosphite.

- According to a further embodiment of the invention, in thermoplastic polymer composition (I) as described above component C, in particular pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate, is present in an amount of 1500 to 1800 ppm, in particular 1600 to 1800 ppm, and stabilizer combination (B) consists of:

- 15 B1: 200 to 500 ppm, preferably 250 to 350 ppm, 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol,
20 B2: 1000 to 1600 ppm, in particular 1400 to 1600 ppm, 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate or mixtures thereof, preferably 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate, and
25 B3: 1000 to 1600 ppm, in particular 1400 to 1600 ppm, tris(2,4-di-tert.-butylphenyl)phosphite.

Preferably, the component (C) is not present.

Additives and/or processing aids D

- 30 Suitable processing aids and additives which can be used as component (D) are such as antiblocking agents, dyes, UV absorbers, plasticizers and waxes (lubricants).
The use of a plasticizer and/or waxes (lubricants) is preferred.

- Preferably used as plasticizer in the inventive thermoplastic polymer composition (I) is a
35 homogeneously miscible oil or oil mixture, in particular mineral oil (or white oil) or dioctyl

adipate. The afore-mentioned plasticizers are preferably used in amounts of 0.05 to 3 wt.-%, more preferably 0.1 to 1 wt.-%, based on thermoplastic polymer composition (I).

5 Examples of waxes (lubricants) which can be used - preferably in amounts of 0.05 to 0.2 wt.-%, based on thermoplastic polymer composition (I) - are fatty acids having 14 to 22 carbon atoms such as stearic acid or behenic acid, their salts (e.g. Ca or Zn stearate) or esters (e.g. stearyl stearate or pentaerythrityl tetrastearate), and also amide derivatives of fatty acids having 14 to 22 carbon atoms (e.g. ethylenebisstearylamine).

10 For better processing, mineral-based antiblocking agents may be added to the thermoplastic polymer composition (I) of the invention. Examples include amorphous or crystalline silica, calcium carbonate, or aluminum silicate.

The maximum concentration of anti-blocking agent is below 1 wt.-%, preferably up to 0.1 wt.-%, based on the thermoplastic polymer composition (I).

15

Thermoplastic Polymers TP (= component (E))

Particularly suitable thermoplastic polymers TP are styrene polymers, such as vinyl-aromatic diene block-copolymers (SBC) different from block-copolymer A, standard polystyrene (GPPS), high impact polystyrene (HIPS), styrene-acrylonitrile copolymers (SAN),
20 styrene-methyl methacrylate copolymers (S/MMA), or polymethacrylates, such as PMMA, polyesters, such as polyethylene terephthalate (PET), polyolefins, such as polyethylene or polypropylene, or polyvinyl chloride (PVC), or semicrystalline materials. Preferably used are styrene polymers, in particular SBC, GPPS and HIPS.

25 It is also possible to use polyacrylates, such as poly-n-butyl acrylate (PnBA), and other acrylate rubbers, ethylvinyl acetate polymers (EVA), etc. The thermoplastic polymers TP can be admixed to improve stiffness, solvent resistance, printability, antiblocking properties, recyclability, and cling properties.

30 It is also possible to use thermoplastic elastomers (TPE), for example linear or star-shaped, hydrogenated or non-hydrogenated styrene-butadiene or styrene-isoprene block copolymers other than block copolymers A. Suitable block copolymers are available commercially as, Kraton® G. Addition of thermoplastic elastomers generally improves the toughness of the polymer composition of the invention.

35

Thermoplastic polymer composition (I)

Often the thermoplastic polymer composition (I) according to the invention comprises (or consists of):

