



(43) International Publication Date
16 March 2017 (16.03.2017)

(51) International Patent Classification:
C08L 23/06 (2006.01)

(21) International Application Number:
PCT/US2016/050650

(22) International Filing Date:
8 September 2016 (08.09.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/216,528 10 September 2015 (10.09.2015) US

(71) Applicant: **DOW GLOBAL TECHNOLOGIES LLC**
[US/US]; 2040 Dow Center, Midland, MI 48674 (US).

(72) Inventors: **HU, Yushan**; 2301 N. Brazosport Blvd., Freeport, TX 77541 (US). **ANDERSON, Kyle**; 2301 N.

Brazosport Blvd., Freeport, TX 77541 (US). **MARCHAND, Gary R.**; 6277 Tezcuco Ct, Gonzales, LA 70737 (US). **WALTON, Kim L.**; 2301 N. Brazosport Blvd., Freeport, TX 77541 (US). **LIPISHAN, Colin**; 2301 N. Brazosport Blvd., Freeport, TX 77541 (US).

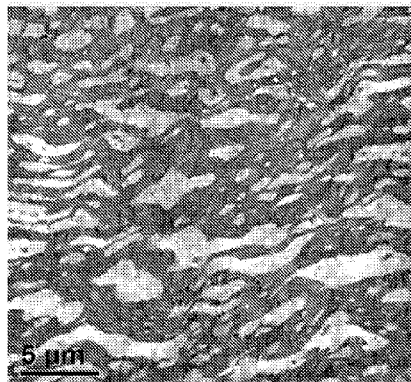
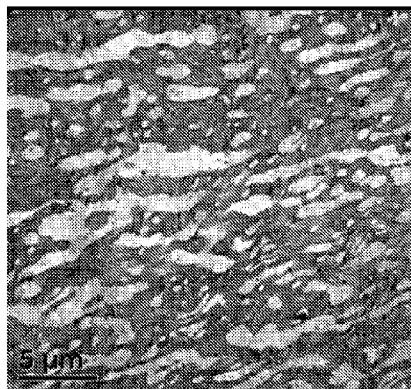
(74) Agent: **HUANG, Cheney**; Dow Global Technologies LLC, 2040 Dow Center, Midland, Michigan 48674 (US).

(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,

[Continued on next page]

(54) Title: POLYOLEFIN BLENDS INCLUDING COMPATIBILIZER

FIG. 1



(57) Abstract: A composition comprising from 10 wt% to 90 wt% of an ethylene component including at least one ethylene based polymer having an ethylene content of at least 50.0 wt%, a melt index from 0.1 g/10 min to 100.0 g/10 min, and a density from 0.935 g/cm³ to 0.965 g/cm³; from 10 wt% to 90 wt% of a propylene component including at least one propylene based polymer having a propylene content of at least 50.0 wt% and a melt flow rate from 0.5 g/10 min to 200.0 g/10 min; and from 1 wt% to 20 wt% of a composite component including a specified block composite, derived from at least ethylene and an alpha-olefin.



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))*

Polyolefin Blends Including Compatibilizer

Field

[0001] Embodiments relate to polyolefin blends that include a specified block copolymer composite (BC) compatibilizer.

Introduction

[0002] Multiphase polymer blends are of major economic importance in the polymer industry. In general, commercial polymer blends consist of two or more polymers. In some cases, they may be combined with small amounts of a compatibilizer or an interfacial agent.

[0003] Polypropylene (PP) homopolymers or PP random copolymers provide the desirable stiffness and temperature resistance for many applications, but suffer from poor impact properties due to having a high T_g (5°C for hPP). To overcome this deficiency, PP homopolymer is blended with PP copolymers and/or elastomers to improve its toughness, but at the expense of its modulus. An improvement would be to blend PP with a tough crystalline material that has a low T_g (such as high density polyethylene (HDPE)) to improve the impact performance without adversely affecting the modulus.

[0004] On the other hand, polyethylene, such as HDPE, possesses excellent toughness and melt strength, but lacks stiffness and temperature resistance for certain applications. An improvement would be to blend, for example, HDPE with PP to improve stiffness and temperature resistance without adversely affecting the toughness.

[0005] Unfortunately, blends of PP and most PE are incompatible and result in immiscible blends with poor mechanical and optical properties. Accordingly, a need exists for compatibilized polyolefin blends that provide the benefits of both PP and PE while minimizing individual trade-off properties.

Summary

[0006] Embodiments may be realized by providing a composition comprising:

(A) from 10 wt% to 90 wt% of an ethylene component including at least one ethylene based polymer having an ethylene content of at least 50.0 wt%, based on the total weight of the ethylene based polymer, a melt index from 0.1 g/10 min to 100.0

g/10 min (ASTM D-1238 at 190°C, 2.16 kg), and a density from 0.935 g/cm³ to 0.965 g/cm³;

(B) from 10 wt% to 90 wt% of a propylene component including at least one propylene based polymer having a propylene content of at least 50.0 wt%, based on the total weight of the propylene based polymer, and a melt flow rate from 0.5 g/10 min to 200.0 g/10 min (ASTM D-1238 at 230°C, 2.16 kg);

(C) from 1 wt% to 20 wt% of a composite component including at least a specified block composite derived from at least ethylene and an alpha-olefin that is one of a C3-10 alpha-olefin. The specified block composite includes an ethylene based polymer having an ethylene content from 69 mol% and to 90 mol%, an alpha-olefin based polymer that is derived from at least the alpha-olefin, and a block copolymer comprising an ethylene block and an alpha olefin block, the ethylene block of the block copolymer having the same composition as the ethylene based polymer in the specified block composite, and the alpha olefin block of the block copolymer having the same composition as the alpha-olefin based polymer of the specified block composite; and

(D) from 1 wt% to 20 wt% of an additional polymer component, such as an elastomer.

Brief Description of the Figures

[0007] FIG. 1 illustrates the transmission electron microscope (TEM) morphology for a PP phase (bright phase) dispersed in an HDPE matrix (grey color phase) for Comparative Example A.

[0008] FIG. 2 illustrates the TEM morphology for a PP phase (bright phase) dispersed in an HDPE matrix (grey color phase) for Working Example 4.

[0009] FIG. 3 illustrates the TEM morphology for CBCA, BC1, BC2, BC3, BC4, and BC5.

Detailed Description

[0010] Embodiments relate to a composition that includes an ethylene based polymer, a propylene based polymer, a specified block composite (BC), and, optionally, an additional polymer component, such as an elastomer.

Terms

[0011] The numerical ranges in this disclosure are approximate, and thus may include values outside of the range unless otherwise indicated. Numerical ranges

include all values from and including the lower and the upper values, in increments of one unit, provided that there is a separation of at least two units between any lower value and any higher value. As used with respect to a chemical compound, unless specifically indicated otherwise, the singular includes all isomeric forms and vice versa.

[0012] "Composition" and like terms mean a mixture or blend of two or more components. "Blend," "polymer blend," and like terms mean a blend of two or more polymers. Such a blend may or may not be miscible. Such a blend may or may not be phase separated. Such a blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and any other method known in the art.

[0013] "Polymer" means a compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, and the term interpolymers and copolymer as defined below. It also encompasses all forms of interpolymers, e.g., random, block, homogeneous, heterogeneous, etc.

[0014] "Interpolymer" and "copolymer" mean a polymer prepared by the polymerization of at least two different types of monomers. These generic terms include both classical copolymers, i.e., polymers prepared from two different types of monomers, and polymers prepared from more than two different types of monomers, e.g., terpolymers, tetrapolymers, etc.

[0015] "Units derived from ethylene", "ethylene content", and like terms mean the units of a polymer that formed from the polymerization of ethylene monomers. "Units derived from α -olefin", "alpha-olefin content", " α -olefin content", and like terms mean the units of a polymer that formed from the polymerization of specific α -olefin monomers, in particular at least one of a C₃₋₁₀ α -olefin. "Units derived from propylene", "propylene content", and like terms mean the units of a polymer that formed from the polymerization of propylene monomers.

[0016] "Propylene based polymer," and like terms mean a polymer that comprises a majority weight percent polymerized propylene monomer, also referred to as units derived from propylene (based on the total amount of polymerizable monomers), and optionally comprises at least one polymerized comonomer different from propylene

(such as at least one selected from a C₂ and C₄₋₁₀ α olefin) so as to form a propylene-based interpolymer. For example, when the propylene-based polymer is a copolymer, the propylene content is greater than 50 wt%, based on the total weight of the copolymer.

[0017] “Ethylene based polymer” and like terms mean a polymer that comprises a majority weight percent polymerized ethylene monomer, also referred to as units derived from ethylene (based on the total weight of polymerizable monomers), and optionally may comprise at least one polymerized comonomer different from ethylene (such as at least one selected from a C₃₋₁₀ α olefin) so as to form an ethylene-based interpolymer. For example, when the ethylene-based polymer is a copolymer, the amount of ethylene is greater than 50 wt%, based on the total weight to the copolymer.

[0018] The term "block copolymer" or "segmented copolymer" refers to a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") joined in a linear manner, that is, a polymer comprising chemically differentiated units, which are joined (covalently bonded) end-to- end with respect to polymerized functionality, rather than in pendent or grafted fashion. The blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the type of crystallinity (e.g. polyethylene versus polypropylene), the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, and/or any other chemical or physical property. The block copolymers are characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn) and block length distribution, e.g., based on the effect of the use of a shuttling agent(s) in combination with catalysts (such as those described in the examples).

[0019] The terms “specified block composite” and “block composite” (BC) refer to composites comprising an ethylene based polymer (may be referred to as EP) having an ethylene content from 69 mol% to 90 mol%, an alpha-olefin based polymer (may be referred AOP), and a block copolymer having an ethylene block (may be referred to EB) and an alpha-olefin block (may be referred to as AOB), wherein the ethylene block of the block copolymer is essentially the same composition as the ethylene based polymer in the block composite and the alpha-olefin block of the block copolymer is

essentially the same composition as the alpha-olefin based polymer of the block composite. The compositional split between the amount of ethylene based polymer and alpha-olefin based polymer will be essentially the same as that between the corresponding blocks in the block copolymer. The alpha-olefin content of the alpha-olefin based polymer and the alpha-olefin block may be from 61 mol% to 90 mol%. In embodiments, the alpha-olefin is propylene. The block composite differs from the crystalline block composite, defined below, based on at least the ethylene content in an ethylene based polymer and the ethylene block. For example, the alpha-olefin block and the ethylene block may be a P-E/E-P (propylene-ethylene and ethylene-propylene) diblock copolymer.

[0020] The term "crystalline block composite" (CBC) refers to composites comprising a crystalline ethylene based polymer (CEP) having an ethylene content of greater than 90 mol%, a crystalline alpha-olefin based polymer (CAOP), and a block copolymer having a crystalline ethylene block (CEB) and a crystalline alpha-olefin block (CAOB), wherein the CEB of the block copolymer is essentially the same composition as the CEP in the crystalline block composite and the CAOB of the block copolymer is essentially the same composition as the CAOP of the crystalline block composite. The compositional split between the amount of CEP and CAOP will be essentially the same as that between the corresponding blocks in the block copolymer. The alpha-olefin content of the CAOP and the CAOB may be greater than 90 mol%. In exemplary embodiments, the alpha-olefin is propylene. For example, the CAOB and the CEB may be an iPP-EP (isotactic polypropylene and ethylene-propylene) diblock copolymer.

[0021] The term "crystalline" refers to a polymer or polymer block that possesses a first order transition or crystalline melting point (T_m) as determined by differential scanning calorimetry (DSC) or equivalent technique. The term may be used interchangeably with the term "semicrystalline".

[0022] The term "crystallizable" refers to a monomer that can polymerize such that the resulting polymer is crystalline. Crystalline propylene polymers may have, but are not limited to, densities of 0.88 g/cm³ to 0.91 g/cm³ and melting points of 100 °C to 170°C.

[0023] The term "amorphous" refers to a polymer lacking a crystalline melting point as determined by differential scanning calorimetry (DSC) or equivalent technique.

[0024] The term "isotactic" is defined as polymer repeat units having at least 70 percent isotactic pentads as determined by ^{13}C -NMR analysis. "Highly isotactic" is defined as polymers having at least 90 percent isotactic pentads.

