

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

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2015/121216 A1

(43) International Publication Date

20 August 2015 (20.08.2015)

WIPO | PCT

(51) International Patent Classification:

C08L 23/00 (2006.01) C08J 3/22 (2006.01)  
C08L 53/02 (2006.01) C08J 5/18 (2006.01)

(21) International Application Number:

PCT/EP2015/052692

(22) International Filing Date:

10 February 2015 (10.02.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

14154638.2 11 February 2014 (11.02.2014) EP

(71) Applicant: STYROLUTION GROUP GMBH [DE/DE];  
Erlenstrasse 2, 60325 Frankfurt (DE).

(72) Inventors: KNOLL, Konrad; Tannhäuserring 71, 68199  
Mannheim (DE). COLOMBO, Andrea; Steubenstr. 8,  
69121 Heidelberg (DE).

(74) Agent: JACOBI, Markus; Isenbruck Bösl Hörschler LLP,  
Patentanwälte, Eastsite One, Seckenheimer Landstraße 4,  
68163 Mannheim (DE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available):

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available):

ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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



WO 2015/121216 A1

(54) Title: BLENDS OF THERMOPLASTIC ELASTOMERS BASED ON STYRENE (S-TPE) AND POLYOLEFINS

(57) Abstract: Polymer blend comprising components A, B and C: A: 1 to 19.5% by weight of an elastomeric block copolymer A based on styrene (S-TPE); B: 0.5 to 8% by weight of a compatibilizer component B; and C: 80 to 98.5 % by weight of at least one semi-crystalline olefin homo- or copolymer C. The invention further relates to a composition comprising thermoplastic elastomers based on styrene (S-TPE) for use as compatibilizer of S-TPE block copolymers and polyolefins, a process for the preparation of the polymer blend, a master batch for the preparation of the polymer blend, and single- and multilayer films comprising said polymer blend and their use for food packaging and as shrink hood.

## Blends of thermoplastic elastomers based on styrene (S-TPE) and polyolefins

## Description

5

The invention relates to a polymer blend comprising thermoplastic elastomers based on styrene (S-TPE) and polyolefins. The invention further relates to a composition comprising thermoplastic elastomers based on styrene (S-TPE) for use as compatibilizer of S-TPE block copolymers and polyolefins, a process for the preparation of the polymer blend, a master batch for the preparation of the polymer blend, and single- and multilayer films comprising said polymer blend and their use.

10

Packaging films are often produced from polyolefins, in particular polyethylene and/or polypropylene films. However, deficits regarding impact properties and other properties are observed.

15

In order to permit production of thinner films, it is desirable to increase the crack propagation resistance, puncture resistance and dart impact properties of the polyolefin film.

20

U.S 5,972,519, WO 96/23823 and WO 98/34783 describe flexible, transparent films comprising styrene-butadiene block copolymers P1 for food packaging. P1 is a S-TPE block copolymer comprising hard blocks (S) and soft blocks (B/S) having random styrene/butadiene distribution. The block copolymers can have a star shaped or linear structure S-(S/B)-S. The films can additionally comprise thermoplastic polymers P2,

25

inter alia homo- and copolymers of olefins. Said polyolefins can additionally contain minor amounts of ethylene-octene copolymers or ethylene-hexene copolymers with a high content of octene or hexene (e.g. commercial products Affinity® or Engage® of the Dow Chemical Company, USA). No example of a film comprising a blend of P1 and an olefin homo- or copolymer P2 is shown.

30

EP-A 1607432 and EP-A 1607431 disclose polymer films comprising a thermoplastic elastomer based on styrene (S-TPE) and a polyolefin. As S-TPE preferably linear styrene-butadiene block copolymers of the general structure S-(S/B)-S are used having, between the two S blocks, one or more (S/B) random blocks having random styrene/butadiene distribution. Said polymer films often have unpredictable and fluctuating film properties due to melt demixing during processing.

Thus, one problem to be solved is to achieve sufficient, reproducible dispersion of an S-TPE in a polyolefin film to gain constantly good results.

35

40

It is one object of the present invention to provide improved polymer blends comprising S-TPE and polyolefins, in particular films, which have a low polymer "fish-eye level", and which even when film thicknesses are low, have adequate puncture resistance, good crack propagation resistance and dart impact properties. It was found that this 5 object is achieved by means of a specific type of compatibilizer comprised in the polymer blend according to the invention.

The invention provides a polymer blend comprising components A, B and C:

10 A: 1 to 19.5% by weight of an elastomeric block copolymer A made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B/S which forms a soft phase and incorporates both units of a vinylaromatic monomer (S) and of a diene (B), where S is the vinylaromatic block and B/S is the soft phase, wherein 15 the block is built up randomly from diene units and vinylaromatic units, and where the glass transition temperature  $T_g$  of the block S is above 25°C, and that of the block B/S is below 25°C, and the phase volume ratio of block S to block B/S is selected so that the proportion of hard phase in the entire block copolymer is from 1 to 40% by volume and the proportion of the diene is less than 20 50% by weight, based on A;

B: 0.5 to 8% by weight of component B comprising components B1 and further optional components B2 and/or B3:

25 B1: at least one elastomeric block copolymer selected from the group consisting of B11, B12 and B13:

B11: block copolymer B11 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block EB which forms a soft phase and incorporates units of ethylene and butylene; and/or

30 B12: block copolymer B12 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block EP which forms a soft phase and incorporates units of ethylene and propylene; and/or

35 B13: block copolymer B13 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B which forms a soft phase and incorporates units of a diene

(B), and the proportion of the hard phase in the entire block copolymer is at most 45% by weight, based on B13;

5 B2: a stiff/tough block copolymer B2 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B which forms a soft phase and incorporates units of a diene (B), and the proportion of the hard phase in the entire block copolymer is more than 50% by weight, based on B2;

10 B3: an ethylene-(C<sub>3</sub>-C<sub>18</sub>)- $\alpha$ -olefin copolymer B3 with a high content of (C<sub>3</sub>-C<sub>18</sub>)- $\alpha$ -olefin, based on B3, and having a crystallinity of less than 50%;

15 C: 80 to 98.5 % by weight of at least one semi-crystalline olefin homo- or copolymer C different from component B3;  
where the entire weight of components A, B and C gives exactly 100% by weight.

20 The polymer blend comprises preferably from 1 to 15%, more preferably 2 to 12% by weight of component A; preferably from 0.8 to 6%, more preferably 1.0 to 4.5 by weight of component B; and preferably 84.2 to 98.2%, more preferably 87 to 97% by weight of component C.

25 According to a further embodiment, the polymer blend comprises preferably from 10 to 17%, more preferably 12 to 16% by weight of component A; preferably from 0.8 to 6.0%, more preferably 1.0 to 6.0 by weight of component B; and preferably 80 to 87%, more preferably 80 to 85% by weight of component C.

30 In particular preferred are polymer blends in which the afore-mentioned amounts of components A and B together are no more than 20%, preferably 2 to 12% by weight and where the entire components A, B and C give exactly 100% by weight.

In the context of the invention the term "diene" refers to a 1,3-diene, in particular 1,3-butadiene and/or isoprene, often butadien.

35

#### Component A

An elastomeric block copolymer A according to the invention is obtained by forming the soft phase within the definition of the above parameters from a random copolymer of a vinylaromatic compound with a diene; random copolymers of vinylaromatic compounds

and dienes are obtained by polymerization in the presence of a polar cosolvent. Further, more detailed information on the preparation of elastomeric block copolymers consisting of or comprising a random copolymer of a vinylaromatic compound and a diene is given in WO 95/35335.

5

According to the present invention the random copolymer block B/S of the block copolymer A also comprise the diene/vinylaromat soft block described in US 7,282,536 (col. 6, l. 36 to col. 8, l. 2 and figures 1 to 3) with controlled diene/vinylaromat composition change along the polymer chain. Preferred is a softblock with a gradient, where the diene content increases from the block center towards the ends of the block, which are attached to a vinylaromat block (col. 8, l. 3 to 15).

