

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:
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- 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 $(B/S)_A-$
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$S_i-(B/S)_B-S_r$, 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. 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. 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. 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 combi-
 nation 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 thermoplastic polymer composition (I) –
 15 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol (CAS
 number: 991-84-4),
 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-
 20 [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 mix-
 tures thereof, and
 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) -
 25 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);
 (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
 30 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;
 where components (A), (B), and, if present, components (C), (D) and/or (E) total
 35 100 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.
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23. A shrink film produced from a thermoplastic polymer composition (I) according to any of claims 1 to 20.
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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.