Block Composites

[0025] The composition includes a specified block composite. The amount of the specified block composite in the composition is from 1 wt% to 20 wt %, from 2 wt% to 15 wt%, from 3 wt% to 10 wt %, and/or from 3 wt% to 9 wt%, based on the total weight of the composition. In exemplary embodiments, the composition includes the specified block composite and optionally includes an additional polymer component, such as an elastomer (e.g., an ethylene-octene based copolymer and/or an octene based polymer), such that only the specified block composite may be included and/or a combination of both the specified block composite and the additional polymer component may be included.

[0026] The specified block composite may have a total ethylene content that is from 30 wt% to 70 wt% (e.g., 35 wt% to 60 wt%, 35 wt% to 55 wt%, 35 wt% to 50 wt%, etc.), based on the total weight of the specified block composite. The remainder of the total weight of the specified block composite may be accounted for by units derived from at least one C_{3-10} α -olefin (referring to a comonomer content). For example, the remainder of the total weight may be accounted for by units derived from propylene.

[0027] The specified block composite (BC) includes the ethylene based polymer (may be referred to as EP), the alpha-olefin based polymer (may be referred to as AOP), and the block copolymer having the ethylene block (may be referred to as EB) and the alpha-olefin block (may be referred to as AOB), where ethylene based polymer is essentially the same composition as the ethylene block of the block copolymer and the alpha-olefin based polymer is essentially the same composition as the alpha-olefin block of the block copolymer. In the specified block composite, the alpha-olefin is at least one selected from the group of C_{3-10} α -olefins (e.g., may be propylene and/or butylene).

[0028] The alpha-olefin based polymer and the alpha-olefin block of the specified block composite may have an alpha-olefin content that is from 61 mol% to 90 mol% (e.g., 65 mol% to 90 mol%, 70 mol% to 90 mol%, 75 mol% to 88 mol%, etc.). The remainder may be essentially accounted for with at least one selected from the group of C₂–C₄₋₁₀ α-olefins as comonomers. For example, the remainder may be essentially accounted for with units derived from ethylene, e.g., such that the ethylene content is from 10 mol% to 39 mol% (e.g., 10 mol% to 35 mol%, 10 mol% to 30 mol%, 12 mol% to 35 mol%, etc.). Said in another way, the alpha-olefin based polymer and the alpha-olefin block may have an alpha-olefin content (such as propylene content) that is from 70 wt% to 93 wt% (e.g., 75 wt% to 93 wt%, 80 wt% to 93 wt%, 85 wt% to 91 wt%, etc.).

[0029] The ethylene based polymer and ethylene block of the block copolymer of the specified block composite may have an ethylene content from 69 mol% to 90 mol% (e.g., 74 mol% to 89 mol%, 78 mol% to 85 mol%, 80 mol% to 85 mol%, etc.). The remainder may be essentially accounted for with at least one selected from the group of C₃₋₁₀ α-olefins as a comonomer, e.g., such that the comonomer content from 10 mol% to 31 mol%, 15 mol% to 20 mol%, etc. Said in another way, the ethylene content of ethylene based polymer and ethylene block of the block copolymer may be from 60 wt% to 85 wt% (e.g., from 65 wt% to 84 wt%, 70 wt% to 84 wt%, 75 wt% to 80 wt%, etc.).

[0030] In exemplary embodiments, the alpha-olefin based polymer and the alpha-olefin block of the block copolymer of the specified block composite includes propylene. For example, the propylene content is from 61 mol% to 90 mol% (e.g., 65 mol% to 90 mol%, 70 mol% to 90 mol%, 70 mol% to 90 mol%, 75 mol% to 88 mol%, etc.). The alpha-olefin based polymer and the alpha-olefin block of the block copolymer may additionally comprise ethylene as a comonomer. Further, the ethylene based polymer and the ethylene block of the block copolymer may comprise propylene as a comonomer. The compositional split between the amount of ethylene based polymer and the alpha-olefin based polymer will be essentially the same as that between the corresponding blocks in the block copolymer. The ethylene block and the alpha-olefin block may be referred to as semi-crystalline and/or amorphous segments/blocks.

[0031] The specified block composite may include from 0.5 wt% to 95.0 wt% EP, from 0.5 wt% to 95.0 wt% AOP, and from 5.0 wt% to 99.0 wt% of the block copolymer. For example, the block composite may include from 5.0 wt% to 80.0 wt% EP, from 5.0 wt% to 80.0 wt% AOP, and from 20.0 wt% to 90.0 wt% of the block copolymer. Weight percents are based on total weight of specified block composite. The sum of the weight percents of EP, AOP, and the block copolymer equals 100%. An exemplary measurement of the relative amount of the block copolymer is referred to as the Modifier Block Composite Index (MBCI). The MBCI is based on HTLC separation (e.g., not xylene separation) to isolate unbounded polypropylene in the block composite, and the methodology and assumptions are similar to the CBCI calculation. The MBCI for the block composite is greater than 0 and less than 1.0. For example, the MBCI is from 0.20 to 0.99, from 0.30 to 0.99, from 0.40 to 0.99, from 0.40 to 0.90, from 0.40 to 0.85, from 0.50 to 0.80, and/or from 0.55 to 0.75.

[0032] In accordance with ASTM D-1238 at 230°C, 2.16 kg, the MFR (melt flow rate) of the specified block composite composites may be from 0.1 to 1000 dg/min, from 1 to 500 dg/min, from 3 to 30 dg/min, and/or from 3 to 10 dg/min.

[0033] In accordance with ASTM D792-00, Method 13, the density of the specified block composite may be between 0.850 and 0.900 g/cc. In exemplary embodiments, the density of the specified block composite may be from 0.860 to 0.900, from 0.865 to 0.890, and/or from 0.870 to 0.890 g/cm³.

[0034] The specified block composite may have a T_m of greater than 60°C, greater than 70°C, and/or greater than 80°C and a T_c of from 35°C to less than 70°C.

[0035] The specified block composite differs from a crystalline block composite, as defined above, in view of the lower mole percent of ethylene in the ethylene based polymer (EP relative to CEP) and the ethylene block (EB relative to CEB) of the corresponding block copolymer. The specified block composite may also differ from a crystalline block composite in view of the lower mole percent of an alpha-olefin (such as propylene) in the alpha-olefin based polymer (AOP relative to CAOP) and the alpha-olefin block (AOB relative to CAOB).

[0036] The specified block composites may be differentiated from conventional, random copolymers, physical blends of polymers, and block copolymers prepared via sequential monomer addition. The specified block composites may be differentiated

from random copolymers and from a physical blend by characteristics such as modified block composite index, better tensile strength, improved fracture strength, finer morphology, improved optics, and/or greater impact strength at lower temperature. The specified block composites may be differentiated from block copolymers prepared by sequential monomer addition by molecular weight distribution, rheology, shear thinning, rheology ratio, and block polydispersity. A unique feature of specified block composites is that they may not be fractionated by conventional means by solvent or temperature such as xylene fractionation, solvent/non-solvent, or temperature rising elution fractionation or crystallization elution fractionation.

[0037] When produced in a continuous process, the crystalline block composites and the specified block composites desirably possess PDI from 1.7 to 15 (e.g., from 1.8 to 10, from 2.0 to 5, and/or from 2.5 to 4.8). Exemplary specified block composites are described in, e.g., U.S. Patent Application Publication Nos. 2014/0174509, incorporated herein by reference with respect to descriptions of the crystalline block composites, processes to make them, and methods of analyzing them. In exemplary embodiments, the specified block composite may have a molecular weight distribution (MWD), defined as weight average molecular weight divided by number average molecular weight (M_w/M_n) of 5.0 or less, 4.0 or less, 3.0 or less, from 2.0 to 4.0, from 2.0 to 3.0, and/or from 2.0 to less than 3.0. The M_w/M_n may be lower for the specified block composite relative to a crystalline block composite.

[0038] The specified block composite polymers may be prepared by a process comprising contacting an addition polymerizable monomer or mixture of monomers under addition polymerization conditions with a composition comprising at least one addition polymerization catalyst, at least one cocatalyst, and a chain shuttling agent, said process being characterized by formation of at least some of the growing polymer chains under differentiated process conditions in two or more reactors operating under steady state polymerization conditions or in two or more zones of a reactor operating under plug flow polymerization conditions. The term, “shuttling agent” refers to a compound or mixture of compounds that is capable of causing polymeric exchange between at least two active catalyst sites under the conditions of the polymerization. That is, transfer of a polymer fragment occurs both to and from one or more of the active catalyst sites. In contrast to a shuttling agent, a “chain transfer agent” causes

termination of polymer chain growth and amounts to a one-time transfer of growing polymer from the catalyst to the transfer agent. In a preferred embodiment, the specified block composites comprise a fraction of block polymer which possesses a most probable distribution of block lengths.

[0039] Suitable processes useful in producing the specified block composites and may be found, e.g., in U.S. Patent Application Publication No. 2008/0269412, published on Oct. 30, 2008. In particular, the polymerization is desirably carried out as a continuous polymerization, preferably a continuous, solution polymerization, in which catalyst components, monomers, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to one or more reactors or zones and polymer product continuously removed therefrom. Within the scope of the terms “continuous” and “continuously” as used in this context are those processes in which there are intermittent additions of reactants and removal of products at small regular or irregular intervals, so that, over time, the overall process is substantially continuous. The chain shuttling agent(s) may be added at any point during the polymerization including in the first reactor or zone, at the exit or slightly before the exit of the first reactor, or between the first reactor or zone and the second or any subsequent reactor or zone. Due to the difference in monomers, temperatures, pressures or other difference in polymerization conditions between at least two of the reactors or zones connected in series, polymer segments of differing composition such as comonomer content, crystallinity, density, tacticity, regio-regularity, or other chemical or physical difference, within the same molecule are formed in the different reactors or zones. The size of each segment or block is determined by continuous polymer reaction conditions, and preferably is a most probable distribution of polymer sizes.

[0040] For example, when producing a block copolymer having the ethylene block (EB) and the alpha-olefin block (AOB) in two reactors or zones it is possible to produce the EB in the first reactor or zone and the AOB in the second reactor or zone or to produce the AOB in the first reactor or zone and the EB in the second reactor or zone. It may be more advantageous to produce EB in the first reactor or zone with fresh chain shuttling agent added. The presence of increased levels of ethylene in the reactor or zone producing EB may lead to much higher molecular weight in that reactor or zone than in the zone or reactor producing AOB. The fresh chain shuttling agent

will reduce the MW of polymer in the reactor or zone producing EB thus leading to better overall balance between the length of the EB and AOB segments.

[0041] When operating reactors or zones in series it is necessary to maintain diverse reaction conditions such that one reactor produces EB and the other reactor produces AOB. Carryover of ethylene from the first reactor to the second reactor (in series) or from the second reactor back to the first reactor through a solvent and monomer recycle system may be preferably minimized. There are many possible unit operations to remove this ethylene, but because ethylene is more volatile than higher alpha olefins one simple way is to remove much of the unreacted ethylene through a flash step by reducing the pressure of the effluent of the reactor producing EB and flashing off the ethylene. A more preferable approach is to avoid additional unit operations and to utilize the much greater reactivity of ethylene versus higher alpha olefins such that the conversion of ethylene across the EB reactor approaches 100%. With respect to the AOB, the overall conversion of monomers across the reactors may be controlled by maintaining the alpha-olefin conversion at a high level (90 to 95%).

[0042] Exemplary catalysts for forming block composites are disclosed in US Patent Publication Nos. 2006/0199930, US 2007/0167578, and US 2008/0311812; U.S. Patent No. 7,355,089; and International Publication No. WO 2009/012215.

Ethylene Component

[0043] The composition includes from 10 wt% to 90 wt% (e.g., 15 wt% to 80 wt%, 20 wt% to 75 wt%, 30 wt% to 70 wt%, 40 wt% to 65 wt%, etc.) of an ethylene component. The ethylene component includes one or more ethylene based polymers having an ethylene content of at least 50.0 wt%, based on the total weight of the ethylene based polymer. The one or more ethylene based polymers have a melt index from 0.1 g/10 min to 100 g/10 min (e.g., from 0.3 g/10 min to 80.0 g/10 min, 0.3 g/10 min to 70.0 g/10 min, 0.5 g/10 min to 60.0 g/10 min, etc.), according to ASTM D-1238 at 190°C, 2.16 kg. The ethylene based polymers have, in accordance with ASTM D792-00, Method 13, a density from 0.935 g/cm³ to 0.965 g/cm³ (e.g., 0.945 g/cm³ to 0.965 g/cm³, 0.950 g/cm³ to 0.965 g/cm³, 0.950 g/cm³ to 0.963 g/cm³, etc.), such that the ethylene based polymer is a high density polyethylene based polymer (HDPE). The ethylene based polymers may consist of heterogeneous polyethylene or homogeneous polyethylene.