A block copolymer A according to the invention can be represented, for example, by one of the formulae 1 to 12:

15 (1) S-B/S-S;

(2) (S-B/S) $n$  ;(3) (S-B/S) $n$  -S;(4) B/S-(S-B/S) $n$  ;(5) X-[(S-B/S) $n$ ] $m+1$  ;20 (6) X-[(B/S-S) $n$ ] $m+1$  ;(7) X-[(S-B/S) $n$  -S] $m+1$  ;(8) X-[(B/S-S) $n$  -B/S] $m+1$  ;(9) Y-[(S-B/S) $n$ ] $m+1$  ;(10) Y-[(B/S-S) $n$ ] $m+1$  ;25 (11) Y-[(S-B/S) $n$  -S] $m+1$  ;(12) Y-[(B/S-S) $n$  -B/S] $m+1$  ;

where S is the vinylaromatic block and B/S is the soft phase, ie. the block built up randomly from diene units and vinylaromatic units, X is the radical of an n-functional initiator, Y is the radical of an m-functional coupling agent and m and n are natural numbers from 1 to 10.

A preferred block copolymer is one of the general formulae S-(B/S)-S, X-[-(B/S)-S] $_2$  and Y-[-(B/S)-S] $_2$  (for the meanings of abbreviations, see above) and a particularly preferred

35 block copolymer is a linear block copolymer of the structure S-(B/S)-S.

The vinylaromatic monomer is preferably chosen from styrene,  $\alpha$ -methylstyrene, vinyltoluene and 1,1-diphenylethylene, and the diene from butadiene and isoprene.

A particularly preferred combination of monomers is butadiene and styrene. All weights and volumes stated below are based on this combination; when technical equivalents of styrene and butadiene are used, the data will have to be correspondingly converted. The B/S block is preferably composed of about 75-30% by weight of styrene and 25-5 70% by weight of butadiene. A flexible block particularly preferably has a butadiene content of from 35 to 70% and a styrene content of from 65 to 30%.

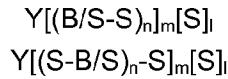
In the case of the monomer combination styrene/butadiene, the amount of the diene in the total block copolymer is preferably 15-65% by weight and that of the vinylaromatic 10 component is correspondingly 85-35% by weight. Butadiene/styrene block copolymers having a monomer composition comprising 25-60% by weight of diene and 75-40% by weight of vinylaromatic compound are particularly preferred.

Particular preference is given to linear styrene-butadiene block copolymers of the general structure S-(S/B)-S having, situated between the two S blocks, one or more (S/B)-random blocks having random styrene/butadiene distribution. These block copolymers are obtainable via anionic polymerization in a non-polar solvent with addition of a polar cosolvent or of a potassium salt, as described by way of example in WO 95/35335 or 15 WO 97/40079.

20 Vinyl content is the relative proportion of 1,2-linkages of the diene units, based on the entirety of 1,2-, 1,4-cis and 1,4-trans linkages. The 1,2-vinyl content in the styrene-butadiene copolymer block (S/B) is preferably below 20%, in particular in the range from 9 to 15%, particularly preferably in the range from 9 to 12%. Suitable block copolymers A having such a 1,2-vinyl content in the styrene-butadiene copolymer block 25 (S/B) are described in detail in WO 97/40079.

Very particular preferred block copolymers A according to the present invention are linear styrene-butadiene block copolymers of the general structure S-(S/B)-S having, 30 situated between the two S blocks, one or more (S/B)-random blocks having random styrene/butadiene distribution, and a 1,2-vinyl content in the styrene-butadiene copolymer block (S/B) of below 20%. The afore-mentioned linear styrene-butadiene block copolymers are commercially available as Styroflex® 2G 66 from Styrolution, Germany.

35 Further preferred block copolymers A have a star-shaped molecular architecture, where the star-shaped molecular architecture has at least two different arms of the star, having the structure one of the following general formulae:



5 where S B/S n and m have the meaning given above Y is the moiety of an (m + l)-functional coupling agent, and l is a natural number from 1 to 10. Said star shaped block copolymers A are described in detail in WO 2012/055919.

Component B

10 Component B comprises component B1 and further optional components B2 and/or B3. Thus, component B can comprise component B1 alone or a combination of B1 with B2 and/or B3 such as: B1 and B2; B1 and B3; and B1, B2 and B3.

Component B1 alone is in particular preferred. Furthermore, preferred are the aforementioned combinations of component B1.

15 The amount of component B1, based on the entire component B, is generally 1 to 100% and preferably 10 to 100%. Furthermore in the interest of cost reduction a reduced amount of component B1, based on the entire component B, of preferably from 15 to 50%, more preferably 25 to 40% by weight is also preferred and effective.

20 The amount of component B2, based on the entire component B, is generally 0 to 99%, preferably 0 to 90, more preferably 20 to 70%, most preferably 30 to 60% by weight. If component B2 is present its minimum amount comprised is usually 0.1% by weight.

25 The amount of component B3, based on the entire component B, is generally 0 to 99%, preferably 0 to 90%, more preferably 10 to 50%, most preferably 15 to 45% by weight. If component B3 is present, its minimum amount comprised is usually 0.1% by weight.

The amounts of components B1, B2 and B3 together give exactly 100% by weight, based on component B.

30

Component B1

According to the invention component B1 can comprise component B11, B12 or B13, each of which alone or in combination with each other. Suitable combinations are: B11 and B12; B11 and B13; B12 and B13; B11, B12 and B13.

The amounts of components B11, B12 and B13 together give exactly 100% by weight, based on component B1.

Component B11

Elastomeric SEBS (Styrene-Ethylene/Butylene-Styrene) block copolymer B11 having at least one elastomeric block EB which forms a soft phase and incorporates units of ethylene and butylene is obtainable by hydrogenation of a SBS (Styrene-Butadiene-Styrene) block copolymer comprising a butadiene soft block and styrene hard blocks. The ethylene-butylene soft phase originates from the center butadiene block with approximately 40-50% by weight 1,2-vinyl content.

The amount of the vinylaromatic component is preferably 20-40% by weight in the total block copolymer and that of ethylene and butylene is correspondingly 60 to 80 % by weight.

Suitable SEBS block copolymers B11 are commercially available as Kraton® G from Kraton Performance Polymers Inc., USA, and as high-performance rubber Septon® from Kuraray, USA.

The amount of component B11, based on the entire component B1, is 0 to 100%, preferably 25 to 100%, more preferably 40 to 100% by weight. Furthermore, the amount of component B11, based on the entire component B1, is 0 to 100%, preferably 25 to 75%, in particular 40 to 60% by weight.

If component B11 is present its minimum amount comprised is usually 0.1% by weight.

Component B12

Elastomeric block copolymer B12 having at least one elastomeric block EP which forms a soft phase and incorporates units of ethylene and propylene is an SEPS (Styrene Ethylene Propylene Styrene) or SEEPS block copolymer which is obtainable by hydrogenation of a (styrene-b-isoprene-b-styrene) block copolymer comprising an isoprene soft block and styrene hard blocks or of a block copolymer of the type poly(styrene-b-isoprene/butadiene-b-styrene) which soft phase is made from an isoprene/butadiene-copolymer.

Suitable SEPS and SEEPS blockcopolymers B12 are commercially available as Septon® from Kuraray.

The amount of component B12, based on the entire component B1, 0 to 100%, preferably 25 to 100%, more preferably 40 to 100% by weight. Furthermore the amount of component B12, based on the entire component B1, is 0 to 100%, preferably 25 to 75%, in particular 40 to 60% by weight.

If component B12 is present its minimum amount comprised is usually 0.1% by weight.

Component B13

Elastomeric block copolymers B13 are made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B which forms a soft phase and incorporates units of a diene (B), and the proportion of the hard phase in the entire block copolymer is at most 45% by weight, based on B13.

Preferred as component B13 are SBS (Styrene Butadiene Styrene) block copolymers wherein the diene is butadiene and the vinylaromatic monomer is styrene.

10

Suitable SBS block copolymers B13 are commercially available as Kraton<sup>®</sup> D from Kraton Performance Polymers Inc. and as Asaprene<sup>®</sup> from Asahi.

Also preferred as component B13 are SIS block copolymers (Styrene Isoprene Styrene) commercially available as Kraton<sup>®</sup> D from Kraton Performance Polymers Inc.

15

The amount of component B13, based on the entire component B1, is 0 to 100%, preferably 0 to 50%, more preferably 0 to 20% by weight. If component B13 is present its minimum amount comprised is usually 0.1% by weight.

20

Component B2

Stiff/tough block copolymers B2 are made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B which forms a soft phase and incorporates units of a diene (B), and the proportion of the hard phase in the entire block copolymer is more than 50% by weight, based on B2.