- 5 (A) 25 to 99.88 wt.-%, preferably 25 to 99.82 wt.-%, - based on the entire thermoplastic polymer composition (I) - of at least one block copolymer A as described above;
- (B) 0.120 to 0.700 wt.-%, preferably 0.170 to 0.600 wt.-%, more preferably 0.225 to 0.550 wt.-%, of a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):
- 10 B1: 0.020 to 0.250 wt.-%, preferably 0.020 to 0.225 wt.-%, more preferably 0.025 to 0.210 wt.-% – based on thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS number: 991-84-4),
- 15 B2: 0.050 to 0.250 wt.-%, preferably 0.075 to 0.175 wt.-%, more preferably 0.100 to 0.160 wt.-% – based on thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate (CAS number: 123968-25-2) or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (CAS number: 61167-58-6) or mixtures thereof, and
- 20 B3: 0.050 to 0.200 wt.-%, preferably 0.075 to 0.175 wt.-%, more preferably 0.100 to 0.160 wt.-% — based on thermoplastic polymer composition (I) - tris(2,4-di-tert.-butylphenyl)phosphite (CAS number: 31570-04-4);
- (C) 0 to 0.50 wt.-%, preferably 0 to 0.20 wt.-%, – based on the entire thermoplastic polymer composition (I) - of one or more stabilizers different from (B1), (B2) and (B3);
- 25 (D) 0 to 6.00 wt.-%, preferably 0.01 wt.-% to 3.00 wt.-%, based on the entire thermoplastic polymer composition (I), one or more additives and/or processing aids other than (B) and (C):
- (E) 0 to 74.88 wt.-%, preferably 0 to 74.82 wt.-%, based on the entire thermoplastic polymer composition (I), - at least one thermoplastic polymer TP other than block copolymer A;
- 30 where components (A), (B), and, if present, components (C), (D) and/or (E) total 100 wt.-%.

Furthermore often the thermoplastic polymer composition (I) according to the invention comprises (or consists of):

35

- (A) 25 to 99.30 wt.-%, preferably 25 to 98.89 wt.-%, - based on the entire thermoplastic polymer composition (I) - of at least one block copolymer A as described above;
- 5 (B) 0.150 to 0.700 wt.-%, preferably 0.250 to 0.600 wt.-%, more preferably 0.300 to 0.550 wt.-%, most preferably 0.350 to 0.500 wt.-%, of a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):
- B1: 0.05 to 0.250 wt.-%, preferably 0.100 to 0.225 wt.-%, more preferably 0.150 to 0.210 wt.-% – based on the entire thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS number: 991-84-4),
- 10 B2: 0.050 to 0.250 wt.-%, preferably 0.075 to 0.175 wt.-%, more preferably 0.100 to 0.160 wt.-% – based on thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate (CAS number: 123968-25-2) or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (CAS number: 61167-58-6) or mixtures thereof, and
- 15 B3: 0.050 to 0.200 wt.-%, preferably 0.075 to 0.175 wt.-%, more preferably 0.100 to 0.160 wt.-% — based on thermoplastic polymer composition (I) - tris(2,4-di-tert.-butylphenyl)phosphite (CAS number: 31570-04-4);
- (C) 0 to 0.500 wt.-% – based on the entire thermoplastic polymer composition (I) - of one or more stabilizers different from (B1), (B2) and (B3);
- 20 (D) 0 to 6.00 wt.-%, preferably 0.01 wt.-% to 3.00 wt.-%, based on the entire thermoplastic polymer composition (I), one or more additives and/or processing aids other than (B) and (C);
- (E) 0 to 74.85 wt.-%, preferably 0.50 to 74.85 wt.-%, based on the entire thermoplastic polymer composition (I), - at least one thermoplastic polymer TP other than block copolymer A;
- 25

where components (A), (B), and, if present, components (C), (D) and/or (E) total 100 wt.-%.

30

One further aspect of the invention is a process for the preparation of thermoplastic polymer composition (I) according to the invention. As described above the at least one block copolymer (A) is generally obtained by an anionic polymerization process. Preferably block copolymer A is obtained by an anionic polymerization process with 1, 2 or 3

35 initiation steps and sequential monomer addition and polymerization.

The preparation of such block copolymers by sequential anionic polymerization is commonly known (cp. e.g. US 6,593,430, col. 3, l. 1 to col. 4, l. 45).