[0044] The ethylene component may include only HDPE type ethylene based polymers, or may include a combination of HDPE with other ethylene based polymers. Exemplary other ethylene based polymers include ultralow density polyethylene (ULDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high melt strength high density polyethylene (HMS-HDPE), ultrahigh density polyethylene (UHDPE), and combinations thereof. In exemplary embodiments, the ethylene component includes at least 50 wt%, 60 wt%, 70 wt%, 80 wt%, 90 wt%, 95 wt%, 99 wt%, etc., and/or includes 100 wt% of HDPE type ethylene based polymers, based on the total amount of one or more ethylene based polymers in the ethylene component.

[0045] The composition may be rich in the ethylene component (i.e., present in a higher amount by weight percent relative to the propylene component) to form an ethylene rich composition. In an ethylene rich composition the amount of the ethylene component may be from 40 wt% to 86 wt%, 40 wt% to 80 wt%, 40 wt% to 75 wt%, 40 wt% to 70 wt%, 42 wt% to 68 wt%, etc. Alternatively, the composition may be rich in the propylene component (i.e., present in a lower amount by weight percent relative to the propylene component) to form a propylene rich composition. In a propylene rich composition the amount of the ethylene component may be from 15 wt% to 45 wt%, 15 wt% to 40 wt%, 20 wt% to 40 wt%, 23 wt% to 36 wt%, etc.).

[0046] The number average molecular weight (M_w) of the ethylene based polymers in the ethylene component may be at least 5,000, at least 10,000, at least 15,000, at least 20,000, at least 25,000, and/or at least 30,000 grams per mole (g/mol). The maximum M_w of the ethylene based polymers may be less than 100,000 and/or less than 60,000 g/mol. The molecular weight distribution or polydispersity or M_w/M_n of these polymers may be less than 5, between 1 and 5, and/or between 1.5 and 4. Weight average molecular weight (M_w) and number average molecular weight (M_n) are well known in the polymer art and can be determined by known methods.

[0047] The ethylene-based polymer may have a crystallinity in the range of from at least 1 percent by weight (a heat of fusion (H_f) of at least 2 Joules/gram (J/g)) to 30 percent by weight (a H_f of less than 50 J/g). For example, the crystallinity range may be from 5% to 25%, from 10% to 20%, and/or from 12% to 18%.

[0048] Exemplary ethylene based polymers may include an ethylene/alpha-olefin interpolpolymer. The ethylene-based polymers are formed without the use of a chain shuttling agent, as discussed below with respect to the crystalline block composite. Such interpolpolymers include polymers polymerized from at least two different monomers. They include, e.g., copolymers, terpolymers and tetrapolymers. Exemplary, interpolpolymers are prepared by polymerizing ethylene with at least one comonomer, such as an alpha-olefin (α -olefin) of 3 to 20 carbon atoms (C_3 - C_{20}), 4 to 20 carbon atoms (C_4 - C_{20}), 4 to 12 carbon atoms (C_4 - C_{12}), 4 to 10 carbon atoms (C_4 - C_{10}), and/or 4 to 8 carbon atoms (C_4 - C_8). The alpha-olefins include, but are not limited to, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, and 1-octene. In embodiments, alpha-olefins such as 1-butene, 1 pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, and/or 1-octene are used. The alpha-olefin may be a C_4 - C_8 alpha-olefin.

[0049] Exemplary, interpolpolymers include ethylene/propylene (EP), ethylene/butene (EB) copolymers, ethylene/hexene (EH), ethylene/octene (EO) copolymers, ethylene/alpha-olefin/diene modified (EAODM) interpolpolymers such as ethylene/propylene/diene modified (EPDM) interpolpolymers, and ethylene/propylene/octene terpolymers. In exemplary embodiments, at least one of the EP, EB, EH, and EO copolymers are used in the hot melt adhesive composition.

[0050] In exemplary embodiments, the ethylene based polymers may be branched and/or unbranched interpolpolymers. The presence or absence of branching in the ethylene based interpolpolymers, and if branching is present, the amount of branching, can vary widely, and may depend on the desired processing conditions and the desired polymer properties. Exemplary types of long chain branching (LCB) in the interpolpolymers include T-type branching and H-type branching.

Propylene Component

[0051] The composition includes from 10 wt% to 90 wt% (e.g., 15 wt% to 80 wt%, 20 wt% to 75 wt%, 20 wt% to 70 wt%, 20 wt% to 65 wt%, 20 wt% to 60 wt%, etc.) of a propylene component. The propylene based component includes one or more propylene based polymers having a propylene content of at least 50.0 wt%, based on the total weight of the propylene based polymer. The one or more propylene based polymer has a melt flow rate from 0.1 g/10 min to 100.0 g/10 min (e.g., from 0.1 g/10 min to 80.0 g/10 min, 0.1 g/10 min to 50.0 g/10 min, 0.5 g/10 min to 50.0 g/10 min, 1.0

g/10 min to 45.0 g/10 min, 1.5 g/10 min to 40.0 g/10 min, 2.0 g/10 min to 35.0 g/10 min, etc.), according to ASTM D-1238 at 230°C, 2.16 kg. The propylene based polymer may have a density, in accordance with ASTM D792-00, Method 13, from 0.870 g/cm³ to 0.910 g/cm³ (e.g., 0.880 g/cm³ to 0.905 g/cm³, 0.885 g/cm³ to 0.905 g/cm³, 0.890 g/cm³ to 0.905 g/cm³, etc.). The propylene based component may consist of heterogeneous polypropylene or homogeneous polypropylene.

[0052] Each of the one or more propylene based polymers may be a propylene homopolymer, propylene based interpolymers, a random copolymer polypropylene (RCPP), an impact copolymer polypropylene (e.g., homopolymer propylene modified with at least one elastomeric impact modifier) (ICPP), a high impact polypropylene (HIPP), a high melt strength polypropylene (HMS-PP), an isotactic polypropylene (iPP), a syndiotactic polypropylene (sPP), or a combination thereof. In exemplary embodiments, the one or more propylene based polymers may be in the isotactic form of homopolymer polypropylene, although other forms of polypropylene may be used (e.g., syndiotactic or atactic).

[0053] Exemplary propylene based interpolymers (such as RCPP), may contain 1 wt% and up to 50 wt% of ethylene and/or an alpha-olefin comonomer of 4 to 20 carbon atoms (e.g., C₂ and C₄-C₁₀ alpha-olefins). All individual values and subranges from 1 and up to 50 wt% are included herein and disclosed herein; e.g., the comonomer content can be from a lower limit of 1 wt%, 3 wt%, 4 wt%, 5 wt%, 7 wt%, or 9 wt% to an upper limit of 40 wt%, 35 wt%, 30 wt%, 27 wt%, 20 wt%, 15 wt%, 12 wt%, or 9 wt%. For example, the propylene/alpha-olefin copolymer comprises from 1 to 35 wt%, 1 to 30 wt%, 3 to 27 wt%, 3 to 20 wt%, and/or 3 to 15 wt% of one or more alpha-olefin comonomers.

[0054] The one or more propylene-based polymers are formed without the use of a chain shuttling agent, as discussed below with respect to the crystalline block composite and the specified block composite. Exemplary comonomers for polymerizing with propylene include ethylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, as well as 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, vinylcyclohexane, and styrene. Exemplary comonomers include ethylene, 1-butene, 1-hexene, and 1-octene. Exemplary propylene based interpolymers include propylene/ethylene, propylene/1-

butene, propylene/1-hexene, propylene/4-methyl-1-pentene, propylene/1-octene, propylene/ethylene/1-butene, propylene/ethylene/ENB, propylene/ethylene/1-hexene, propylene/ethylene/1-octene, propylene/styrene, and propylene/ethylene/styrene. Optionally, the propylene-based polymer include a monomer having at least two double bonds such as dienes or trienes.

[0055] An exemplary discussion of various polypropylene polymers is contained in Modern Plastics Encyclopedia/89, mid October 1988 Issue, Volume 65, Number 11, pp. 86-92, the entire disclosure of which is incorporated herein by reference. Examples of such propylene based polymers include VERSIFY™ (available from The Dow Chemical Company), Vistamaxx™ (available from Exxon Mobil), INSPIRE™ (available from Braskem), and Pro-Fax (available from LyondellBasell).

[0056] In exemplary embodiments, the propylene-based polymer may be a propylene-alpha-olefin copolymer, which is characterized as having substantially isotactic propylene sequences. "Substantially isotactic propylene sequences" means that the sequences have an isotactic triad (mm) measured by ¹³C NMR of greater than 0.85; in the alternative, greater than 0.90; in another alternative, greater than 0.92; and in another alternative, greater than 0.93.

[0057] Similarly as discussed with respect to the ethylene-based polymers, the propylene-based polymers may contain LCB. For example, the propylene-based polymer may contain an average of at least 0.001, an average of at least 0.005 and/or an average of at least 0.01, long chain branches/1000 total carbons. The term long chain branch, as used herein, refers to a chain length of at least one (1) carbon more than a short chain branch, and short chain branch, as used herein with regard to propylene/alpha-olefin copolymers, refers to a chain length of two (2) carbons less than the number of carbons in the comonomer. For example, a propylene/1-octene interpolymer has backbones with long chain branches of at least seven (7) carbons in length, but these backbones also have short chain branches of only six (6) carbons in length.

Optional Polymer Component

[0058] The composition may include from 0 wt% to 22 wt% (e.g., 1 wt% to 20 wt%, 5 wt% to 15 wt%, 5 wt% to 10 wt%, etc.) of an optional polymer component that includes at least one ethylene-octene based polymer and/or at least one octene based

polymer. “Ethylene-octene based polymer” and the like terms mean a polymer that comprises ethylene and a minority percent of units derived from octene (based on the total weight of the polymerizable monomers). “Octene based polymer” and the like terms mean a polymer that comprises a majority weight percent polymerized octene polymer, also referred to as units derived from octene (based on the total weight of the polymerizable monomers), and optionally may comprise at least one polymerized comonomer different from octene (such as at least one selected from a C₂₋₇ and C₉₋₁₀ α olefin) so as to form an octene-based interpolymer. For example, when the octene-based polymer is a copolymer, the amount of octene is greater than 50 wt%, based on the total weight to the copolymer.

[0059] For example, the ethylene-octene based polymer may be a copolymer with an ethylene content of at least 50 wt% (e.g., at least 60 wt%, at least 70 wt%, at least 80 wt%, at least 85 wt%, etc., with the remainder of the total weight of the polymerizable monomers being accounted for with units derived from octene. The ethylene-based polymer may be derived from one or more alpha-olefins (C_{2-7,9, and 10}) in addition to ethylene and octene.

[0060] For example, the optional polymer component may include at least one octene based polymer having an octene content of at least 80.0 wt% (i.e., units derived from octene), based on the total weight of the octene based polymer. The octene component may include one or more octene based polymers, of which at least one octene based polymer has the octene content of at least 80.0 wt%. In exemplary embodiments, each of the one or more octene based polymers of the octene component has the octene content of at least 80 wt%. In exemplary embodiments, the octene content may be at least 54 mol%, based on the total weight of the octene based polymer. The octene based polymer may be a copolymer with an alpha olefin content of less than 20.0 wt% (e.g., less than 15.0 wt%, less than 10.0 wt%, less than 5.0 wt%, less than 2.0 wt%, less than 1.0 wt%, and/or less than 0.1 wt%), whereas the alpha olefin is at least one selected from the group of C_{2-7,9, and 10} alpha-olefins (e.g., the alpha olefin is ethylene and/or propylene). The octene based polymer may be derived from one or more alpha-olefins (C_{2-7,9, and 10}) in addition to the octene. The octene based polymer may be differentiated from some ethylene-octene copolymers based on the

high octene content of at least 80.0 wt%. In exemplary embodiments, the alpha olefin is excluded or less than 5.0 wt%.