Preferred as component B2 are SBS (Styrene Butadiene Styrene) block copolymers wherein the diene is butadiene and the vinylaromatic monomer is styrene.

Suitable SBS block copolymers B2 are commercially available as Styroclear<sup>®</sup> GH 62, Styrolux<sup>®</sup> 3G33 and Styrolux<sup>®</sup> 693 D from Styrolution; K-Resin<sup>®</sup> from Chevron Phillips Chemical; Asaflex<sup>®</sup> from Asahi Kasei, Clearen<sup>®</sup> from Denka (DENKI KAGAKU KOUGYO KABUSHIKI KAISYA).

Component B3

Copolymers suitable as component B3 have a crystallinity of less than 50%, preferably of less than 45%, and have a high content, preferably 10 to 30% by weight, more preferably 20 to 25%, most preferred 25% by weight, of the (C<sub>3</sub>-C<sub>18</sub>)- $\alpha$ -olefin comonomer.

Component B3 is preferably at least one ethylene-(C<sub>3</sub>-C<sub>12</sub>)- $\alpha$ -olefin copolymer, more preferably an ethylene-(C<sub>3</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer, such as copolymers of ethylene with comonomers such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene and 1-dodecene.

5

In particular preferred are ethylene-hexene copolymers and most preferred ethylene-octene copolymers, which are commercially available as Affinity<sup>®</sup> or Engage<sup>®</sup> from DOW Chemical Co. Most preferred is Engage<sup>®</sup>.

10 Component C

Examples of suitable olefin homo- or copolymers C are semicrystalline polyolefins, such as homo- or copolymers of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 3-methyl-1-butene, 4-methyl-1-butene, 4-methyl-1-pentene and 1-octene. Homo- or copolymers C are preferably made from ethylene, propylene, 1-butene, 4-methyl-1-pentene.

15 The olefin homo- or copolymers C can be used alone or as their mixtures.

Olefin homo- or copolymers C are more preferably a high-density polyethylene (HDPE), a low-density polyethylene (LDPE), a linear low-density polyethylene (LLDPE)

20 or a propylene homo- or copolymer (PP), preferably with an ethylene comonomer.

In particular preferable are LDPE, LLDPE or PP.

According to a first embodiment of the invention polymer blends comprising components A, B1 and C are in particular preferred.

25

According to a second embodiment of the invention polymer blends comprising components A, B1, B2 and C are preferred.

30 According to a third embodiment of the invention polymer blends comprising components A, B1, B3 and C are preferred.

According to a fourth embodiment of the invention polymer blends comprising components A, B1, B2, B3 and C are preferred.

35 In said embodiments the components are used in the afore-mentioned amounts.

More preferable are inventive polymer blends of said afore-mentioned embodiments wherein component B1 is B11 and/or B12, in particular B11.

Furthermore preferable are inventive polymer blends of said afore-mentioned embodiments wherein A is a linear styrene-butadiene block copolymer of the general structure S-(S/B)-S.

Particular preferred are inventive polymer blends comprising components A, B11, B2,  
5 B3 and C.

Furthermore particular preferred are inventive polymer blends comprising components A, B12, B2, B3 and C.

Furthermore particular preferred are inventive polymer blends comprising components A, B11, B12, B2, B3 and C.

10

Most preferred are inventive polymer blends comprising components A, B11 and C; A,  
B12 and C; and A, B11, B12 and C.

In particular preferred are blends of the following composition:

15 1 to 10% by weight of component A,  
0.8 to 2.5% by weight of component B11 and/or B12, in particular B11, and  
87.5 to 98.2% by weight of component C,  
where A, B11, B12 and C give exactly 100% by weight.

20 Furthermore preferred are blends of the following composition:

10 to 17% by weight of component A,  
1.0 to 6.0% by weight of component B11 and/or B12, in particular B11, and  
80 to 87% by weight of component C,  
where A, B11, B12 and C give exactly 100% by weight.

25

Furthermore preferred are blends of the following composition:

1 to 10% by weight of component A,  
0.1 to 0.8% by weight of component B11 and/or B12, in particular B11,  
30 0.1 to 0.8% by weight of component B2,  
0.1 to 0.8% by weight of component B3, and  
87.6 to 98.7% by weight of component C,  
where A, B11, B12, B2, B3 and C give exactly 100% by weight.

35 Furthermore more preferred are blends of the following composition:

1 to 10% by weight of component A,  
0.2 to 0.8% by weight of component B11 and/or B12, in particular B11,  
0.2 to 1.0% by weight of component B2,  
0.1 to 0.8% by weight of component B3, and

87.4 to 98.5% by weight of component C,  
where A, B11, B12, B2, B3 and C give exactly 100% by weight.

Furthermore preferred are blends of the following composition:

1 to 10% by weight of component A,

5 0.8 to 2.5% by weight of component B11 and/or B12, in particular B11,  
0.8 to 2.5% by weight of component B2,  
85 to 94% by weight of component C,  
where A, B11, B12, B2 and C give exactly 100% by weight.

10 Furthermore preferred are blends of the following composition:

10 to 17% by weight of component A,

0.8 to 3.0% by weight of component B11 and/or B12, in particular B11,

0.8 to 3.0% by weight of component B2,

80 to 87% by weight of component C,

15 where A, B11, B12, B2 and C give exactly 100% by weight.

Furthermore preferred are blends of the following composition:

1 to 10% by weight of component A,

20 0.8 to 2.5% by weight of component B11 and/or B12, in particular B11,  
0.8 to 2.5% by weight of component B3,  
85 to 94% by weight of component C,  
where A, B11, B12, B3 and C give exactly 100% by weight.

25 Furthermore preferred are blends of the following composition:

10 to 17% by weight of component A,

0.8 to 3.0% by weight of component B11 and/or B12, in particular B11,

0.8 to 3.0% by weight of component B3,

80 to 87% by weight of component C,

30 where A, B11, B12, B2 and C give exactly 100% by weight.

Furthermore preferable are inventive polymer blends of said afore-mentioned embodiments and compositions wherein A is a linear linear styrene-butadiene block copolymer of the general structure S-(S/B)-S; B1 is B11 and/or B12, in particular B11; C is polyethylene, in particular LDPE or LLDPE; or polypropylene, or their mixtures; and, if present, B3 is an ethylene-octene copolymer, and B2, if present, is a SBS block copolymer.

The inventive polymer blend may also comprise the usual auxiliaries and additives as component D, such as lubricants, antiblocking agents, antifogging agents, release agents, stabilizers, antioxidants, UV-absorbers, antistatic agents, flame retardants, colorants, etc.

5 The additional use of UV-absorbers is preferred, in particular by use of the polymer blend as a weather resistant film.

10 The auxiliaries and additives D can be present in the inventive polymer blend in a proportion of from 0 to 50% by weight, preferably from 0 to 45% by weight, more preferably 0 to 30% by weight, and particularly preferably from 0 to 10% by weight, based on the entire polymer blend. If component D is present its minimum amount comprised is usually 0.1% by weight.

15 A further subject of the invention is at least one compatibilizer comprising or consisting of the afore-mentioned component B comprising or consisting of components B1 and further optional components B2 and/or B3, which is in particular suitable as compatibilizer for blends comprising S-TPE of the type of component A and polyolefins C. Thus, a further subject of the invention is the use of said compatibilizer as compatibilizer for blends comprising S-TPE of the type of component A and polyolefins C.

20 Suitable inventive compatibilizers B are selected from the group comprising the following components or combination of components: B1; B1 and B2; B1, B2 and B3; and B1 and B3.

25 Among said afore-mentioned compatibilizers B such wherein B1 is B11 and/or B12, in particular B11, are preferred.

More preferred are inventive compatibilizers B comprising or consisting of: B11 and B2; B11 and B3; and/or B11, B2 and B3.

In said compatibilizers B2, if present, is preferably a SBS block copolymer, and B3, if present, is an ethylene-octene copolymer.

30 In particular preferred are inventive compatibilizers B comprising or consisting of: B11, B2 and B3.

35 The composition of the compatibilizer B in respect to the amounts of components B1, and, if present, components B2 and/or B3, is as herein before described for component B.