Preferred star-shaped block copolymers (A) are prepared by sequential anionic polymerization method using double or triple initiation. After chain termination or after coupling of the living anionic polymer chain ends the obtained linear or star shaped block copolymers can be further worked-up. Optionally a small amount of alcohol, such as isopropanol, can be used to protonate the possible small amounts of residual carbanions and the polymer-bonded alcoholates which may have been produced in the termination or coupling step, in order to avoid formation of deposits in the tank and discoloration of the product, and to lower the viscosity of the solution, and, prior to further work-up, CO₂/water can be used in a conventional manner to acidify the product slightly, so that the product subsequently obtained is glass-clear with no color tinge.

Preferably after chain termination or after coupling of the living anionic polymer chain ends, and after optional addition of alcohol, and CO₂ and water as described hereinbefore, the obtained linear or star shaped block copolymers (A) are stabilized with the hereinbefore described stabilizer combination (B) consisting of stabilizer components (B1), (B2) and (B3), and optionally one or more hereinbefore described stabilizers (C) different from (B1), (B2) and (B3). Stabilizer components (B1), (B2), (B3) and optional stabilizers (C) can also be added at a later stage of the process for the preparation of thermoplastic polymer composition (I). Optional components (D) and/or (E) can also be added after chain termination or after coupling of the living anionic polymer chain ends, but can also be added at a later stage of the process for the preparation of thermoplastic polymer composition (I).

Then, preferably the solvent may be removed by use of conventional methods, and optionally the obtained thermoplastic polymer composition (I) may be extruded and pelletized by use of conventional methods (cp. e.g. WO 2018/153808 A1, p. 12, l. 1 to 38).

In particular in case thermoplastic polymer TP (component (E)) is present, the thermoplastic molding composition (I) according to the invention can be obtained by mixing components A, B, E and optional components C and/or D by any known method. However, it is preferable when the components are blended by melt mixing, for example joint extrusion, kneading or preferably a twin screw extruder, more preferably a counter-

rotating twin screw extruder. For this process block copolymer A can be used as a pre-mixture with component B and further optional components C and/or D as described hereinbefore and blended as stated hereinbefore by addition of component E. This is usually done at temperatures in the range of from 160°C to 300°C, preferably from 180°C to 250°C, in particular 200 to 220°C.

Capillary rheology tests show that thermoplastic polymer compositions (I) according to the invention have low crosslinking and exhibit a low gel/fish-eye content. Thermoplastic polymer compositions (I) have a final die pressure (die of 16 mm length and 1 mm diameter ($L/D = 16$) of 2.5 MPa or lower when using a capillary rheology at a temperature of 250 °C, a constant shear of 100 s^{-1} and over a time of 63 min.

A further aspect of the invention is the use of thermoplastic polymer composition (I) for the production of films, in particular shrink films.

15 A further aspect of the invention is a shrink film produced from thermoplastic polymer composition (I) according to the invention.

The preparation of shrink films is commonly known. Processing may be carried out using the known processes for thermoplastic polymer - in particular SBC - processing, in particular production may be effected by thermoforming, extrusion, injection molding, calendaring, blow molding, or compression molding, preferably by extrusion, thermoplastic polymer composition (I) to films.

The invention is further illustrated by the claims and the following examples.

Examples

Styrene-butadiene block-copolymer A

In a batch reactor (stainless steel reactor, stirred, 50 m³) 21300 L of cyclohexane at 40 °C was used as initial charge and 165 L styrene (S1) was added at 20 m³/h. When 16 L of S1 had been dosed, 30.00 L of a 1.4 M sec-butyllithium solution (BuLi 1) for initiation and 3.88 L of a 5 wt% potassium tert-amylate solution in cyclohexane as randomizer had been dosed at once. The reaction was allowed to proceed under continuous stirring to complete monomer consumption (identified by no further temperature increase of the reaction mixture).

In a next step, 3139 L styrene (S2) and 538 L butadiene (B1) were added together and the polymerization reaction, under continuous stirring, was allowed to run to complete monomer consumption (identified by no further temperature increase of the reaction mixture). After complete monomer consumption, the polymerization mixture was cooled by means of reflux cooling to a temperature below 70 °C.

In a next step, 65.26 L of a 1.4 M sec-butyllithium solution (BuLi 2) for initiation and 8.73 L of a 5 wt% potassium tert-amylate solution in cyclohexane as randomizer had been dosed at once.