[0061] The one or more octene based polymers may be prepared in one or more reactors (e.g., a continuous stirred tank reactor - CSTR) using at least octene as a monomer (an optional another alpha-olefin as additional monomer/comonomer), a solvent, a catalyst, a cocatalyst-1, and a cocatalyst-2 that are flowed to the reactor. In exemplary embodiments, the octene based polymer is prepared in a single reactor.

[0062] The optional polymer component may have a melt index from 0.1 g/10 min to 100 g/10 min (e.g., from 0.3 g/10 min to 80.0 g/10 min, 0.3 g/10 min to 70.0 g/10 min, 0.5 g/10 min to 60.0 g/10 min, etc.), according to ASTM D-1238 at 190°C, 2.16 kg. The optional polymer component may have, in accordance with ASTM D792-00, Method 13, a density from 0.850 g/cm³ to 0.900 g/cm³.

Composition

[0063] The polyolefin blend composition may be useful for preparing articles using known processes. For example, the compositions may be fabricated into parts, sheets or other article of manufacture, using any extrusion, calendering, blow molding, compression molding, injection molding, or thermoforming processes. The components of the composition may be fed to the process either pre-mixed, or the components may be fed directly into the process equipment, such as a converting extruder, such that the composition is formed therewithin. The compositions may be blended with another polymer, prior to fabrication of an article. Such blending may occur by any of a variety of conventional techniques, one of which is dry blending of pellets of the compositions with pellets of another polymer.

[0064] The polyolefin blend compositions can optionally include one or more additives and/or fillers. Non-limiting examples of additives and/or fillers include plasticizers, thermal stabilizers, light stabilizers (e.g., UV light stabilizers and absorbers), antioxidants, slip agents, process aids, optical brighteners, antistats, lubricants, catalysts, rheology modifiers, biocides, corrosion inhibitors, dehydrators, organic solvents, colorants (e.g., pigments and dyes), surfactants, antiblocking agents, nucleating agents, flame retardants and combinations thereof.

[0065] The polyolefin blend compositions may be compounded using, for example, a twin screw extruder, batch mixer, or single screw extruder.

Examples

[0066] Approximate conditions, properties, formulations etc., for the preparation of the Examples are provided below.

Test Methods

[0067] Density is measured in accordance with ASTM D-792. The result is reported in grams (g) per cubic centimeter, or g/cc.

[0068] Melt index (MI) is measured in accordance with ASTM D-1238 (190°C; 2.16 kg). The result is reported in grams/10 minutes.

[0069] Melt flow rate (MFR) is measured in accordance with ASTM D-1238 (230°C; 2.16 kg). The result is reported in grams/10 minutes.

[0070] Tensile Properties are measured using ASTM D-1708 microtensile specimens or ASTM D-638. For ASTM D-1708, the gauge length of the samples is 22

mm and samples are stretched with an Instron® at 554% min⁻¹ at 23°C. Tensile strength, tensile strain, and percent elongation at break are reported for an average of 5 specimens. For the compression molded examples, the plaques used for microtensile test are prepared by compression molding using a Tetrahedron press. The polymer is pre-melted at 190°C for 1 minute at 5 klb and then pressed for 5 minutes at 30 klb and then quenched to ice water bath. The nominal plaque thickness was 2.9 mm. For ASTM D-638, the gauge length of samples is 25 mm and the samples are stretched with an Instron® at 20 in/min at 23°C. Tensile strength, tensile strain, and percent elongation at break are reported for an average of 5 specimens. The plaques used for testing of tensile properties are prepared by injection molding and the tensile bars are cut from the plaque (type IV) in the cross direction.

[0071] Izod Impact, including at 23 °C, at 0 °C, and at -18 °C are measured according to ASTM D-256, at a thickness as indicated in the respective examples. Samples are prepared by compression molding or injection molding. For compression molding, the samples are cut from the same plaques used for tensile test to have the dimensions 63.5 mm x 12.7mm x 2.9 mm. The samples are notched using a notcher to produce a notch depth 2.54 +/- 0.05 mm in accordance with ASTM D-256. Five specimens of each sample are tested at 23°C and at 0°C. For injection molding, the samples are cut from the same plaques used for tensile test to have the dimensions 63.5mm x 12.7mm x 2.9mm. The samples are notched using a notcher to produce a notch depth 2.54 +/- 0.05 mm in accordance with ASTM D-256. Five specimens of each sample are tested at 23°C, 0°C and -18°C.

[0072]

[0073] Molecular weight distribution (MWD) is measured using Gel Permeation Chromatography (GPC). In particular, conventional GPC measurements are used to determine the weight-average (M_w) and number-average (M_n) molecular weight of the polymer, and to determine the MWD (which is calculated as M_w/M_n). Samples are analyzed with a high-temperature GPC instrument (Polymer Laboratories, Inc. model PL220). The method employs the well-known universal calibration method, based on the concept of hydrodynamic volume, and the calibration is performed using narrow polystyrene (PS) standards, along with four Mixed A 20µm columns (PLgel Mixed A from Agilent (formerly Polymer Laboratory Inc.)) operating at a system temperature of

140°C. Samples are prepared at a “2 mg/mL” concentration in 1,2,4-trichlorobenzene solvent. The flow rate is 1.0 mL/min, and the injection size is 100 microliters.

[0074] As discussed, the molecular weight determination is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968) to derive the following equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b.$$

[0075] In this equation, $a = 0.4316$ and $b = 1.0$ (as described in Williams and Ward, J. Polym. Sc., Polym. Let., 6, 621 (1968)). Polyethylene equivalent molecular weight calculations were performed using VISCOTEK TriSEC software Version 3.0.

[0076] Differential Scanning Calorimetry (DSC) is used to measure crystallinity in the polymers (e.g., polyethylene (PE) polymers). About 5 to 8 mg of polymer sample is weighed and placed in a DSC pan. The lid is crimped on the pan to ensure a closed atmosphere. The sample pan is placed in a DSC cell, and then heated, at a rate of approximately 10°C/min, to a temperature of 180°C for PE (230°C for polypropylene or “PP”). The sample is kept at this temperature for three minutes. Then the sample is cooled at a rate of 10°C/min to -60°C for PE (-40°C for PP), and kept isothermally at that temperature for three minutes. The sample is next heated at a rate of 10°C/min, until complete melting (second heat). The percent crystallinity is calculated by dividing the heat of fusion (H_f), determined from the second heat curve, by a theoretical heat of fusion of 292 J/g for PE (165 J/g, for PP), and multiplying this quantity by 100 (for example, % cryst. = $(H_f / 292 \text{ J/g}) \times 100$ (for PE)).

[0077] Unless otherwise stated, melting point(s) (T_m) of each polymer is determined from the second heat curve (peak T_m), and the crystallization temperature (T_c) is determined from the first cooling curve (peak T_c).

[0078] High Temperature Liquid Chromatography: High Temperature Liquid Chromatography Experimental Method Instrumentation is the HTLC experiment, which is done according to the published method with minor modifications (Lee, D.;

Miller, M. D.; Meunier, D. M.; Lyons, J. W.; Bonner, J. M.; Pell, R. J.; Shan, C. L. P.; Huang, T. J. *Chromatogr. A* 2011, *1218*, 7173). Two Shimadzu (Columbia, MD, USA) LC-20AD pumps are used to deliver decane and trichlorobenzene (TCB) respectively. Each pump is connected to a 10:1 fixed flow splitter (Part #: 620-PO20-HS, Analytical Scientific Instruments Inc., CA, USA). The splitter has a pressure drop of 1500 psi at 0.1 mL/min in H₂O according to the manufacturer. The flow rates of both pumps are set at 0.115 mL/min. After the splitting, the minor flow is 0.01 mL/min for both decane and TCB, determined by weighing the collected solvents for more than 30 min. The volume of the collected eluent is determined by the mass and the densities of the solvents at room temperature. The minor flow is delivered to the HTLC column for separation. The main flow is sent back to the solvent reservoir. A 50- μ L mixer (Shimadzu) is connected after the splitters to mix the solvents from Shimadzu pumps. The mixed solvents are then delivered to the injector in the oven of Waters (Milford, MA, USA) GPCV2000. A HypercarbTM column (2.1 $\times$ 100 mm, 5 μ m particle size) is connected between the injector and a 10-port VICI valve (Houston, TX, USA). The valve is equipped with two 60- μ L sample loops. The valve is used to continuously sample eluent from the first dimension (D1) HTLC column to the second dimension (D2) SEC column. The pump of Waters GPCV2000 and a PLgel RapidTM-M column (10 $\times$ 100 mm, 5 μ m particle size) are connected to the VICI valve for D2 size exclusion chromatography (SEC). The symmetric configuration is used for the connections as described in the literature (Brun, Y.; Foster, P. *J. Sep. Sci.* 2010, *33*, 3501). A dual-angle light scattering detector (PD2040, Agilent, Santa Clara, CA, USA) and an IR5 inferred absorbance detector are connected after the SEC column for measurement of concentration, composition, and molecular weight.

[0079] *Separation for HTLC:* Approximately 30 mg are dissolved in 8-mL decane by gently shaking the vial at 160 °C for 2 hours. The decane contains 400 ppm BHT(2,6-Di-tert-butyl-4-methylphenol) as the radical scavenger. The sample vial is then transferred to the autosampler of GPCV2000 for injection. The temperatures of the autosampler, the injector, both the Hypercarb and the PLgel columns, the 10-port VICI valve, and both the LS and IR5 detectors are maintained at 140 °C throughout the separation.

[0080] The initial conditions before injection are as follows. The flow rate for the HTLC column is 0.01 mL/min. The solvent composition in the D1 Hypercarb column is 100% decane. The flow rate for the SEC column is 2.51 mL/min at room temperature. The solvent composition in the D2 PLgel column is 100% TCB. The solvent composition in the D2 SEC column does not change throughout the separation.

[0081] A 311- μ L aliquot of sample solution is injected into the HTLC column. The injection triggers the gradient described below:

From 0 – 10 min, 100% decane/ 0% TCB;

From 10 – 651 min, TCB is increased linearly from 0% TCB to 80% TCB.

The injection also triggers the collection of the light scattering signal at 15° angle (LS15) and the “measure” and “methyl” signals from IR5 detector (IR_{measure} and IR_{methyl}) using EZChrom™ chromatography data system (Agilent). The analog signals from detectors are converted to digital signals through a SS420X analog-to-digital converter. The collection frequency is 10 Hz. The injection also triggers the switch of the 10-port VICI valve. The switch of the valve is controlled by the relay signals from the SS420X converter. The valve is switched every 3 min. The chromatograms are collected from 0 to 651 min. Each chromatogram consist of $651/3 = 217$ SEC chromatograms.

[0082] After the gradient separation, 0.2 mL of TCB and 0.3 mL of decane are used to clean and re-equilibrate the HTLC column for next separation. The flow rate of this step is 0.2 mL/min, delivered by a Shimadzu LC-20 AB pump connected to the mixer.

[0083] *Data Analysis for HTLC:* The 651 min raw chromatogram is first unfolded to give 217 SEC chromatograms. Each chromatogram is from 0 to 7.53 mL in the unit of 2D elution volume. The integration limit is then set and the SEC chromatograms undergo spike removal, baseline correction, and smoothing. The process is similar to batch analysis of multiple SEC chromatograms in conventional SEC. The sum of all the SEC chromatograms is inspected to ensure both left side (upper integration limit) and right side (lower integration limit) of the peak were at the baseline as zero. Otherwise, the integration limit is adjusted to repeat the process.

[0084] Each SEC chromatogram n from 1 to 217 yields an X-Y pair in the HTLC chromatogram, where n is the fraction number:

$$X_n = \text{elution volume (mL)} = \text{D1 flow rate} \times n \times t_{\text{switch}}$$

where $t_{\text{switch}} = 3\text{min}$ is the switch time of the 10-port VICI valve.

$$Y_n = \text{signal intensity (Voltage)} = \sum_{\text{peak start}}^{\text{peak end}} IR_{\text{measure},n}$$

[0085] The above equation uses IR_{measure} signal as the example. The obtained HTLC chromatogram shows the concentrations of the separated polymeric components as a function of elution volume. The normalized IR_{measure} HTLC chromatogram includes Y represented by dW/dV , meaning the normalized weight fractions with respect to the elution volume.

[0086] X-Y pairs of data are also obtained from IR_{methyl} and LS15 signals. The ratio of $IR_{\text{methyl}}/IR_{\text{measure}}$ is used to calculate composition after calibration. The ratio of $LS15/IR_{\text{measure}}$ is used to calculate weight-average molecular weight (M_w) after calibration.