Preferably compatibilizer B comprises:

15 to 50%, more preferably 25 to 40% by weight of component B1  
20 to 70%, most preferably 30 to 60% by weight of component B2 and  
10 to 50%, most preferably 15 to 45% by weight of component B3,  
where the entire components B1, B2 and B3 together give exactly 100% by weight.

5

More preferably compatibilizer B comprises:  
25 to 40% by weight of component B1  
30 to 60% by weight of component B2 and  
15 to 45% by weight of component B3,

10 where the entire components B1, B2 and B3 together give exactly 100% by weight.

The polymer blends according to the invention can generally be obtained by any usual method, eg. by joint extrusion and calendering.

15 The calendering is expediently carried out firstly in kneaders or extruders (softening) and, if desired, on mixing rolls, followed by the actual calendering process with, if desired, addition of suitable stabilizers. Blowmolding and injection molding are carried out on the usual machinery.

20 The extrusion can be carried out on single- or twin-screw extruders. However, sometimes mixing and homogeneity problems of the components used for the inventive polymer blend occur under the usual extrusion temperature conditions (200 to 210°C) due to the high viscosity of component B1 particularly in case of single-screw extruders with limited mixing capability. Preferred are twin-screw extruders particular equipped with screws containing kneading elements beside transport elements. Therefore, in case of  
25 direct feeding of the components of the inventive polymer blend advantageously a twin screw extruder is used for the extrusion and the temperature of the middle zones of the twin screw extruder (e.g. FTS 16) is preferably set to 230 to 260°C, in particular to 250°C.

30 It has been a further object of the invention to provide an improved process for the preparation of the polymer blend according to the invention.

According to the inventive process for the preparation of the inventive polymer blend, in a first step pre-compounds of components A and B1 and, if present, components B2 and B3 are prepared and pelletized in an extruder. In a second step said pre-  
35 compound is pre-mixed with polyolefin pellets of component C and then this mixture is extruded, preferably by cast film extrusion, to give the inventive polymer blend, preferably as cast film. Said inventive process can be carried out on single- or twin-screw extruders, under usual extrusion temperature conditions.

For the inventive process preferably a twin screw extruder is used. Advantageously a FTS 16 twin screw extruder having an L/D ratio of 40 with eight 5D shots and ten zones can be used.

5 For pre-compounding the feeding zone of the single- or twin-screw extruder is preferably set to a temperature in the range of 130 to 150°C, the mixing/kneading zones to 180 to 200°C and the final zones to 200 to 220°C.

For workup the extruder can be equipped with a hole-plate, water-bath and pelletizer for making pellets, preferably micro-pellets.

10

For making cast films the same extruder can be used by mounting a slit die of a suitable slit width (e.g. 0.2 to 0.5 mm) and the temperatures are preferably set as mentioned for the extrusion before, the chill roll is preferably kept at 30 to 50°C.

15 A further subject of the invention is a masterbatch for the preparation of the inventive polymer blend. The masterbatch is preferably prepared by twin screw extrusion as herein before mentioned.

20 According to a first embodiment the masterbatch comprises a pre-compound of components A and B1 and, if present, components B2 and B3, which can be used as such for mixing with component C, or alternatively to said masterbatch and component C further amounts of component A can be added, provided that the total amount of component A, comprised in the inventive blend, is as defined herein before.

An inventive master batch comprising components A, B1, B2 and B3 is preferred.

25

Preferably said inventive master batch comprises 50 to 60% by weight of component A, 10 to 20% by weight of component B1, 5 to 15% by weight of component B2 and 15 to 30% by weight of component B3, where the entire components A, B1, B2 and B3 give exactly 100% by weight.

30 More preferred is a master batch of said composition, wherein A is a linear S-(S/B)-S block copolymer; B1 is B11 and or B12, in particular B11, B2 is an SBS-block copolymer and B3 is an ethylene-octene copolymer.

35 According to a second embodiment the masterbatch comprises a pre-compound of components C and B1 and, if present, components B2 and B3, which can be used as such for mixing with component A, or, alternatively, to said masterbatch and component A further amounts of component C can be added, provided that the total amount of component C, comprised in the inventive blend, is as defined herein before.

Said inventive master batch comprises preferably 30 to 70%, more preferably 40 to 60% by weight of component C, and correspondingly preferably 70 to 30%, more preferably 60 to 40% by weight of component B.

In said masterbatch the entire components C and B give exactly 100% by weight.

5

The polymer blends according to the invention are useful in producing films of all types, such as cast-film, chill-roll, coextruded, blown- and extruded films or calendered films.

Thin films can be produced by cast-film, blown-film, chill-roll or other usual processes.

10 Thin films in the range from 5 to 200 µm can be obtained which are in some cases very tough and have high resilience.

15 Blends according to the invention can be used to make single layer films e.g. by blow molding or sheet extrusion using a slit die. By controlling the speed of the chill roll the film can be further stretched and thinned. E.g. starting with a 200 µm film after the slit die one can easily obtain films with preferred 10 to 100 µm, more preferred 20 to 50 µm by adjusting the chill roll speed.

Blends according to the invention are also preferred part of a bi- or multilayer film produced as described for single-layer films. In a bilayer film with the layers L and M, layer L comprises or consists of a blend according to the invention with a total component A and B content of preferred 5 to 50%, layer M can comprise or consist predominantly or essentially of component C. The relative thickness of the layers can vary preferentially between 10 and 90%. Layer M can further comprise or consist predominantly or essentially of component A. In a tri-layer film with the layers L, M and N one or two of the layers can be a blend according to the invention, the other or others respectively may comprise or consist predominantly or essentially of component C and/or predominantly or essentially of component A. One or two layers can also be a blend of components C and B3.

30 In a preferred embodiment layer L comprises or consists predominantly or essentially of component C, layer M comprises or consists of component B3 or a blend of the components C and B3, and layer N comprises or consists of a blend according to the invention. The relative layer thickness varies preferentially between 5 and 90%. One particularly preferred embodiment is a relative thickness of layer L of 40 to 75%, of layer M of 10 to 20% and of layer N of 10 to 40%.

35 In another preferred embodiment layers L and N comprise or consist predominantly or essentially of component C and layer M comprises or consists of a blend according to the

invention. The relative layer thickness varies preferentially between 5 and 90%. One particularly preferred embodiment is a relative thickness of layers L and N of 5 to 25% and of layer M of 50 to 90%. In a particularly preferred embodiment layers L and N contain UV-absorbers as additional additives.

- 5 Preferred are further films with four, five and more layers with one or more layers comprising or consisting of blends according to the invention. In a layer sequence L, M, N, O and P as preferential embodiment layers L and P comprise or consist of a blend according to the invention, layers M and O of component B3 or a blend of components C and B3 and layer N predominantly or essentially of component A.
- 10 In another preferred embodiment layer N comprises or consists of a polyamide, particularly preferred of polyamide 6, layers M and O comprise or consist predominantly or essentially of component A and layers L and N of blends according to the invention.
- 15 The inventive polymer blends and films produced therefrom have an improved crack-propagation resistance, puncture resistance and dart impact properties.

A further subject of the invention is the use of films comprising the inventive polymer blend for food packaging or as barrier film for gases such as oxygen and water vapour or, in particular as weather resistant film, as shrink hood for packaging pallets.

- 20 Single layer-films comprising the inventive polymer are preferably used as thin food packaging films; multi-layer films are used as barrier films and as weather resistant strong elastic films for shrink hood applications e.g. for packaging pallets.
- 25 The following examples and claims further illustrate the present invention.