In a next step, 1758 L styrene (S3) was added and the polymerization reaction, under continuous stirring, was allowed to run to complete monomer consumption (identified by no further temperature increase of the reaction mixture). After complete monomer consumption, the polymerization mixture was cooled by means of reflux cooling to a temperature below 56 °C.

In a next step, 677 L styrene (S4) and 2956 L butadiene (B2) were added together and the polymerization reaction, under continuous stirring, was allowed to run to complete monomer consumption (identified by no further temperature increase of the reaction mixture). After complete monomer consumption, the polymerization mixture was cooled by means of reflux cooling to a temperature below 90 °C.

In a next step, 121 L styrene (S5) was added and the polymerization reaction, under continuous stirring, was allowed to run to complete monomer consumption (identified by no further temperature increase of the reaction mixture).

Then, 10 minutes after the last complete monomer consumption, 12.7 L Edeno[®] D82 (epoxydized soybean oil) was added to the block copolymer polymer solution and allowed to react for 10 minutes while stirring.

Then, the reaction mixture was stabilized by acidification with 0.06 phm (= parts (g) per 100 g monomers) demineralized water and a 0.43 phm CO₂ gas stream.

In a next step, samples of this block copolymer solution were taken. Then to each polymer sample stabilizers were added in amounts (based on the polymer content in the solution) as shown in Table 1 and each sample was homogenized by means of stirring to obtain a block copolymer composition as defined in Table 1. Thereafter, the cyclohexane solvent was removed from the block copolymer composition in a co-rotating degassing twin screw extruder.

Irganox[®] 1010, Sumilizer[®] GS, Irgafos[®] 168, Irganox[®] 1141 and Irganox[®] 565 were received from BASF SE, Germany. Hostanox[®] O3 and Hostanox SE10 were received from Clariant International Ltd, Switzerland. CPD-650 was received from Guangdong Xinhua Yue Petrochemical Incorporated Company.

TABLE 1

	Polymer Sample	Irganox® 1010	Sumilizer® GS	Irgafos® 168	Irganox® 1141	Irganox® 565	Hostanox® O3	Hostanox® SE10	CPD-650	Total Sum	Final pressure at 250°C	Final pressure at 270°C
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	MPa	MPa
Inventive example	A	0	1500	1500	0	2000	0	0	0	5000	2.1	9.9
Inventive example	B	0	1500	1500	0	2000	0	0	0	5000	2.1	10.3
Inventive example	C	1000	1500	1500	0	1000	0	0	0	5000	2.3	/
Comparative example	D	2000	1500	1500	0	0	0	0	0	5000	2.6	11.2
Comparative example	E	750	1500	1500	0	0	1250	0	0	5000	2.6	/
Comparative example	F	0	1500	1500	2000	0	0	0	0	5000	3.0	/
Comparative example	G	1000	1500	1500	0	0	0	0	1000	5000	3.1	/
Comparative example	H	750	1500	1500	0	0	0	1250	0	5000	3.4	/
Inventive example	X	1750	1500	1500	0	250	0	0	0	5000		10.3

ppm = parts per million (mg/kg) based on entire thermoplastic polymer composition (I)

In a next step, the stabilized block copolymer samples were subjected to a capillary rheology experiment to evaluate the resistance of the product against crosslinking upon energy input. The material was loaded to the barrel of the capillary rheometer at 250 °C and preheated for 3 minutes (Inventive examples A, B, C and comparative examples D to H). Next, a force was applied at ram (piston) to push the material through a die of 16 mm length and 1 mm diameter ($L/D = 16$) at a constant shear rate of 100 s^{-1} over a time of 63 min. During this experiment, the pressure at the die is measured to maintain this shear rate. The more crosslinking appears in the sample during the experiment, the more difficult it becomes to press the material through the die at a constant shear rate. This is reflected as a pressure increase at the die. Therefore, the pressure at the die is a direct correlation for the degree of crosslinking in the sample. The higher the final pressure, the higher is the degree of crosslinking.