[0087] Calibration follows the procedures of Lee et al., *ibid.* High density polyethylene (HDPE), *isotactic* polypropylene (*iPP*), and ethylene-propylene copolymer with propylene contents of 20.0, 28.0, 50.0, 86.6, 92.0, and 95.8 wt% P are used as the standards for $IR_{\text{methyl}}/IR_{\text{measure}}$ calibration. The composition of the standards are determined by NMR. The standards are run by SEC with IR5 detector. The obtained $IR_{\text{methyl}}/IR_{\text{measure}}$ ratios of the standards are plotted as a function of their compositions, yielding the calibration curve.

[0088] The HDPE reference is used for routine LS15 calibration. The M_w of the reference is predetermined by GPC as 104.2 kg/mol with LS and RI (refractive index) detectors. GPC uses NBS 1475 as the standard in GPC. The standard has a certified value of 52.0 kg/mol by NIST. Between 7 to 10 mg of the standard is dissolved in 8-mL decane at 160 °C. The solution is injected to the HTLC column in 100% TCB. The polymer is eluted under constant 100% TCB at 0.01 mL/min. Therefore, the peak of the polymer appears at the HTLC column void volume. A calibration constant, Ω , is determined from the total LS15 signals (A_{LS15}) and the total IR_{measure} signals ($A_{IR, \text{measure}}$):

$$\Omega = \frac{A_{LS15}}{A_{IR, \text{measure}} M_w}$$

[0089] The experimental $LS15/IR_{\text{measure}}$ ratio is then converted to M_w through Ω .

[0090] C¹³ Nuclear Magnetic Resonance (NMR): For Sample Preparation, samples are prepared by adding approximately 2.7g of a 50/50 mixture of tetrachloroethane-d₂/orthodichlorobenzene that is 0.025M in chromium acetylacetonate (relaxation agent) to 0.21g sample in a 10mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150°C.

[0091] For Data Acquisition Parameters, data is collected using a Bruker 400 MHz spectrometer equipped with a Bruker Dual DUL high-temperature CryoProbe. The data is acquired using 320 transients per data file, a 7.3 sec pulse repetition delay (6 sec delay + 1.3 sec acq. time), 90 degree flip angles, and inverse gated decoupling with a sample temperature of 125°C. All measurements are made on non-spinning samples in locked mode. Samples are homogenized immediately prior to insertion into the heated (130°C) NMR Sample changer, and are allowed to thermally equilibrate in the probe for 15 minutes prior to data acquisition. The NMR may be used to determine total weight percent of ethylene, e.g., with respect to the crystalline block composite index and modified block composite index discussed below.

[0092] Gel permeation chromatographic (GPC) system consists of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140°C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160°C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

[0093] Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 “cocktail” mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80°C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular

weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

$$M_{\text{polypropylene}} = 0.645(M_{\text{polystyrene}}).$$

[0094] Transmission Electron Microscopy (TEM) is for morphology determination. Polymer films are prepared by compression molding followed by fast quenching. The polymer is pre-melted at 190°C for 1 minute at 1000 psi and then pressed for 2 minutes at 5000 psi and then quenched between chilled platens (15-20°C) for 2 minutes. The compression molded films are trimmed so that sections could be collected near the core of the films. The trimmed samples are cryopolished prior to staining by removing sections from the blocks at -60°C to prevent smearing of the elastomer phases. The cryo-polished blocks are stained with the vapor phase of a 2% aqueous ruthenium tetroxide solution for 3hrs at ambient temperature. The staining solution is prepared by weighing 0.2gm of ruthenium (III) chloride hydrate ($\text{RuCl}_3 \times \text{H}_2\text{O}$) into a glass bottle with a screw lid and adding 10ml of 5.25% aqueous sodium hypochlorite to the jar. The samples are placed in the glass jar using a glass slide having double sided tape. The slide is placed in the bottle in order to suspend the blocks about 1 inch above the staining solution. Sections of approximately 90 nanometers in thickness are collected at ambient temperature using a diamond knife on a Leica EM UC6 microtome and placed on 600 mesh virgin TEM grids for observation.

[0095] Image Collection - TEM images are collected on a JEOL JEM-1230 operated at 100kV accelerating voltage and collected on a Gatan-791 and 794 digital cameras.

[0096] Polymer Characterization Methods, a discussion of the methods used may also be found in, e.g., U.S. Patent Publication Nos. 2011/0313106, 2011/0313107, and 2011/0313108. For example, these methods are used with respect to the crystalline block composite and block composite materials discussed below.

Block Composite Preparation and Characterization

[0097] BC1, BC2, BC3, BC4, and BC5 (Block Composite) are each propylene-ethylene/ethylene-propylene (P-E/E-P) based block composite samples that are prepared using two continuous stirred tank reactors (CSTR) connected in series. The first reactor is approximately 12 gallons in volume while the second reactor is

approximately 26 gallons. Each reactor is hydraulically full and set to operate at steady state conditions. Monomers, Solvent, Catalyst, Cocatalyst-1, Cocatalyst-2, and CSA 1 are flowed to the first reactor according to the process conditions outlined in Table 1. Then, the first reactor contents, as described in Table 1A, below, are flowed to a second reactor in series. Additional Catalyst, Cocatalyst-1, and Cocatalyst-2 are added to the second reactor.

[0098] Catalyst, ([rel-2',2''-[(1R,2R)-1,2-cyclohexanediylbis(methyleneoxy-κO)]bis[3-(9H-carbazol-9-yl)-5-methyl[1,1'-biphenyl]-2-olato-κO]](2-)]dimethyl-hafnium) and Cocatalyst-1, a mixture of methyldi(C₁₄₋₁₈ alkyl)ammonium salts of tetrakis(pentafluorophenyl)borate, prepared by reaction of a long chain trialkylamine (Armeen™ M2HT, available from Akzo-Nobel, Inc.), HCl and Li[B(C₆F₅)₄], substantially as disclosed in U.S. Patent No. 5,919,9883, Ex. 2., are purchased from Boulder Scientific and used without further purification.

[0099] CSA-1 (diethylzinc or DEZ) and Cocatalyst-2 (modified methylalumoxane (MMAO)) are purchased from Akzo Nobel and used without further purification.

[00100] The Solvent is a hydrocarbon mixture (ISOPAR®E) obtainable from ExxonMobil Chemical Company and purified through beds of 13-X molecular sieves prior to use.

[00101] The resultant block composites for BC1, BC2, and BC3 each have an ethylene content of greater than 5 wt% in the propylene-ethylene and an ethylene content greater than 65 wt% in the ethylene-propylene. The process conditions for preparing BC1, BC2, and BC3 are shown in Table 1, below.

Table 1

Material	BC1		BC2		BC3	
Reactor	1st Reactor	2nd Reactor	1st Reactor	2nd Reactor	1st Reactor	2nd Reactor
Reactor Control Temp.(°C)	105	117	105	114	105	117
Solvent Feed (lb/hr)	485	569	351	462	471	545
Propylene Feed (lb/hr)	13.4	68.8	13.3	53.0	21.4	71.1
Ethylene Feed (lb/hr)	68.6	10.5	48.5	6.1	62.2	8.8
Hydrogen Feed SCCM)	0	0	0	0	0	0
Reactor Ethylene Conc. (g/L)	6.43	0.05	5.46	0.14	5.32	0.17
Reactor Propylene Conc. (g/L)	2.04	2.09	2.34	2.08	3.09	2.07
Catalyst Efficiency (gPoly/gM) *1.0E6	1.78	0.46	1.44	0.50	1.78	0.44
Catalyst Flow (lb/hr)	0.57	0.58	0.81	2.42	0.88	1.24
Catalyst Conc. (ppm)	75	300	50	50	50	150
Cocatalyst-1 Flow (lb/hr)	0.26	0.34	0.23	0.24	0.27	0.38
Cocatalyst-1 Conc. (ppm)	1794	4693	1795	4693	1794	4693
Cocatalyst-2 Flow (lb/hr)	0.39	0.87	0.37	0.62	0.4	0.89
Cocatalyst-2 Conc. (ppm)	494	397	494	397	494	397
DEZ Flow (lb/hr)	3.74	0	2.75	0	3.29	0
DEZ Conc. (ppm)	25998	0	26000	0	25998	0

[00102] BC1 is a propylene-ethylene/ethylene-propylene (P-E/E-P) based block composite having 50 wt% of propylene-ethylene (having an ethylene content of 15 wt%) and 50 wt% of ethylene-propylene (having ethylene content of 84 wt%).

[00103] BC2 is a propylene-ethylene/ethylene-propylene (P-E/E-P) based block composite having 50 wt% of propylene-ethylene (having an ethylene content of 12 wt%) and 50 wt% of ethylene-propylene (having an ethylene content of 79 wt%).

[00104] BC3 is a propylene-ethylene/ethylene-propylene (P-E/E-P) based block composite having 50 wt% of propylene-ethylene (having an ethylene content of 12 wt%) and 50 wt% of ethylene-propylene (having an ethylene content of 75 wt%).

[00105] The resultant block composites for BC4 and BC5, each have an ethylene content of 9 wt% in the propylene-ethylene and an ethylene content greater than 65 wt% in the ethylene-propylene. The process conditions for preparing BC4 and BC5, are shown in Table 2, below.

Table 2

Material	BC4		BC5	
	1st Reactor	2nd Reactor	1st Reactor	2nd Reactor
Reactor Control Temp.(°C)	107	119	115	116
Solvent Feed (lb/hr)	618	690	556	633
Propylene Feed (lb/hr)	24.6	101.1	30.6	91.9
Ethylene Feed (lb/hr)	88.9	8.1	70.6	8.4
Hydrogen Feed SCCM)	0	0	0	0
Reactor Ethylene Conc. (g/L)	5.26	0.14	0.75	0.08
Reactor Propylene Conc. (g/L)	2.63	2.47	2.04	2.32
Catalyst Efficiency (gPoly/gM) *1.0E6	1.69	0.36	1.47	0.35
Catalyst Flow (lb/hr)	1.26	2.06	0.34	1.41
Catalyst Conc. (ppm)	50	150	200	200
Cocatalyst-1 Flow (lb/hr)	0.37	0.62	0.26	0.57
Cocatalyst-1 Conc. (ppm)	1794	4693	2496	4693
Cocatalyst-2 Flow (lb/hr)	0.58	1.35	0.32	0.43
Cocatalyst-2 Conc. (ppm)	494	397	995	995
DEZ Flow (lb/hr)	4.85	0	3.31	0
DEZ Conc. (ppm)	25998	0	34997	0

[00106] BC4 is a propylene-ethylene/ethylene-propylene (P-E/E-P) based block composite having 50 wt% of propylene-ethylene (having an ethylene content of 9 wt%) and 50 wt% of ethylene-propylene (having an ethylene content of 79 wt%).

[00107] BC2 is a propylene-ethylene/ethylene-propylene (P-E/E-P) based block composite having 50 wt% of propylene-ethylene (having an ethylene content of 9 wt%) and 50 wt% of ethylene-propylene (having an ethylene content of 70 wt%).

[00108] A comparative Crystalline Block Composite CBCA (Block Composite) is synthesized in dual reactors in series, using a similar method as described above with respect to the BC1 to BC5 samples.

[00109] The process conditions for preparing CBCA are shown in Table 3, below.

Table 3

Material	CBCA	
	1st Reactor	2nd Reactor
Reactor Control Temp.(°C)	153	130
Solvent Feed (lb/hr)	343	101
Propylene Feed (lb/hr)	3.40	44.10
Ethylene Feed (lb/hr)	47.1	0.0
Hydrogen Feed SCCM)	0.0	0.0
Reactor Ethylene Conc. (g/L)	2.06	0
Reactor Propylene Conc. (g/L)	0	2.42
Catalyst Efficiency (gPoly/gM) *1.0E6	0.247	0.138
Catalyst Flow (lb/hr)	0.31	0.53
Catalyst Conc. (ppm)	600	600
Cocatalyst-1 Flow (lb/hr)	0.62	0.53
Cocatalyst-1 Conc. (ppm)	2729	7082
Cocatalyst-2 Flow (lb/hr)	0.72	0.73
Cocatalyst-2 Conc. (ppm)	3442	1893
DEZ Flow (lb/hr)	1.49	0
DEZ Conc. (ppm)	30000	0

[00110] Referring to the above, the resultant CBCA is an isostatic polypropylene/ethylene-propylene (iPP/E-P) based crystalline block composite that include 50 wt% of iPP and 50 wt% of the ethylene-propylene (having an ethylene content of 92 wt%).