#### Examples

##### Starting Materials:

- 30 Component A: Styroflex<sup>®</sup> 2G 66 from Styrolution (Frankfurt, Germany), a linear styrene-butadiene triblock copolymer of the structure S-(S/B)-S, the amount of the monomers in the total block copolymer is 35% by weight of butadiene and 65% by weight of styrene; the weight ratio of the blocks is 16/68/16 ; MFI: 14 (200°C/5 kg) g/10 min
- 35

Component B11: Kraton® G 1650 from Kraton Performance Polymers Inc., a linear symmetrical SEBS block copolymer, the amount of ethylene/butylene in the total block copolymer is 70.8% by weight and that of styrene is 29.2% by weight, solution viscosity (20% in toluene, 25°C (BMS 0380)): 1,0 bis 1,9 Pas

5

Component B13-1: Kraton® D 1101 from Kraton Performance Polymers Inc., a linear symmetrical SBS block copolymer, the amount of butadiene in the total block copolymer is 68 bis 70% by weight and that of styrene is 30 bis 32% by weight, MFI: < 1 (200°C/5 kg) g/10 min, solution viscosity (20% in toluene, 25°C (BMS 0380)): 4

10

Component B13-2: Kraton® D 1102 from Kraton Performance Polymers Inc., a linear symmetrical SBS block copolymer, the amount of butadiene in the total block copolymer is 70 bis 73% by weight and that of styrene is 27 bis 30% by weight, MFI: 12 (200°C/5 kg) g/10 min

15

Component B2: Styrclear® GH 62 from Styrolution, a star shaped SBS (Styrene Butadiene Styrene) block copolymer, the amount of butadiene in the total block copolymer is 26% by weight and that of styrene is 74% by weight, MFI: 15 (200°C/5 kg) g/10 min

20 Component B3: Engage® 8480 from DOW Chemical Co., an ethylene-octene copolymer; density: 0.902 g/cm<sup>3</sup>; shore A hardness: 89; MFI 1.0 (190°C/2.16 kg) g/10 min)

Component C-1: Lupolen® 2420, a low density polyethylene (LDPE); density: 0.923 g/cm<sup>3</sup>, MFI 0.25 (190°C/2.16 kg) g/10 min) of Lyondell Basell Industries

25

Component C-2: Moplen® HP500N, a polypropylene (PP) homopolymer; density: 0.90 g/cm<sup>3</sup>, MFI: 12 (230°C/2.16 kg) g/10 min of Lyondell Basell Industries

### Test Methods

30 The test specimens for the mechanical and optical tests were cut out longitudinally and transversely from the films.

Crack propagation resistance was determined according to DIN ISO 34-1:04-07 method B, process (b) with notch.

The puncture resistance test was carried out in accordance with the proposed standard

35 FNK 403.3.

Tensile strength at break ( $\sigma$ -B) and tensile strain at break ( $\epsilon$ -B) were determined in the ISO 527-2 tensile test.

The dart drop test was determined in accordance with DIN 53373.

Haze: ASTM D 1003-13

Transmission: ASTM D 1003-13

Yellowness Index (YI): determined according to ASTM E 313

Shore A hardness: DIN ISO 7619-1

MFI: ISO 1133

5 Density: ISO 1183-1

Preparation of Polymer Blends

Pre-compounds of component A with compatibilizers B have been made on a 16 mm twin-screw extruder (FTS16) and micro-pelletized. The composition of the pre-

10 compound is shown in table 1. In a second step the obtained pre-compound has been pre-mixed with polyolefin micro-pellets in a weight ratio 20/80 and 0.5 mm cast films have been made on the same extruder using a slit die.

The FTS 16 twin screw extruder had an L/D ratio of 40 with eight 5D shots and ten

15 zones. The screws (combination 26) were equipped with two kneading elements at zone 3 and 6. For pre-compounding the feeding zone 1 was kept at 140°C, the mixing/kneading zones 2 to 6 190°C and the final zones 210°C. For workup the extruder was equipped with a hole-plate, water-bath and pelletizer for making micro-pellets. For making cast films a 0.5 mm slit die was mounted and the temperatures set to

20 150°/200°/210°C, the chill roll was kept at 40°C.

Crack propagation resistance parallel to extrusion (CPR //) and perpendicular to extrusion (CPR ⊥) and puncture resistance (PRW = puncture resistance work) of the inventive polymer blend has been tested as well as optics (transparency, haze, yellow-

25 ness index YI).

Table 1 shows the composition of the pre-compounds in parts by weight.

The mechanical data are listed in table 1-a PP (polypropylene); the optical data are shown in table 1-b PP; in these tables the composition of the pre-compounds is shown in parts.

Table 1 Precompounds

Precompound	B1			B2	A
	B13-1	B13-2	B11		
A1	100	-	-	-	400
A2	50	-	-	50	400
A3	-	100	-	-	400
A4	-	50	-	50	400
A5	-	-	100	-	400
A6	-	-	50	50	400
A8	33	-	33	33	400
A9	-	33	33	33	400
A10	-	50	50	-	400
A11	50	-	50	-	400
	components in parts				

Table 1-a PP - Mechanical properties

Crack propagation resistance DIN ISO 34-1:04-07 Method B, Process (b) with cut				Puncture Resistance			
Example	CPR MD N/mm	Fmax Lm N	CPR TD N/mm	Fmax Lm N	Fmax N	W Break Nmm	Pre compound An
12	248,7	113,93	60,8	28,1	51,49	254,7	A1
13	275,2	125,15	58,1	26,72	56,06	269,1	A2
14	259,1	118	57,1	25,96	53,34	230,1	A3
15	274	126,14	56,4	26,1	55,08	230,8	A4
16	270,6	131,99	75,9	37,83	61,14	319,6	A5
17	210,8	101,89	73,4	37,04	63,16	330,1	A6
19	246,4	118,55	67,9	33,7	60,51	318,5	A8
20	256,3	125,31	69,6	35,23	60,44	297	A9
21	252,3	123,28	72,3	36,02	61,23	321,3	A10
22	275,2	136,24	71,7	35,6	61,51	323,8	A11
C1	89,4	44,67	30,7	15,61	35,25	142,2	pure PP

The examples are blends of 20% precompound A and 80% polypropylene C

Table 1-b PP – optical Properties

Example	Haze	Transmission Y %	Yellowness YI	
	H %			Precompound An
12	98,91	55,10	16,23	A1
13	98,85	52,53	16,88	A2
14	98,50	51,25	17,15	A3
15	98,64	53,60	17,01	A4
16	98,98	53,97	16,28	A5
17	98,83	51,64	16,55	A6
19	98,95	52,00	17,20	A8
20	98,83	52,96	16,99	A9
21	98,74	53,70	16,94	A10
22	98,96	52,41	17,26	A11

The examples are blends of 20% precompound A and 80% polypropylene C.

5 The mechanical data show that the inventive polymer blends are better than reference. The strongest effect both in PE and PP has an inventive blend comprising precompound A5 and A6 as shown by examples 16 and 17.

10 Further pre-compounds and inventive polymer blends comprising additionally component B3 have been prepared. The experiments have been performed under the same conditions as described before.

Tables 2-PE (polyethylene) and 2-PP (polypropylene) show the composition of the pre-compounds in parts. The weight ratio polyolefin/pre-compound was 80/20.

15 The mechanical data are listed in tables 2-a PP and 2-a PE; the optical data are shown in tables 2-b PP and 2-b PE.

Table 2-PE Precompounds PE

	B1			B2	A	B3
	B13-1	B13-2	B11			
A12	-	-	-	-	400	-
A13	85,71	-	-	-	400	-
A14	71,43	71,43	-	-	400	-
A15	71,43	-	71,43	-	400	-
A16	-	71,43	71,43	-	400	-
A17	71,43	-	-	71,43	400	-
A18	-	71,43	-	71,43	400	-
A19	-	-	71,43	71,43	400	-
A20	71,43	-	-	-	400	71,43
A21	-	71,43	-	-	400	71,43
A22	-	-	71,43	-	400	71,43
A23	-	-	-	71,43	400	71,43
A24	-	-	-	50	400	100

components in parts

Table 2-a PE - Mechanical properties

Example	Crack propagation resistance DIN ISO 34-1:04-07				Puncture Resistance		
	CPR MD N/mm	Fmax N	CPR TD N/mm	Fmax N	Fmax N	W Break Nmm	Precompound
C2	76,8	37,1	18,5	9,2	46,6	162,9	A12
23	71	35,3	22,2	10,9	45,5	174,9	A13
24	71,3	34,9	20,2	10	42,9	141,1	A14
25	73,7	35,9	25,8	12,6	47,7	204,8	A15
26	72,5	34,5	22,2	10,7	47,3	172,3	A16
27	73,5	36	22,2	11	45,7	167,8	A17
28	75,3	36,8	15,6	7,7	46,6	170	A18
29	77,4	38	24,8	12,4	48,7	204,1	A19
30	80,3	39,6	21,4	10,5	46,4	170,2	A20
31	85,2	41,7	15,8	7,7	35,5	103,1	A21
32	84,6	41,9	28	13,8	48,4	179,6	A22
C3	80,3	39,8	18,8	9,3	40,8	115,9	A23
C4	89,0	44,4	22,9	11,4	42,7	126,3	A24