Furthermore, a sample of inventive examples A, B, comparative example D and of inventive example X, respectively, was loaded to the barrel of the capillary rheometer at 270 °C and preheated for 3 minutes and then a force was applied to each sample as hereinbefore described.

The final pressure per sample can be found in Table 1 and Figures 1 and 2.

Figure 1: The Y-axis of the graph shows the pressure in MPa and the X-axis shows the time in minutes. The measured values (at 250°C) obtained for polymer samples A to H are shown by different continuous, dashed and dotted lines.

Figure 2: The Y-axis of the graph shows the pressure in MPa and the X-axis shows the time in minutes. The measured values (at 270°C) obtained for polymer samples A; B, D and X are shown by different continuous, dashed and dotted lines.

Samples A and B have the same composition and give an indication of the consistency of the experiment. Table 1 and Figures 1 and 2 show that the final pressure of the inventive examples according to samples A, B, C and X is significantly lower than the final pressure obtained for comparative examples (samples D to H).

Thus, it has been proven that by use of the stabilizer combination as used in the block copolymer composition according to the invention (samples A, B, C, and X) the crosslinking of the block copolymers can be reduced.

Patent Claims

1. Thermoplastic polymer composition (I) comprising (or consisting of) components (A), (B), and optionally (C), (D) and/or (E):
- 5 (A) at least one block copolymer A comprising (or consisting of):
- A1: 60 to 95 wt.-% - based on block copolymer A - polymerized units of at least one vinyl aromatic monomer, preferably styrene, and
- A2: 5 to 40 wt.-% - based on block copolymer A - polymerized units of at least one conjugated diene, preferably butadiene or isoprene;
- 10 (B) a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):
- B1: 200 to 2500 ppm (0.020 to 0.250 wt.-%) – based on the entire thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS number: 991-84-4),
- 15 B2: 500 to 2500 ppm (0.050 to 0.250 wt.-%) – based on the entire thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate (CAS number: 123968-25-2) or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (CAS number: 61167-58-6) or mixtures thereof, and
- 20 B3: 500 to 2000 ppm (0.050 to 0.200 wt.-%) — based on the entire thermoplastic polymer composition (I) - tris(2,4-di-tert.-butylphenyl)phosphite (CAS number: 31570-04-4);
- (C) 0 to 5000 ppm (0 to 0.500 wt.-%) – based on the entire thermoplastic polymer composition (I) - of one or more stabilizers different from (B1), (B2) and (B3);
- 25 (D) optionally one or more additives and/or processing aids other than (B) and (C);
- (E) optionally at least one, preferably 1, 2 or 3, more preferably one, thermoplastic polymer TP other than block copolymer A.
- 30 2. Thermoplastic polymer composition (I) according to claim 1 wherein stabilizer combination (B) consists of stabilizer components (B1), (B2) and (B3) in the following amounts:
- B1: 200 to 2250 ppm, preferably 250 to 2100 ppm,
- B2: 750 to 1750 ppm, preferably 1000 to 1600 ppm, and
- 35 B3: 750 to 1750 ppm, preferably 1000 to 1600 ppm.