[00111] The measured properties of BC1 to BC5 and CBCA are provided in Table 4, below.

Table 4

	MFR (230°C/ 2.16 kg)	wt% PP from HTLC Separation	Mw Kg/mol	Mw/ Mn	Total wt% C ₂	T _m (°C) Peak 1 (Peak 2)	T _c (°C)	Melt Enthalpy (J/g)	Modified Block Composite Index	Crystalline Block Composite Index
BC1	5.2		107	2.42	49.8	90	69	49	0.681	not applicable
BC2	5.8	17.0	110	2.65	45.8	73	55	44	0.691	not applicable
BC3	4.7		118	2.64	44	62	48	37	0.630	not applicable
BC4	5.6		114	2.63	44.1	76	56	55	0.665	not applicable
BC5	6.029		127	2.90	39.9	84	38	51	0.664	not applicable
CBCA	10.1	20.3	92	3.48	48.1	130 (105)	90	103	not applicable	0.566

Modified Block Composite Index Calculations and Crystalline Block Composite Index Calculations

[00112] CBCI and MBCI provide an estimate of the quantity of block copolymer within the block composite under the assumption that the ratio of CEB/EB to CAO/BO within the diblock is the same as the ratio of ethylene to alpha-olefin in the overall block composite. This assumption is valid for these statistical olefin block copolymers based on the understanding of the individual catalyst kinetics and the polymerization mechanism for the formation of the diblocks via chain shuttling catalysis as described in the specification. This CBCI and MBCI analysis shows that the amount of isolated PP is less than if the polymer was a simple blend of a propylene homopolymer (in this example the CAOP/AOP) and polyethylene (in this example the CEP/EP). Consequently, the polyethylene fraction contains an appreciable amount of propylene that would not otherwise be present if the polymer was simply a blend of polypropylene and polyethylene. To account for this "extra propylene", a mass balance calculation can be performed to estimate the CBCI/MBCI from the amount of the polypropylene and polyethylene fractions and the weight % propylene present in each of the fractions that are separated by HTLC.

[00113] The corresponding MBCI calculations for BC1, BC2, BC3, BC4, and BC5 are provided in Table 5, below.

Table 5

Line #	Variable	Source	MBCI				
			BC1	BC2	BC3	BC4	BC5
1	Overall wt% C3 Total	Measured	50.2	54.2	56	55.9	60.1
2	wt% C3 in PP block/polymer	Measured	85	88	88	91	91
3	wt% C3 in PE block/polymer	Measured	16	21	25	21	30
4	wt fraction PP (in block or polymer)	Eq. 2 below	0.496	0.496	0.492	0.499	0.493
5	wt fraction PE (in block or polymer)	1-Line 4	0.504	0.504	0.508	0.501	0.507
	Analysis of HTLC Separation						
6	wt fraction isolated PP	Measured	0.158	0.153	0.182	0.167	0.166
7	wt fraction PE fraction	Measured	0.842	0.847	0.818	0.833	0.834
8	wt% C3 in PE-fraction	Eq. 4 below	43.7	48.1	48.9	48.9	53.9
9	wt fraction PP-diblock in PE fraction	Eq. 6 below	0.401	0.404	0.379	0.398	0.393
10	wt fraction PE in PE fraction	1-Line 10	0.599	0.596	0.621	0.602	0.607
11	wt fraction Diblock in PE fraction	10/Line 4	0.809	0.816	0.77	0.798	0.796
12	Modified Block Composite Index (MBCI)	Eq. 7.1 below	0.681	0.691	0.630	0.665	0.664

[00114] The corresponding CBCI calculations for comparative CBCA are provided in Table 6, below.

Table 6

Line #	Variable	Source	CBCI
			CBCA
1	Overall wt% C3 Total	Measured	51.900
2	wt% C3 in PP block/polymer	Measured	99.000
3	wt% C3 in PE block/polymer	Measured	10.500
4	wt fraction PP (in block or polymer)	Eq. 2 below	0.468
5	wt fraction PE (in block or polymer)	1-Line 4	0.532
	Analysis of HTLC Separation		
6	wt fraction isolated PP	Measured	0.203
7	wt fraction PE fraction	Measured	0.797
8	wt% C3 in PE-fraction	Eq. 4 below	39.903
9	wt fraction PP-diblock in PE fraction	Eq. 6 below	0.332
10	wt fraction PE in PE fraction	1-Line 10	0.668
11	wt fraction Diblock in PE fraction	10/Line 4	0.710
12	Crystalline Block Composite Index (CBCI)	Eq. 7.2 below	0.566

[00115] Referring to Tables 5 and 6, above, the MBCI/CBCI is measured by first determining a summation of the weight % propylene from each component in the polymer according to Equation 1, below, which results in the overall weight % propylene/C3 (of the whole polymer). This mass balance equation can be used to quantify the amount of the PP and PE present in the block copolymer. This mass balance equation can also be used to quantify the amount of PP and PE in a binary blend or extended to a ternary, or n-component blend. For the BCs and CBCs, the overall amount of PP or PE is contained within the blocks present in the block copolymer and the unbound PP and PE polymers.

$$\text{Wt \% C3}_{\text{Overall}} = w_{\text{PP}}(\text{wt\%C3}_{\text{PP}}) + w_{\text{PE}}(\text{wt\%C3}_{\text{PE}}) \quad \text{Eq. 1}$$

where

w_{PP} = weight fraction of PP in the polymer

w_{PE} = weight fraction of PE in the polymer

$\text{wt\%C3}_{\text{PP}}$ = weight percent of propylene in PP component or block

$\text{wt\%C3}_{\text{PE}}$ = weight percent of propylene in PE component or block

[00116] Note that the overall weight % of propylene (C3) is measured from C¹³ NMR or some other composition measurement that represents the total amount of C3 present in the whole polymer. The weight % propylene in the PP block ($\text{wt\%C3}_{\text{PP}}$) is set to 100 (if applicable) or if otherwise known from its DSC melting point, NMR measurement, or other composition estimate, that value can be put into its place. Similarly, the weight % propylene in the PE block ($\text{wt\%C3}_{\text{PE}}$) is set to 100 (if applicable) or if otherwise known from its DSC melting point, NMR measurement, or other composition estimate, that value can be put into its place. The weight % of C3 is shown in Table 6.

[00117] Calculating the Ratio of PP to PE in the crystalline block composite and/or the specified block composite: Based on Equation 1, the overall weight fraction of PP present in the polymer can be calculated using Equation 2 from the mass balance of the total C3 measured in the polymer. Alternatively, it could also be estimated from a mass balance of the monomer and comonomer consumption during the polymerization. Overall, this represents the amount of PP and PE present in the polymer regardless of whether it is present in the unbound components or in the block copolymer. For a conventional blend, the weight fraction of PP and weight fraction of PE corresponds to

the individual amount of PP and PE polymer present. For the crystalline block composite and the block composite, it is assumed that the ratio of the weight fraction of PP to PE also corresponds to the average block ratio between PP and PE present in this statistical block copolymer.

$$w_{PP} = \frac{wt\%C3_{Overall} - wt\%C3_{PE}}{wt\%C3_{PP} - wt\%C3_{PE}} \quad \text{Eq. 2}$$

where

w_{PP} = weight fraction of PP present in the whole polymer

$wt\%C3_{PP}$ = weight percent of propylene in PP component or block

$wt\%C3_{PE}$ = weight percent of propylene in PE component or block

[00118] To estimate the amount of the block copolymer (diblock) in the Block Composite and/or the Crystalline Block Composite, apply Equations 3 through 5, and the amount of the isolated PP that is measured by HTLC analysis is used to determine the amount of polypropylene present in the diblock copolymer. The amount isolated or separated first in the HTLC analysis represents the ‘unbound PP’ and its composition is representative of the PP block present in the diblock copolymer. By substituting the overall weight % C3 of the whole polymer in the left hand side of Equation 3, and the weight fraction of PP (isolated from HTLC) and the weight fraction of PE (separated by HTLC) into the right hand side of Equation 3, the weight % of C3 in the PE fraction can be calculated using Equations 4 and 5. The PE fraction is described as the fraction separated from the unbound PP and contains the diblock and unbound PE. The composition of the isolated PP is assumed to be the same as the weight % propylene in the PP block as described previously.

$$wt\%C3_{Overall} = w_{PP\ isolated} (wt\%C3_{PP}) + w_{PE-fraction} (wt\%C3_{PE-fraction}) \quad \text{Eq. 3}$$

$$wt\%C3_{PE-fraction} = \frac{wt\%C3_{Overall} - w_{PP\ isolated} (wt\%C3_{PP})}{w_{PE-fraction}} \quad \text{Eq. 4}$$

$$w_{PE-fraction} = 1 - w_{PP\ isolated} \quad \text{Eq. 5}$$

where

$w_{PP\ isolated}$ = weight fraction of isolated PP from HTLC

$w_{PE-fraction}$ = weight fraction of PE separated from HTLC, containing the diblock and unbound

PE

$wt\%C3_{PP}$ = weight % of propylene in the PP; which is also the same amount of propylene present in the PP block and in the unbound PP

$wt\%C3_{PE-fraction}$ = weight % of propylene in the PE-fraction that was separated by HTLC

$wt\%C3_{Overall}$ = overall weight % propylene in the whole polymer

[00119] The amount of wt% C3 in the polyethylene fraction from HTLC represents the amount of propylene present in the block copolymer fraction that is above the amount present in the ‘unbound polyethylene’. To account for the ‘additional’ propylene present in the polyethylene fraction, the only way to have PP present in this fraction is for the PP polymer chain to be connected to a PE polymer chain (or else it would have been isolated with the PP fraction separated by HTLC). Thus, the PP block remains adsorbed with the PE block until the PE fraction is separated.

[00120] The amount of PP present in the diblock is calculated using Equation 6.

$$w_{PP-diblock} = \frac{wt\%C3_{PE-fraction} - wt\%C3_{PE}}{wt\%C3_{PP} - wt\%C3_{PE}} \quad \text{Eq. 6}$$

Where

$wt\%C3_{PE-fraction}$ = weight % of propylene in the PE-fraction that was separated by HTLC

(Equation 4)

$wt\%C3_{PP}$ = weight % of propylene in the PP component or block (defined previously)

$wt\%C3_{PE}$ = weight % of propylene in the PE component or block (defined previously)

$w_{PP-diblock}$ = weight fraction of PP in the diblock separated with PE-fraction by HTLC

[00121] The amount of the diblock present in this PE fraction can be estimated by assuming that the ratio of the PP block to PE block is the same as the overall ratio of PP to PE present in the whole polymer. For example, if the overall ratio of PP to PE is 1:1 in the whole polymer, then it assumed that the ratio of PP to PE in the diblock is also 1:1. Thus, the weight fraction of diblock present in the PE fraction would be weight fraction of PP in the diblock ($w_{PP-diblock}$) multiplied by two. Another way to calculate this is by dividing the weight fraction of PP in the diblock ($w_{PP-diblock}$) by the weight fraction of PP in the whole polymer (Equation 2).

[00122] To further estimate the amount of diblock present in the whole polymer, the estimated amount of diblock in the PE fraction is multiplied by the weight fraction of the PE fraction measured from HTLC. To estimate the crystalline block composite index or the modified block composite index, the amount of diblock copolymer is determined by Equation 7.1 or 7.2, respectively. To estimate the MBCI and the CBCI, the weight fraction of diblock in the PE fraction calculated using Equation 6 is divided

by the overall weight fraction of PP (as calculated in Equation 2) and then multiplied by the weight fraction of the PE fraction. The value of the MBCI and/or CBCI can range from 0 to 1.0, wherein 1.0 would be equal to 100% diblock and zero would be for a material such as a traditional blend or random copolymer.

$$MBCI = \frac{w_{PP-diblock}}{w_{PP}} \cdot w_{PE-fraction} \quad \text{Eq. 7.1 (MBCI)}$$

$$CBCI = \frac{w_{PP-diblock}}{w_{PP}} \cdot w_{PE-fraction} \quad \text{Eq. 7.2 (CBCI)}$$

Where

$w_{PP-diblock}$ = weight fraction of PP in the diblock separated with the PE-fraction by HTLC (Equation 6)

w_{PP} = weight fraction of PP in the polymer

$w_{PE-fraction}$ = weight fraction of PE separated from HTLC, containing the diblock and unbound PE (Equation 5)

[00123] For example, if an isotactic polypropylene block/ethylene-propylene block polymer (diblock polymer) contains a total of 53.3 wt% C3 and is made under the conditions to produce an iPP polymer containing 99 wt% C3 and an PE polymer with 10 wt% C3, the weight fractions of PP and PE are 0.487 to 0.514, respectively (as calculated using Equation 2).