The examples are blends of 20% precompound A and 80% polyethylene C

Table 2-b PE - Optical properties

Example	Haze H %	Transmission Y %	Yellowness YI	Precompound
C2	94,65	59,13	16,96	A12
23	93,21	59,56	17,34	A13
24	89,89	61,20	17,27	A14
25	80,28	61,14	18,11	A15
26	76,03	62,36	16,86	A16
27	93,21	59,32	18,53	A17
28	90,31	59,43	17,32	A18
29	84,37	61,36	17,42	A19
30	86,96	61,46	17,37	A20
31	83,63	61,76	16,22	A21
32	68,60	64,43	17,36	A22
C3	90,41	60,76	16,99	A23
C4	87,77	61,55	15,95	A24

The examples are blends of 20% precompound A and 80% polyethylene C

5

Table 2-PP Precompounds PP

	B1			B2	A	B3
	B13-1	B13-2	B11			
A25	-	-	-	-	400	-
A26	85,71	57,14	-	-	400	-
A27	-	71,43	71,42	-	400	-
A28	71,43	-	-	71,43	400	-
A29	-	71,43	-	71,43	400	-
A30	71,43	-	-	-	400	71,43
A31	-	-	71,43	-	400	71,43
A32	-	-	-	71,43	400	71,43
A33	-	57,14	-	-	400	85,71
A34	-	-	-	-	400	100

components in parts

Table 2-a PP - Mechanical properties

Crack propagation resistance DIN ISO 34-1:04-07 Method B, Process (b) with cut				Puncture Resistance			
Example	CPR MD N/mm	Fmax Lm N	CPR TD N/mm	Fmax Lm N	Fmax N	W Break Nm	Precom- pound
C5	187,5	91,3	58,3	28,9	56,1	234,1	A25
33	260,0	125,2	61,3	30,0	61,0	301,6	A26
34	234,9	111,5	67,5	33,0	63,9	334,4	A27
35	267,3	129,3	58,3	28,3	62,0	321,0	A28
36	262,1	126,5	58,6	28,7	62,8	311,7	A29
37	269,1	132,0	69,2	33,5	61,4	319,8	A30
38	249,6	122,4	75,7	37,6	64,5	335,7	A31
C6	263,2	124,7	62,3	30,3	63,7	333,6	A32
39	278,6	134,1	65,9	31,5	62,4	322,4	A33
C7	254,7	122,5	67,4	32,4	62,4	330,8	A34

Table 2-b PP Optical properties

Example	Haze H %	Transmission Y %	Yellowness YI
C5	98,56	51,25	17,49
33	98,74	55,15	16,71
34	98,04	55,3	17,17
35	98,78	55,87	16,1
36	98,3	55,65	16,12
37	98,67	56,02	16,56
38	98,41	56,94	16,53
C6	98,62	53,03	16,54
39	97,88	54,84	16,6
C7	97,96	55,65	15,87

5

Table 2-a PE shows that the strongest effects can be achieved by the use of precompound A15, A19 and A22 (examples 25, 29 and 32). Table 2-a PP shows that the strongest effects can be achieved by the use of precompound 31 (example 38).

10

Table 3 shows further compositions of pre-compounds and inventive polymer blends with PE and PP wherein binary and ternary compatibilizer systems have been used. The obtained mechanical data are summarized in Tables 3-a PE and 3a-PP. The polymer blends and films have been prepared according to the standard procedure as described herein-before.

15

Table 3-a PE - Mechanical properties

Example	Precompound				Puncture Resistance Method B, Process (b) with cut					
	B11	B2	A	B3	PE	CPR MD N/mm	Fmax N	CPR TD N/mm	Fmax N	W Break Nmm
40	1,962	3,066	14	0,972	80	66,1	41,5	55,0	34,0	163,2
41	1,308	2,044	16	0,648	80	63,1	38,3	55,7	33,3	179,1
42	0,981	1,533	17	0,486	80	64,1	31,8	53,6	25,2	169,7
43	0,981	1,533	7	0,486	90	64,0	37,9	60,2	29,6	163,0
44	0,654	1,022	8	0,324	90	66,2	35,0	60,9	33,3	163,6
45	0,4905	0,7665	8,5	0,243	90	67,1	36,3	59,3	32,8	152,5
46	0,5886	0,9198	4,2	0,2916	94	65,9	36,6	62,1	31,6	157,7
47	0,3924	0,6132	4,8	0,1944	94	67,5	35,6	62,1	32,9	155,9
48	0,2943	0,4599	5,1	0,1458	94	69,0	40,7	61,1	33,1	155,4
49	2,704	0	16	1,296	80	64,0	33,8	53,7	28,5	169,6
50	2,028	0	7	0,972	90	65,9	35,2	59,7	31,8	163,5
51	1,352	0	8	0,648	90	65,9	34,5	61,2	32,6	182,4
52	1,014	0	8,5	0,486	90	66,9	35,2	60,1	33,7	172,3
53	0,8112	0	4,8	0,3888	94	67,8	36,0	62,2	32,5	184,2

components in % by weight

Table 3-a PP - Mechanical properties

Example	Precompound				Puncture Resistance Method B, Process (b) with cut					
	B11	B2	A	B3	PP	CPR MD N/mm	Fmax N	CPR TD N/mm	Fmax N	W Break Nmm
54	1,728	2,568	14	1,704	80	116,4	76,6	113,8	70,2	335,5
55	1,152	1,712	16	1,136	80	78,3	61,0	113,7	65,0	335,5
56	0,864	1,284	17	0,852	80	109,0	63,5	112,2	61,5	340,5
57	0,864	1,284	7	0,852	90	91,1	53,5	93,0	48,3	357,1
58	0,576	0,856	8	0,568	90	102,4	66,9	96,3	68,9	357,0
59	0,432	0,642	8,5	0,426	90	84,9	47,7	96,8	49,0	367,1
60	0,5184	0,7704	4,2	0,5112	94	94,6	49,7	89,7	45,8	400,2
61	0,3456	0,5136	4,8	0,3408	94	96,2	53,8	85,9	48,0	388,1
62	0,2592	0,3852	5,1	0,2556	94	88,0	50,1	82,8	44,9	394,8
63	1,468	0	16	2,532	80	108,3	69,7	111,0	67,3	368,9
64	1,101	0	7	1,899	90	171,2	100,9	69,9	43,0	377,8
65	0,734	0	8	1,266	90	152,2	79,6	89,5	47,5	366,3
66	0,5505	0	8,5	0,9495	90	183,0	101,4	79,4	43,6	374,6
67	0,4404	0	4,8	0,7596	94	161,3	88,1	95,1	54,0	386,0
C9	0	0	0	0	100	71,2	36,8	69,9	36,5	359,2

components in %

Table 3-a PE shows that the best results were obtained for inventive polymer PE blends according to examples 46, 47, 48 and 53.

Table 3-a PP shows that the best results were obtained for inventive polymer PP blends according to examples 60, 61, 62 and 67.

In the following examples (tables 4 a-c) films of inventive polyethylene (PE) blends stretched by 500% have been tested.

10 The blends of this test-series have not been pre-compounded; the pellet mixture was directly fed to the film extruder. The middle zones of the afore-mentioned FTS 16 twin screw extruder have been set to 250°C in order to homogenize component B11, the other temperatures have been kept on standard level. Homogenous stretched films were obtained. The composition of the blends (% by weight) is shown in table 4

15

Table 4 composition of the blends

Example	B11	B2	A	B3	PE
C10	0,00	0,00	0,00	0,00	100,00
C25	0,00	0,00	5,33	2,00	92,67
69	2,00	0,00	8,00	0,00	90,00
C11	0,00	0,00	4,00	0,00	96,00
70	0,67	0,67	5,33	0,67	92,67
C12	0,00	0,00	5,33	0,00	94,67
C13	0,00	0,00	8,00	2,00	90,00
71	2,00	0,00	5,33	0,00	92,67
C14	0,00	1,33	8,00	2,00	88,67
C15	0,00	2,00	8,00	1,33	88,67
C16	0,00	0,00	1,33	0,33	98,33
C17	0,00	1,67	4,00	0,00	94,33
C18	0,00	0,00	4,00	1,67	94,33
72	1,33	2,00	8,00	0,00	88,67
73	1,33	0,00	8,00	2,00	88,67
C19	0,00	0,00	8,00	0,00	92,00
74	1,00	0,67	8,00	0,67	89,67
75	1,67	0,00	4,00	0,00	94,33
76	2,00	1,33	8,00	0,00	88,67
C20	0,00	2,00	8,00	0,00	90,00
C21	0,00	1,00	8,00	0,00	91,00
77	2,00	0,00	8,00	1,33	88,67
78	1,00	0,00	8,00	0,00	91,00
C22	0,00	0,00	8,00	1,00	91,00

C23	0,00	0,33	1,33	0,00	98,33
C24	0,00	2,00	5,33	0,00	92,67
79	0,53	0,53	4,27	0,53	94,13
80	0,47	0,47	3,73	0,47	94,87
81	0,40	0,40	3,20	0,40	95,60
82	0,33	0,33	2,67	0,33	96,33

Besides standard mechanical and optical testing (table 4a), a tensile test (table 4b) and a dart drop test (table 4c) were performed.