3. Thermoplastic polymer composition (I) according to claim 1 wherein stabilizer combination (B) consists of stabilizer components (B1), (B2) and (B3) in the following amounts:
- 5 B1: 500 to 2500 ppm (0.05 to 0.250 wt.-%),
B2: 500 to 2500 ppm (0.050 to 0.250 wt.-%), and
B3: 500 to 2000 ppm (0.050 to 0.200 wt.-%).
- 10 4. Thermoplastic polymer composition (I) according to claim 3 wherein stabilizer combination (B) consists of stabilizer components (B1), (B2) and (B3) in the following amounts:
- B1: 1000 to 2250 ppm (0.100 to 0.225 wt.-%),
B2: 750 to 1750 ppm (0.075 to 0.175 wt.-%), and
15 B3: 750 to 1750 ppm (0.075 to 0.175 wt.-%).
5. Thermoplastic polymer composition (I) according to claim 3 or 4 wherein stabilizer combination (B) consists of stabilizer components (B1), (B2) and (B3) in the following amounts:
- 20 B1: 1500 to 2100 ppm (0.150 to 0.210 wt.-%), preferably 1900 to 2100 ppm (0.190 to 0.210 wt.-%),
B2: 1000 to 1600 ppm (0.100 to 0.160 wt.-%), preferably 1400 to 1600 ppm (0.140 to 0.160 wt.-%),
B3: 1000 to 1600 ppm (0.100 to 0.160 wt.-%), preferably 1400 to 1600 ppm (0.140 to 0.160 wt.-%).
- 25 6. Thermoplastic polymer composition (I) according to claim 1 or 2 wherein component C is present in an amount of 500 to 1900 ppm, preferably 750 to 1800 ppm, and the amount of component B1 is 200 to 1500 ppm (0.020 to 0.015 wt.-%), preferably 250 to 1100 ppm (0.025 to 0.110 wt.-%).
- 30 7. Thermoplastic polymer composition (I) according to claim 3 wherein component C is present in an amount of 500 to 1500 ppm (0.050 to 0.150 wt.-%), preferably 750 to 1100 ppm (0.075 to 0.110 wt.-%), more preferably 950 to 1050 ppm (0.095 to 0.105 wt.-%), and stabilizer combination (B) consists of stabilizer components (B1), (B2) and (B3) in the following amounts:
- 35

- B1: 500 to 1500 ppm (0.050 to 0.150 wt.-%), preferably 750 to 1100 ppm (0.075 to 0.110 wt.-%), more preferably 950 to 1050 ppm (0.095 to 0.105 wt.-%)
B2: 1000 to 1600 ppm (0.100 to 0.160 wt.-%), preferably 1400 to 1600 ppm (0.140 to 0.160 wt.-%), and
5 B3: 1000 to 1600 ppm (0.100 to 0.160 wt.-%), preferably 1400 to 1600 ppm (0.140 to 0.160 wt.-%).
8. Thermoplastic polymer composition (I) according to any of claims 1 to 7 wherein
10 component B2 is 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate.
9. Thermoplastic polymer composition (I) according to any of claims 1 to 8 wherein
15 component C is pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]-propionate.
10. Thermoplastic polymer composition (I) according to any of claims 1 to 5, or 8
wherein optional component C is not present.
11. Thermoplastic polymer composition (I) according to any of claims 1 to 10 wherein
20 block copolymer A comprises (consists of):
- A1: 60 to 80 wt.-%, preferably 60 to 76 wt.-%, most preferred 65 to 76 wt.-%, -
based on block copolymer A - polymerized units of at least one vinyl aromatic
monomer, in particular styrene, and
A2: 20 to 40 wt.-%, preferably 24 to 40 wt.-%, most preferred 24 to 35 wt.-%, -
25 based on block copolymer A - polymerized units of at least one conjugated diene,
in particular butadiene or isoprene.
12. Thermoplastic polymer composition (I) according to any of claims 1 to 11 wherein
30 block copolymer A comprises at least one hard polymer block S composed of
from 95 to 100 wt.-% of vinylaromatic monomers and of from 0 to 5 wt.-% of
conjugated dienes, optionally one or more hard copolymer blocks (B/S) each
composed of conjugated dienes and vinylaromatic monomers having a B/S-ratio
(= diene/vylaromatic monomer-ratio) < 0.25, preferably 0.1 to 0.2, more pref-
erably 0.1 to 0.15, and a glass transition temperature $T_g > 37^\circ\text{C}$, and one or
35 more soft blocks B composed of 100 wt.-% conjugated diene and/or one or more
soft copolymer blocks (S/B) each composed of vinylaromatic monomers and of

conjugated dienes having a S/B-ratio (= vinylaromatic monomer/diene-ratio) < 0.5, preferably 0.15 to 0.45, more preferably 0.2 to 0.4, and a glass transition temperature $T_g < 37^\circ\text{C}$.