Blend Compositions

[00124] The following materials are principally used in the blends compositions and the corresponding appropriate properties are provided below:

[00125] PP: A polypropylene homopolymer having typical properties of a MFR of 35 grams/10 minutes (230°C/2.16 kg) (available from LyondellBasell and having the designation Pro-fax PD702).

[00126] HDPE: A high density polyethylene having typical properties of a MI of 4.4 grams/10 minutes (190°C/2.16 kg) and a density of 0.952 g/cm³ (available from The Dow Chemical Company and having the designation DOW™ HDPE DMDA-8904).

[00127] E-O: An ethylene-octene polymer having typical properties of a MI of 1.0 grams/10 minutes (190°C/2.16 kg) and a density of 0.870 g/cm³ (available from The Dow Chemical Company and having the designation ENGAGE™ 8100).

[00128] AO: An antioxidant (available as Irganox® B 225 from Ciba).

[00129] All blends were compounded via twin screw extrusion and pelletized for compression and injection molding.

Compression Molded Examples

[00130] Blends for preparation of compression molded samples corresponding to Working Examples 1 to 8 (Table 7) and Comparative Examples A to C (Table 8), are prepared according to the following approximate formulations and are analyzed with respect to the following properties. The compounding of the components is performed on a HAAKE™ Rheomix 3000 lab mixer, with the rotation set at 50 RPM. The mixer is preheated to 190°C, and the mixing is maintained for 5 minutes at 190°C after the ram is secured down. During mixing, an additional amount of 0.2 wt% of the AO is added to each of the formulations. Following compounding and pelletizing, plaques were prepared by compression molding using a Tetrahedron press where the pellets are pre-melted at 190°C for 1 minute at 5,000 pounds of pressure and then pressed at 190°C for 4 minutes at 40,000 pounds of pressure using a 12x12x0.126" mold. The plaques were subsequently quick quench cooled in an ice bath immediately upon removal from the press. The nominal plaque thickness was about 0.125".

[00131] In particular, Working Examples 1 to 8 are prepared according to the following formulations and are analyzed with respect to the following properties:

Table 7

Materials		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
Formulation (wt%)									
BC1		9.0	--	--	--	--	--	--	--
BC2		--	9.0	--	--	--	--	--	--
BC3		--	--	9.0	--	--	5.0	--	--
BC4		--	--	--	9.0	--	--	5.0	--
BC5		--	--	--	--	9.0	--	--	5.0
CBCA		--	--	--	--	--	--	--	--
E-O		--	--	--	--	--	6.0	6.0	6.0
PP		30.5	30.5	30.5	30.5	30.5	29.5	29.5	29.5
HDPE		60.4	60.4	60.4	60.4	60.4	59.4	59.4	59.4
AO		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Properties									
Flexural	Flex Modulus at 1% (ksi)	105	108	105	89	106	90	71	87
Flexural	Flex Modulus at 2% (ksi)	92	95	92	79	94	79	62	76
Tensile	Strain @ Break (%)	21.2	10.4	20.1	33.9	9.7	91.0	116.8	98.6
Tensile	Stress @ Yield (psi)	2620	2681	2660	2811	2798	2250	2360	2288
Izod	Strength ² @ 23°C (kJ/m ²)	58.3	60.8	59.1	55.3	29.9	49.9	65.8	55.9
Izod	Strength ² @ 0°C (kJ/m ²)	18.0	15.0	45.7	11.9	13.0	73.9	68.7	No Break
Izod	Strength ² @ -18°C (kJ/m ²)	10.3	10.4	12.3	8.7	11.3	68.7	51.1	No Break

[00132] Similarly, Comparative Examples A to C are prepared according to the following formulations and are analyzed with respect to the following properties:

Table 8

Materials		Ex. A	Ex. B	Ex. C
Formulation (wt%)				
BC1		--	--	--
BC2		--	--	--
BC3		--	--	--
BC4		--	--	--
BC5		--	--	--
CBCA		--	9.0	--
E-O		--	--	9.0
PP		35.0	30.5	30.5
HDPE		64.9	60.4	60.4
AO		0.1	0.1	0.1
Properties				
Flexural	Flex Modulus at 1% (ksi)	151	135	90
Flexural	Flex Modulus at 2% (ksi)	135	121	79
Tensile	Strain @ Break (%)	2.5	126.7	58.4
Tensile	Stress @ Yield (psi)	3417	3129	2337
Izod	Strength ² @ 23°C (kJ/m ²)	2.2	10.6	40.9
Izod	Strength ² @ 0°C (kJ/m ²)	2.1	5.7	19.7
Izod	Strength ² @ -18°C (kJ/m ²)	2.4	4.9	13.4

[00133] Referring to Tables 7 and 8, each of Working Examples 1 to 8 shows improvement with respect to Izod impact strength at each of 23°C, 0°C, -18°C, compared to Comparative Example A (which includes the HDPE and PP), while still showing comparatively good flexural properties and tensile properties. Similarly, each of Working Examples 1 to 8 shows improvement with respect to Izod impact strength at each of at each of 23°C, 0°C, -18°C, compared to Comparative Example B (which includes the HDPE, PP, and CBCA), while still showing comparatively good flexural properties and other tensile properties.

[00134] Further, Working Examples 1 to 8 show improvement with respect to Izod impact strength at each of at each of 23°C, 0°C, -18°C, compared to Comparative Example C (which includes the HDPE, PP, and E-O), while still showing relatively good flexural properties and tensile properties.

[00135] In addition, FIG. 1 illustrates TEM Morphology for a PP phase (bright phase) dispersed in an HDPE matrix (grey color phase) for Comparative Example A. FIG. 2 illustrates the TEM Morphology for a PP phase (bright phase) dispersed in an HDPE matrix (grey color phase) for Working Example 4. Referring to Working Example 4, the PP phase size is significantly smaller, showing the effect of compatibilization by BC4.

[00136] FIG. 3 illustrates the morphology of CBCA and BC1-5 obtained using TEM. Based on the staining applied, the darker domains are PE and the lighter domains are PP. The worm like, co-continuous phase morphology and fine dispersion of PE and PP phase strongly suggests the presence of high level of block copolymers which acted to compatibilize the PP and PE phases. Standard polymer/polymer blends of PP and PE exhibit gross and phase separated morphologies with an order of magnitude higher domain size.

[00137] Testing of properties is carried out in the ASTM lab according to standard ASTM methods. For the compression molding data, quenched cooled type plaque testing is reported. Flexural Testing (including Flex Modulus, Secant Modulus at 1%, and Secant Modulus at 2%) is measured according to ASTM D790 @ 0.5 in/min. Tensile Properties (including Tensile Modulus, Strain at Break, and Stress at Yield) are measured according to ASTM D636 @ 20 in/min. Izod Impact Testing (at each of 23°C, 0°C, -18°C) is performed according to ASTM D256.

Injection Molded Examples

[00138] Blends for preparation of injection molded samples according to Working Examples 9 to 16, and Comparative Examples D and E, are prepared according to the following approximate formulations and are analyzed with respect to the following properties. Blending and compounding of the examples is performed on a ZSK30 twin screw extruder using a general purpose screw. Temperature is maintained at 200°C and screw RMP of 200. The product is pelletized and injection molded into 4"x6"x0.126" plaques using a mirrored finished mold on a KRAUSS MAFFEI KM110 injection molding machine. Polymer is melted at 200°C and injected at a pressure of 2000 bar over 3.0 to 3.5 seconds. The mold temperature is held at 15-38°C. Mold pressure is maintained at 200-300 bars depending on the material composition for 30 seconds. Cooling time is 20 seconds. The nominal plaque thickness is 0.125 inches. The

specimens were cut in machine direction from the center of the plaques to minimize any impact by edge non-uniformities.

[00139] In particular, Working Examples 9 to 16 (having the same formulation as Working Examples 1 to 8, respectively) are prepared according to the following formulations and are analyzed with respect to the following properties:

Table 9

Materials		Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16
Formulation (wt%)									
BC1		9.0	--	--	--	--	--	--	--
BC2		--	9.0	--	--	--	--	--	--
BC3		--	--	9.0	--	--	5.0	--	--
BC4		--	--	--	9.0	--	--	5.0	--
BC5		--	--	--	--	9.0	--	--	5.0
CBCA		--	--	--	--	--	--	--	--
E-O		--	--	--	--	--	6.0	6.0	6.0
PP		30.5	30.5	30.5	30.5	30.5	29.5	29.5	29.5
HDPE		60.4	60.4	60.4	60.4	60.4	59.4	59.4	59.4
AO		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Properties									
Flexural	Flex Modulus at 1% (ksi)	143	144	135	142	132	131	130	127
Flexural	Flex Modulus at 2% (ksi)	126	127	119	125	117	114	115	112
Tensile	Strain @ Break (%)	74	74	87	84	86	107	127	106
Tensile	Stress @ Yield (psi)	3652	3798	3714	3817	3695	3503	3428	3440
Izod	Strength ² @ 23°C (kJ/m ²)	6.1	6.2	7.2	5.9	7.0	41.2	52.7	49.5
Izod	Strength ² @ 0°C (kJ/m ²)	5.3	5.2	5.6	5.1	5.6	8.0	8.5	9.0
Izod	Strength ² @ -18°C (kJ/m ²)	4.6	4.5	5.0	4.3	5.2	6.9	7.2	7.7

[00140] Similarly, Comparative Examples D and E (having the same formulations as Comparative Examples A to C) are prepared according to the following formulations and are analyzed with respect to the following properties:

Table 10

Materials		Ex. D	Ex. E
Formulation (wt%)			
BC1		--	--
BC2		--	--
BC3		--	--
BC4		--	--
BC5		--	--
CBCA		--	9.0
E-O		--	--
PP		35.0	30.5
HDPE		64.9	60.4
AO		0.1	0.1
Properties			
Flexural	Flex Modulus at 1% (ksi)	170	156
Flexural	Flex Modulus at 2% (ksi)	154	138
Tensile	Strain @ Break (%)	53	86
Tensile	Stress @ Yield (psi)	6639	4018
Izod	Strength ² @ 23°C (kJ/m ²)	3.6	4.3
Izod	Strength ² @ 0°C (kJ/m ²)	3.2	3.5
Izod	Strength ² @ -18°C (kJ/m ²)	3.4	3.6

[00141] Referring to Tables 9 and 10, each of Working Examples 9 to 16 shows improvement with respect to Izod impact strength at each of 23°C, 0°C, -18°C, compared to Comparative Example D (which includes the HDPE and PP), while still showing comparatively good flexural properties and tensile properties. Similarly, each of Working Examples 9 to 16 shows improvement with respect to Izod impact strength at each of 23°C, 0°C, -18°C, compared to Comparative Example E (which includes the

HDPE, PP, and CBCA), while still showing comparatively good flexural properties and other tensile properties.

[00142] Testing of properties is carried out in the ASTM lab according to standard ASTM methods. For the injection molding data, machine direction type plaque testing is reported. Flexural Testing (including Flex Modulus, Secant Modulus at 1%, and Secant Modulus at 2%) is measured according to ASTM D790 @ 0.5 in/min. Tensile Properties (including Tensile Modulus, Strain at Break, and Stress at Yield) are measured according to ASTM D636 @ 2 in/min. Izod Impact Testing (at each of 23°C, 0°C, -18°C) is performed according to ASTM D256.

[00143] Polypropylene rich blends may also be prepared for compression and injection molded samples using the same methods as discussed above with respect to the polyethylene rich blends.