5 The dart drop test indicates the film stability under fast impact conditions as opposed to the slow tear and puncture resistance as well as tensile tests.

Table 4-a PE - Mechanical properties and transparency of 40 µm film

Example	Crack propagation resistance DIN ISO 34-1:04-07 Method B, Process (b) with cut				Puncture Resistance		Optics
	CPR MD N/mm	Fmax N	CPR TD N/mm	Fmax N	Fmax N	W Break Nmm	Transmisson %
C10	76,8	3,5	45,5	2,1	4,60	20,71	89,04
C25	78,7	3,95	36,1	1,7	5,18	29,09	87,27
69	64,7	6,72	52,5	4,95	7,76	45,28	84,32
C11	76,8	4	37,4	2,06	5,27	27,80	88,48
70	69,7	3,35	50,3	2,26	4,68	25,07	88,07
C12	80,7	3,82	39,9	1,78	4,90	26,27	88,41
C13	80,6	4,11	36,7	1,66	5,55	31,30	86,11
71	75,9	4,04	53,3	2,37	4,98	27,02	87,91
C14	83,1	4,1	36,0	1,67	5,58	29,27	85,43
C15	84,2	4,2	32,2	1,45	4,88	26,39	85,52
C16	82,6	4,05	40,1	1,94	5,05	24,79	88,89
C17	84,4	3,65	38,6	1,66	4,90	26,00	87,74
C18	79,9	4,13	40,0	1,9	5,45	29,20	88,29
72	72,0	3,4	48,0	2,14	4,73	25,93	84,54
73	78,6	3,58	49,3	2,17	5,07	29,31	85,70
C19	80,4	3,68	36,6	1,69	5,01	26,96	85,61
74	75,4	3,37	47,5	2,1	4,80	26,75	84,87
75	70,0	3,86	48,8	2,4	4,91	27,61	87,78
76	65,4	3,27	41,7	1,8	3,87	18,80	84,01
C20	76,9	3,82	32,8	1,5	4,84	23,80	84,89
C21	79,9	3,61	35,1	1,6	4,97	23,81	85,61

77	70,9	3,41	49,8	2,41	3,94	19,89	83,94
78	66,9	3,32	45,5	2,08	3,09	12,37	86,80
C22	83,1	3,7	35,1	1,65	5,55	30,20	86,08
C23	72,5	3,63	37,2	1,85	4,96	24,28	89,00
C24	81,6	3,84	36,0	1,66	5,37	27,68	86,77
79	73,9	3,86	49,3	2,26	3,70	17,47	88,06
80	78,8	3,85	54,7	2,67	3,56	17,61	88,53
81	74,1	3,66	49,1	2,3	4,05	19,29	88,48
82	79,6	3,71	52,4	2,47	4,44	22,54	88,48

Table 4-a PE shows the best results for examples 69, 70, 71, 72, 73, 75, 77 and 82.

Table 4-b PE - tensile testing of 40 µm film

Example	machine direction		transversal direction	
	$\sigma$ -B [N]	$\epsilon$ -B [%]	$\sigma$ -B [N]	$\epsilon$ -B [%]
C10	78,32	532,07	48,99	831,97
C25	81,47	648,50	44,37	784,73
69	48,51	797,72	33,61	643,80
C11	78,10	595,85	47,13	766,82
70	70,09	631,48		
C12	78,40	579,74	43,45	725,20
C13	90,61	695,80	40,05	661,90
71	65,45	614,16	53,49	848,85
C14	88,91	685,08	38,49	529,87
C15	74,47	550,12	32,88	386,03
C16	81,17	568,89	49,19	804,02
C17	80,28	616,00	44,90	645,75
C18	83,44	617,05	36,07	521,50
72	64,55	635,05	42,01	617,13
73	68,09	604,58	44,92	535,93
C19	84,03	632,89	42,85	651,58
74	65,39	591,81	52,19	823,87
75	73,62	572,74	37,77	528,98
76	67,06	645,74	44,55	670,44
C20	85,20	663,40	36,54	507,05
C21	81,59	600,41	41,87	644,15
77	70,34	653,52	37,72	531,89

78	67,82	623,23	40,07	601,89
C22	85,01	644,39	41,65	689,36
C23	78,13	575,47	45,99	715,70
C24	76,55	568,41	43,72	687,21
79	68,21	607,86	44,31	649,42
80	70,59	629,97	48,07	710,44
81	74,15	627,91	40,68	672,63
82	62,29	535,81	43,74	675,76

Table 4-b PE shows the best results for examples 69, 70, 71, 72, 73, 75, 77 and 82.

Table 4-c PE - dart drop test on 40 µm film

Example	DIN 53 373		
	Force F [ N ]	Energy E [ J ]	Strain s [ mm ]
C10	20,66	0,072	6,116
C25	23,286	0,118	2,564
69	32,746	0,132	7,32
C11	20,996	0,104	7,356
70	20,754	0,082	6,52
C12	23,772	0,118	8,186
C13	24,292	0,134	8,86
71	21,362	0,09	6,856
C14	22,704	0,104	7,63
C15	23,164	0,126	8,37
C16	25,452	0,124	8,304
C17	23,986	0,118	8,004
C18	22,674	0,102	7,598
72	19,136	0,074	6,22
73	19,47	0,09	6,998
C19	23,136	0,096	7,262
74	20,448	0,08	6,432
75	20,008	0,238	15,744
76	16,54	0,214	15,388
C20	28,168	0,192	10,518
C21	26,368	0,148	9,05
77	17,182	0,12	8,49

78	16,51	0,068	4,604
C22	26,856	0,144	8,91
C23	25,484	0,134	8,428
C24	25,634	0,134	8,462
79	18,988	0,224	14,458
80	18,342	0,238	15,392
81	17,764	0,184	15,392
82	18,006	0,158	9,268

Table 4-c PE shows the best results for examples 69, 75 and 82.

Furthermore tables 4a-c show that ductility and impact properties are not going parallel  
 5 for micromechanic reasons connected with the particle size of component A. The inventive polymer blends have the advantage that their properties can be adjusted to the customer's needs in putting more emphasis either on crack propagation or impact properties, e.g. by reducing the compatibilizer content in respect to the amount of component A.

10

The examples show that the polymer blends of the present invention and films produced therefrom have an improved crack propagation resistance, puncture resistance and dart impact properties. Beside said mechanical properties, the optical properties are also good.