- 5 13. Thermoplastic polymer composition (I) according to claim 12 wherein the hard and soft copolymer blocks (B/S) and (S/B) are random random copolymer blocks.
- 10 14. Thermoplastic polymer composition (I) according to claim 12 or 13 wherein block copolymer A comprises at least one hard block S composed of from 95 to 100 wt.-% of vinylaromatic monomers, preferably styrene, and of from 0 to 5 wt.-% of conjugated dienes, preferably isoprene and/or butadiene, and comprises one or more copolymer blocks (B/S)_A each composed of from 65 to 95% by weight of vinylaromatic monomers, preferably styrene, and of from 35 to 5% by weight of conjugated dienes, preferably isoprene and/or butadiene, and of a glass transition temperature T_{gA} in the range from 40° to 90°C , and comprises one or more copolymer blocks (B/S)_B each composed of from 1 to 60 wt.-%, preferably 1 to 30 wt.-%, of vinylaromatic monomers, preferably styrene, and of from 99 to 40 wt.-%, preferably 99 to 70 wt.-%, of conjugated dienes, preferably isoprene and/or butadiene, and of a glass transition temperature T_{gB} in the range from -90° to -40°C , preferably -80° to -65°C .
- 15 15. Thermoplastic polymer composition (I) according to any of claims 1 to 14 wherein block copolymer A is a star shaped block copolymer.
- 20 16. Thermoplastic polymer composition (I) according to claim 15 wherein the stars of block copolymer A have:

short branches of structure $S_e-(B/S)_B\sim$ and long branches of structure $(B/S)_A-S_i-(B/S)_B\sim$, linked to one another via a coupling agent by way of the soft blocks (B/S)_B. or

short branches of structure $S_e-(B/S)_B\sim$ and long branches of structure $S_e-(B/S)_A-S_i-(B/S)_B\sim$, linked to one another via a coupling agent by way of the soft blocks (B/S)_B, or

short branches of structure $S_e-(B/S)_B-S_r\sim$ and long branches of structure $(B/S)_A-$
- 25 30

$S_i-(B/S)_B-S_r$, linked to one another via a coupling agent by way of the blocks S_i ,
or

5 short branches of structure $S_e-(B/S)_B-S_r$ and long branches of structure $S_e-(B/S)_A-S_i-(B/S)_B-S_r$, linked to one another via a coupling agent by way of the blocks S_i ,

10 where S_e and S_i are blocks S having a number-average molar mass M_n of 5000 to 30000 g/mol, S_r and S_e are blocks S having M_n of less than 4000 g/mol, and $(B/S)_A$ and $(B/S)_B$ are as defined above, where M_n of block $(B/S)_A$ is 30000 to 300000 and M_n of block $(B/S)_B$ is 5000 to 50000 g/mol.

17. 17. Thermoplastic polymer composition (I) according to any of claims 1 to 16 having a final die pressure (die of 16 mm length and 1 mm diameter ($L/D = 16$)) of 2.5 MPa or lower when using a capillary rheology at a temperature of 250 °C at a
15 constant shear of 100 s⁻¹ over a time of 63 min.

18. 18. Thermoplastic molding composition (i) according to any of claims 1 to 17 wherein thermoplastic polymer TP is at least one polymer selected from: styrene polymers, such as vinylaromatic diene block-copolymer (SBC), standard polystyrene
20 (GPPS), styrene-acrylonitrile copolymers (SAN), styrene-methyl methacrylate copolymers (S/MMA), or polymethacrylates, such as PMMA, polyesters, such as polyethylene terephthalate (PET), polyolefins, such as polyethylene or polypropylene, or polyvinyl chloride (PVC), or semicrystalline materials, or polyacrylates, or thermoplastic elastomers (TPE) .

25 19. 19. Thermoplastic polymer composition (I) according to any of claims 1, 2, 6 and 8 to 18 comprising (or consisting of) comprising (or consisting of) components (A), (B), and optionally (C), (D) and/or (E) in the following amounts:

(A) 25 to 99.88 wt.-%, preferably 25 to 99.82 wt.-%;
30 (B) 0.120 to 0.700 wt.-%, preferably 0.170 to 0.600 wt.-%, of a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):

B1: 0.020 to 0.250 wt.-%, preferably 0.020 to 0.225 wt.-%,

B2: 0.050 to 0.250 wt.-%, preferably 0.075 to 0.175 wt.-%, and

B3: 0.050 to 0.200 wt.-%, preferably 0.075 to 0.175 wt.-%;

35 (C) 0 to 0.50 wt.-%, preferably 0 to 0.20 wt.-%;

(D) 0 to 6.00 wt.-%, preferably 0.01 wt.-% to 3.00 wt.-%;

(E) 0 to 74.88 wt.-%, preferably 0 to 74.82 wt.-%,

where components (A), (B), and, if present, components (C), (D) and/or (E) total 100 wt.-%.