What is claimed is:

1. A composition, comprising:

(A) from 10 wt% to 90 wt% of an ethylene component including at least one ethylene based polymer having an ethylene content of at least 50.0 wt%, based on the total weight of the ethylene based polymer, a melt index from 0.1 g/10 min to 100.0 g/10 min (ASTM D-1238 at 190°C, 2.16 kg), and a density from 0.935 g/cm³ to 0.965 g/cm³;

(B) from 10 wt% to 90 wt% of a propylene component including at least one propylene based polymer having a propylene content of at least 50.0 wt%, based on the total weight of the propylene based polymer, and a melt flow rate from 0.5 g/10 min to 200.0 g/10 min (ASTM D-1238 at 230°C, 2.16 kg);

(C) from 1 wt% to 20 wt% of a composite component including a specified block composite, derived from at least ethylene and an alpha-olefin that is one of a C₃₋₁₀ alpha-olefin, wherein:

the specified block composite includes an ethylene based polymer having an ethylene content from 69 mol% and to 90 mol%, an alpha-olefin based polymer that is derived from at least the alpha-olefin, and a block copolymer comprising an ethylene block and an alpha-olefin block, the ethylene block of the block copolymer having the same composition as the ethylene based polymer in the block composite, and the alpha-olefin block of the block copolymer having the same composition as the alpha-olefin based polymer of the block composite.

2. The composition as claimed in claim 1, wherein the alpha-olefin is propylene.

3. The composition as claimed in claim 1 or claim 2, wherein:

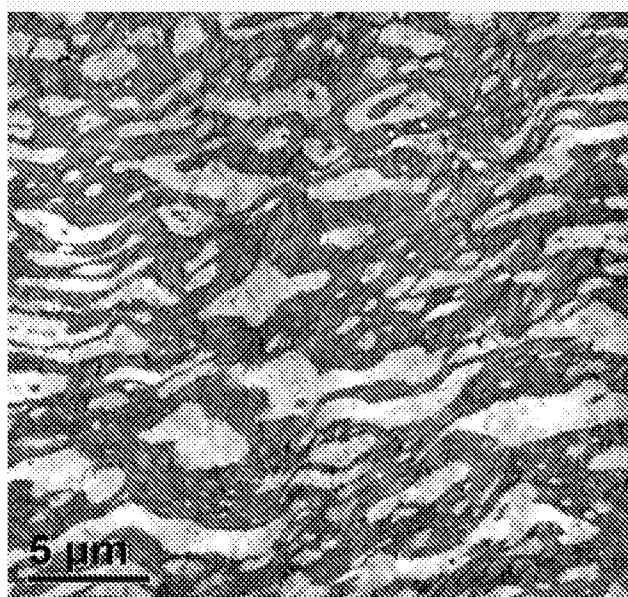
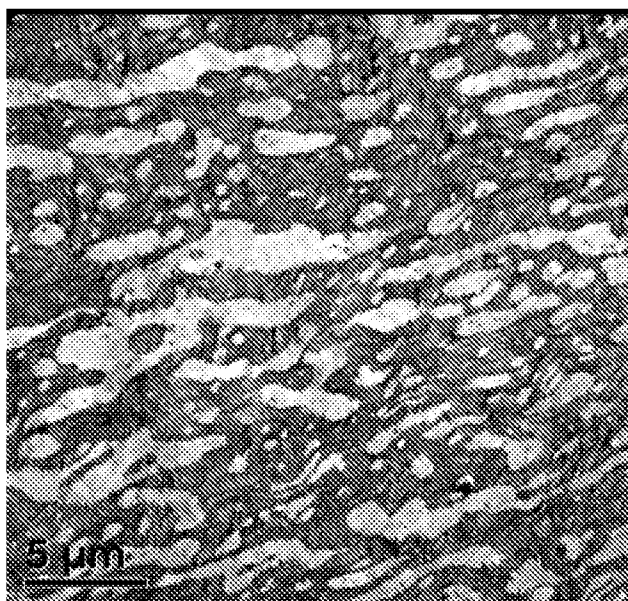
at least the specified block composite is present in the composite component and the alpha-olefin based polymer has an alpha-olefin content of from 61 mol% to 90 mol%; and

the specified block composite has a modified block composite index that is greater than 0 and less than 1.0.

4. The composition as claimed in any one of claims 1 to 3, wherein the propylene based polymer has a density from 0.870 g/ cm³ to 0.910 g/ cm³.
5. The composition as claimed in any one of claims 1 to 4, further comprising an additional polymer component that includes at least one ethylene-octene copolymer.

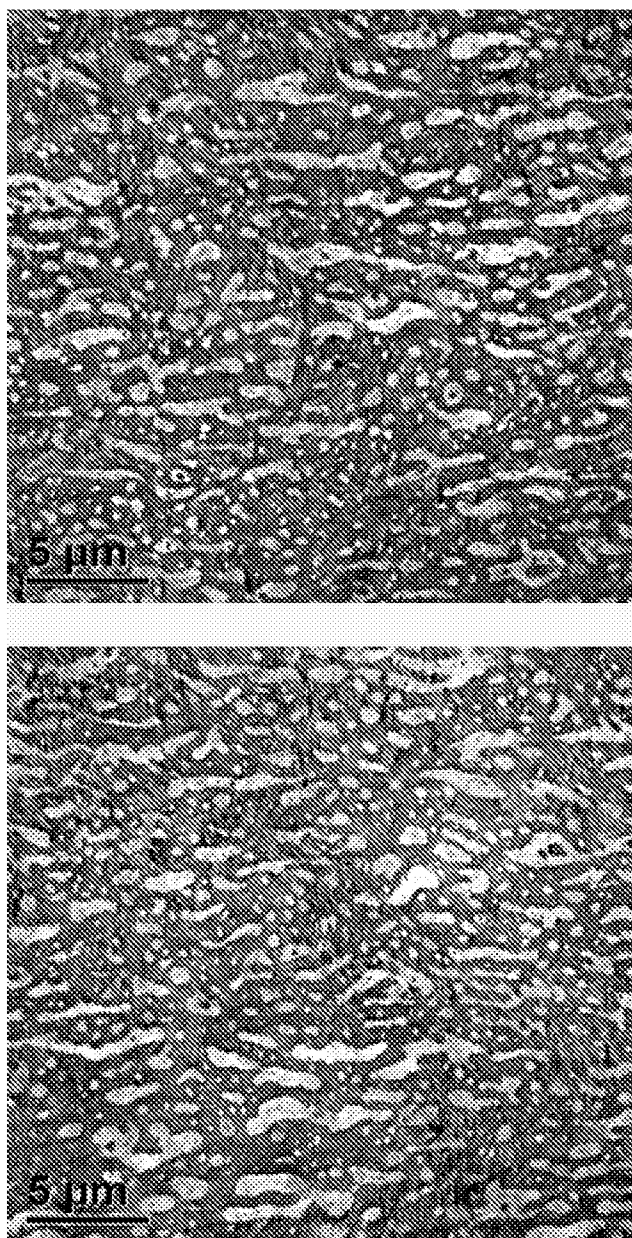
1/3

FIG. 1



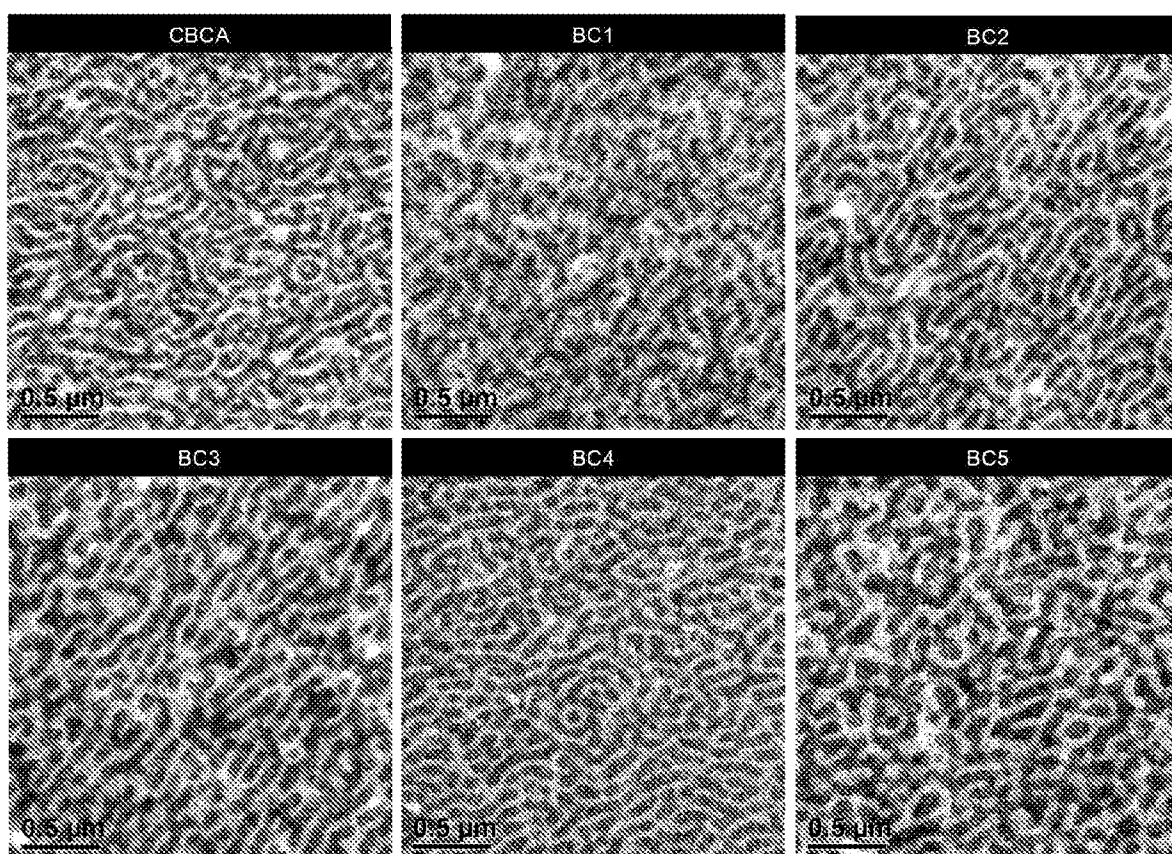
2/3

FIG. 2



3/3

FIG. 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/050650

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L23/06
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 C08F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/044730 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; LIANG WENBIN [US]; WALTON KIM L [US]) 5 April 2012 (2012-04-05) claims 1-15 paragraphs [0025], [0033], [0040], [0045], [0046] page 33; examples Ex V1, Ex V2; table 6 -----	1-5
A	WO 2011/163191 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]; LI PI SHAN COLIN [US]; WALTON KIM L) 29 December 2011 (2011-12-29) claims 1-8 page 38; examples 1-4; table 6 paragraphs [0031], [0041], [0042], [0127], [0132] - [0134] page 36 - page 37; tables 3, 4 page 32; table 1 ----- -/--	1-5



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

25 November 2016

Date of mailing of the international search report

08/12/2016

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

Lippert, Sigrid

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/050650

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2015/057423 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 23 April 2015 (2015-04-23) claim 1 page 45 - page 47; tables C,1,2 -----	1-5
A	WO 2015/094516 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 25 June 2015 (2015-06-25) page 2, line 20 - line 30 page 7, line 3 - line 5 page 7, line 14 - page 11, line 23 page 18, line 19 - line 31 page 20; example BC B; table 2 page 22; examples S1-S5; table 5 page 20 - page 25; examples 1-4 -----	1-5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/050650

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012044730 A1	05-04-2012	BR 112013007286 A2 CN 103228723 A EP 2622014 A1 JP 2013542284 A RU 2013119976 A US 2013183465 A1 WO 2012044730 A1	14-06-2016 31-07-2013 07-08-2013 21-11-2013 10-11-2014 18-07-2013 05-04-2012
WO 2011163191 A1	29-12-2011	CN 103080206 A EP 2582749 A1 JP 5860043 B2 JP 2013529707 A KR 20130026477 A SG 186416 A1 WO 2011163191 A1	01-05-2013 24-04-2013 16-02-2016 22-07-2013 13-03-2013 30-01-2013 29-12-2011
WO 2015057423 A1	23-04-2015	CN 105593286 A EP 3058027 A1 KR 20160072128 A TW 201527382 A US 2016264765 A1 WO 2015057423 A1	18-05-2016 24-08-2016 22-06-2016 16-07-2015 15-09-2016 23-04-2015
WO 2015094516 A1	25-06-2015	CA 2933637 A1 CN 105793347 A EP 3083816 A1 KR 20160100991 A US 2016289433 A1 WO 2015094516 A1	25-06-2015 20-07-2016 26-10-2016 24-08-2016 06-10-2016 25-06-2015