15

## Claims

## 1. Polymer blend comprising components A, B and C:

5 A: 1 to 19.5% by weight of an elastomeric block copolymer A made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B/S which forms a soft phase and incorporates both units of a vinylaromatic monomer (S) and of a diene (B), where S is the vinylaromatic block and B/S is the soft phase, wherein  
10 the block is built up randomly from diene units and vinylaromatic units, and where the glass transition temperature Tg of the block S is above 25°C, and that of the block B/S is below 25°C, and the phase volume ratio of block S to block B/S is selected so that the proportion of hard phase in the entire block copolymer is from 1 to 40% by volume and the proportion of the diene is less than  
15 50% by weight, based on A;

B: 0.5 to 8% by weight of component B comprising components B1 and further optional components B2 and/or B3:

20 B1: at least one elastomeric block copolymer selected from the group consisting of B11, B12 and B13:

B11: block copolymer B11 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block EB which forms a soft phase and incorporates units of ethylene and butylene; and/or

25 B12: block copolymer B12 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block EP which forms a soft phase and incorporates units of ethylene and propylene; and/or

30 B13: block copolymer B13 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B which forms a soft phase and incorporates units of a diene (B), and the proportion of the hard phase in the entire block copolymer is at most 45% by weight, based on B13;

5 B2: a stiff/tough block copolymer B2 made from at least one block S which forms a hard phase and incorporates units of a vinylaromatic monomer, and at least one elastomeric block B which forms a soft phase and incorporates units of a diene (B), and the proportion of the hard phase in the entire block copolymer is more than 50% by weight, based on B2;

10 B3: an ethylene-(C<sub>3</sub>-C<sub>18</sub>)- $\alpha$ -olefin copolymer B3 with a high content of (C<sub>3</sub>-C<sub>18</sub>)- $\alpha$ -olefin, based on B3, and having a crystallinity of less than 50%;

15 2. Polymer blend according to claim 1, wherein component A is a block copolymer having one of the general formulae S-(B/S)-S, X-[-(B/S)-S]<sub>2</sub>, Y-[-(B/S)-S]<sub>2</sub> Y[(B/S-S)<sub>n</sub>]<sub>m</sub>[S]<sub>l</sub> and Y[(S-B/S)<sub>n</sub>-S]<sub>m</sub>[S]<sub>l</sub>, where S is the vinylaromatic block and B/S is the soft phase, X is the radical of an n-functional initiator, Y is the radical of an m-functional or (m + l)-functional coupling agent, and l, m and n are natural numbers from 1 to 10.

20 3. A polymer blend according to claim 1 or 2, wherein component A is a linear styrene-butadiene block copolymer of the general structure S-(S/B)-S having, situated between the two S blocks, one or more (S/B)-random blocks having random styrene-butadiene distribution, and a 1,2-vinyl content in the styrene-butadiene copolymer block (S/B) of below 20%.

25 4. Polymer blend according to any of claims 1 to 3, comprising combinations of components A, B1, C and optionally B2 and/or B3 selected from the group consisting of: A, B1 and C; A, B1, B2 and C; A, B1, B3 and C; and A, B1, B2, B3 and C.

5. Polymer blend according to any of claims 1 to 4, wherein, based on the entire component B, the amount of component B1 is 1 to 100%, preferably 10 to 100%, more preferably 15 to 50% by weight;  
5 the amount of component B2 is 0 to 99%, preferably 0 to 90, more preferably 20 to 70%, by weight; and the amount of component B3 is 0 to 99%, preferably 0 to 90%, more preferably 10 to 50% by weight,  
where the entire amounts of components B1, B2 and B3 together give exactly 100% by weight.
- 10 6. Polymer blend according to any of claims 1 to 5, wherein component B1 is B11 and/or B12, in particular B11; C is polyethylene and/or polypropylene, B3, if present, is an ethylene-octene copolymer, and B2, if present, is a SBS block copolymer.
- 15 7. Polymer blend according to any of claims 1 to 6, having the following composition:  
1 to 10% by weight of component A,  
0.8 to 2.5% by weight of component B11 and/or B12, in particular B11, and  
20 87.5 to 98.2% by weight of component C,  
where A, B11, B12 and C give exactly 100% by weight.
8. Polymer blend according to any of claims 1 to 6, having the following composition:  
25 1 to 10% by weight of component A,  
0.1 to 0.8% by weight of component B11 and/or B12, in particular B11,  
0.1 to 0.8% by weight of component B2,  
0.1 to 0.8% by weight of component B3, and  
30 87.6 to 98.7% by weight of component C,  
where A, B11, B12, B2, B3 and C give exactly 100% by weight.
- 35 9. Polymer blend according to any of claims 1 to 6, having the following composition:  
1 to 10% by weight of component A,  
0.8 to 2.5% by weight of component B11 and/or B12, in particular B11,  
0.8 to 2.5% by weight of component B2,  
85 to 94% by weight of component C,

where A, B11, B12, B2 and C give exactly 100% by weight.

10. Polymer blend according to any of claims 1 to 6, having the following composition:

5      1 to 10% by weight of component A,  
0.8 to 2.5% by weight of component B11 and/or B12, in particular B11,  
0.8 to 2.5% by weight of component B3,  
85 to 94% by weight of component C,  
where A, B11, B12, B3 and C give exactly 100% by weight.

10      11. Polymer blend according to any of claims 1 to 6, having the following composition:

15      10 to 17% by weight of component A,  
1.0 to 6.0% by weight of component B11 and/or B12, in particular B11, and  
80 to 87% by weight of component C,  
where A, B11, B12 and C give exactly 100% by weight.

12. Polymer blend according to any of claims 1 to 6, having the following composition:

20      1 to 10% by weight of component A,  
0.2 to 0.8% by weight of component B11 and/or B12, in particular B11,  
0.2 to 1.0% by weight of component B2,  
0.1 to 0.8% by weight of component B3, and  
87.4 to 98.5% by weight of component C,  
where A, B11, B12, B2, B3 and C give exactly 100% by weight.

13. Polymer blend according to any of claims 1 to 6, having the following composition:

30      10 to 17% by weight of component A,  
0.8 to 3.0% by weight of component B11 and/or B12, in particular B11,  
0.8 to 3.0% by weight of component B2,  
80 to 87% by weight of component C,  
where A, B11, B12, B2 and C give exactly 100% by weight.

14. Polymer blend according to any of claims 1 to 6, having the following composition:
  - 10 to 17% by weight of component A,
  - 0.8 to 3.0% by weight of component B11 and/or B12, in particular B11,
  - 5 0.8 to 3.0% by weight of component B3,
  - 80 to 87% by weight of component C,
  - where A, B11, B12, B2 and C give exactly 100% by weight.
15. Compatibilizer comprising component B as defined in claim 1 or 5.
- 10 16. A process for the preparation of a polymer blend according to any of claims 1 to 14, wherein:
  - a pre-compound of components A and B1 and, if present, components B2 and B3 is prepared in an extruder;
  - the obtained pre-compound is pre-mixed with a polyolefin component C, and
  - 15 then this mixture is extruded to give the polymer blend.
17. A master batch comprising a pre-compound of components A and B1 and, if present, components B2 and B3, as defined in claim 1.
- 20 18. A master batch according to claim 17, comprising 50 to 60% by weight of component A, 10 to 20% by weight of component B1, 5 to 15% by weight of component B2 and 15 to 30% by weight of component B3, where the entire components A, B1, B2 and B3 give exactly 100% by weight.
- 25 19. Single-, bi- or multi layer-films comprising a polymer blend according to any of claims 1 to 14.
20. Use of a film according to claim 19 for food packaging and as shrink hood.

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2015/052692

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. C08L23/00 C08L53/02 C08J3/22 C08J5/18  
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)  
C08L C08J

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

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

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 607 432 A1 (BASF AG [DE]) 21 December 2005 (2005-12-21) cited in the application the whole document -----	1-20
X	US 4 479 989 A (MAHAL MOHAN S [US]) 30 October 1984 (1984-10-30)	15
A	examples -----	1-14, 16-20
X	US 2007/240605 A1 (IYER SRIVATSAN S [US] ET AL IYER SRIVATSAN SRINIVAS [US] ET AL) 18 October 2007 (2007-10-18)	15
A	paragraph [0042] tables VI, VII, VIII, IX -----	1-14, 16-20



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 April 2015	29/04/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Friebe, Lars

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/052692

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 1607432	A1	21-12-2005	DE 102004029132 A1 EP 1607432 A1 US 2005282965 A1	29-12-2005 21-12-2005 22-12-2005
<hr/>				
US 4479989	A	30-10-1984	AU 558081 B2 AU 2154183 A CA 1245788 A1 DE 3367323 D1 EP 0114964 A1 JP S59109542 A US 4479989 A	15-01-1987 07-06-1984 29-11-1988 11-12-1986 08-08-1984 25-06-1984 30-10-1984
<hr/>				
US 2007240605	A1	18-10-2007	CA 2577290 A1 CN 101432356 A EP 1778781 A1 JP 5060952 B2 JP 2008510031 A SG 155215 A1 US 2007240605 A1 WO 2006020309 A1	23-02-2006 13-05-2009 02-05-2007 31-10-2012 03-04-2008 30-09-2009 18-10-2007 23-02-2006
<hr/>				