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20. Thermoplastic polymer composition (I) according to any of claims 3 to 5, and 7 to 18 comprising (or consisting of):

(A) 25 to 99.30 wt.-%, preferably 25 to 98.89 wt.-%, - based on thermoplastic polymer composition (I) - of at least one block copolymer A;

10 (B) 0.150 to 0.700 wt.-%, preferably 0.250 to 0.600 wt.-%, more preferably 0.300 to 0.550 wt.-%, most preferably 0.350 to 0.500 wt.-%, of a stabilizer combination consisting of stabilizer components (B1), (B2) and (B3):

15 B1: 0.05 to 0.250 wt.-%, preferably 0.100 to 0.225 wt.-%, more preferably 0.150 to 0.210 wt.-% – based on thermoplastic polymer composition (I) – 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS number: 991-84-4),

20 B2: 0.050 to 0.250 wt.-%, preferably 0.075 to 0.175 wt.-%, more preferably 0.100 to 0.160 wt.-% – based on thermoplastic polymer composition (I) – 2-[1-(2-hydroxy-3,5-di-tert-pentylphenyl)ethyl]-4,6-di-tert-pentylphenyl acrylate (CAS number: 123968-25-2) or 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-4-methylphenyl acrylate (CAS number: 61167-58-6) or mixtures thereof, and

25 B3: 0.050 to 0.200 wt.-%, preferably 0.075 to 0.175 wt.-%, more preferably 0.100 to 0.160 wt.-% — based on thermoplastic polymer composition (I) - tris(2,4-di-tert.-butylphenyl)phosphite (CAS number: 31570-04-4);

(C) 0 to 0.500 wt.-% – based on thermoplastic polymer composition (I) - of one or more stabilizers different from (B1), (B2) and (B3);

30 (D) 0 to 6.00 wt.-%, preferably 0.01 wt.-% to 3.00 wt.-%, based on thermoplastic polymer composition (I), one or more additives and/or processing aids other than (B) and (C):

(E) 0 to 74.85 wt.-%, preferably 0.50 to 74.85 wt.-%, based on thermoplastic polymer composition (I), - at least one thermoplastic polymer TP other than block copolymer A;

35 where components (A), (B), and, if present, components (C), (D) and/or (E) total 100 wt.-%.

21. Process for the preparation of a thermoplastic polymer composition (I) according to any of claims 1 to 20 which comprises:
- 5 i) sequential anionic polymerization of a monomer composition, comprising:
A1: 60 to 95 wt.-% of at least one vinyl aromatic monomer, preferably styrene,
and,
A2: 5 to 40 wt.-% of at least one conjugated diene, preferably butadiene, to obtain living anionic polymer chains;
- 10 ii) then, chain termination or coupling of the living anionic polymer chains produced in step i) to obtain - linear or star shaped - block copolymer A;
- iii) then, optionally addition of alcohol, and CO₂ and water; and
- 15 iv) - after step ii) or iii) - addition of stabilizer components (B1), (B2) and (B3), and, if present, addition of stabilizers (C), additives and/or processing aids (D) and/or component (E) to obtain composition (I).
22. A process for the preparation of shrink films wherein a thermoplastic polymer composition (I) according to any of claims 1 to 20 is formed to films by thermoforming, extrusion, injection molding, calendaring, blow molding or compression molding.
- 20
23. A shrink film produced from a thermoplastic polymer composition (I) according to any of claims 1 to 20.
- 25
24. Use of a thermoplastic polymer composition (I) according to any of claims 1 to 20 for the production of films, in particular shrink films.