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

(72) Inventor; and
(71) Applicant *(for US only)*: **HU, Yushan** [CN/US]; 11311 Palm Bay St., Pearland, Texas 77584 (US).

(72) Inventors: **LORENZO, Arnaldo**; 5201 Kendall Glen Ct., Rosharon, Texas 77583 (US). **PATEL, Rajen**; 220 Arrowhead Drive, Lake Jackson, Texas 77566 (US). **MARCHAND, Gary**; 6277 Tezcuco Ct., Gonzales, Louisiana 70737 (US). **YUN, Xiaobing**; Room 101, Unit 2, 3rd Building, Lecheng International Apartment, South 2nd Road, Baiziwang, Chaoyang District, Beijing 100022 (CN).

(74) Agent: **WU, FENG & ZHANG CO.**; Room 305, Tower B, BEIJING AEROSPACE CPMIEC BUILDING, No.30 Haidian South Road, Haidian District, Beijing 100080 (CN).

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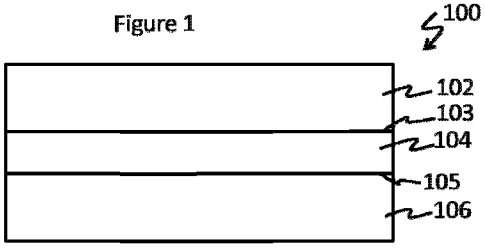
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Figure 1



(57) Abstract: Disclosed herein is a multilayer film comprising a first layer and a second layer; and a tie layer; where the tie layer comprises a crystalline block composite and where the tie layer is disposed between the first layer and the second layer; the first layer being disposed on a first surface of the tie layer; the second layer being disposed on a second surface of the tie layer; where the second surface is opposedly disposed to the first surface; where the crystalline block composite comprises a crystalline ethylene based polymer, a crystalline alpha-olefin based polymerand a block copolymer comprising a crystalline ethylene block and a crystalline alpha- olefin block.

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MULTILAYER FILM, METHODS OF MANUFACTURE THEREOF AND ARTICLES COMPRISING THE SAME

BACKGROUND

This disclosure relates to multilayer film, methods of manufacture thereof and to articles comprising the same.

Cast polypropylene (CPP) films have been available for many years. Raw material prices and new packaging concepts have also had a big influence in promoting CPP films as a good alternative for the packaging industry that uses flexible films. CPP films aregenerally coextruded with propylene-based polymer with a lower melting range than homopolypropylene as a sealant layer, to facilitate a lower heat seal initiation temperature– e.g., random polypropylene copolymers, or terpolymers of propylene-ethylene-butene. However, the seal initiation temperature is high for random polypropylene copolymers or terpolymer-polypropylene.

On the other hand, linear low density polyethylene (LLDPE), particularly metallocene based polyethylenes, provides high seal performance. However, inherent incompatibility between the PP and LLDPE causes delamination between PP and LLDPE layers, resulting in poor adhesion and seal strength. It is therefore desirable to have packaging films that do not undergo delamination.

SUMMARY

Disclosed herein is a multilayer film comprising a first layer and a second layer; and a tie layer; where the tie layer comprises a crystalline block composite and where the tie layer is disposed between the first layer and the second layer; the first layer being disposed on a first surface of the tie layer; the second layer being disposed on a second surface of the tie layer; where the second surface is opposedly disposed to the first surface; where the crystalline block composite comprises a crystalline ethylene based polymer, a crystalline alpha-olefin based polymerand a block copolymer comprising a crystalline ethylene block and a crystalline alpha-olefin block, and where the crystalline ethylene based polymer is present in an amount of at least 80 mole percent, based on the total number of moles of the crystalline ethylene based polymer.

Disclosed herein too is a method of manufacturing a multilayer film comprisingcoextruding a multilayer film comprisinga first layer and a second layer; and a tie

layer; where the tie layer comprises a crystalline block composite and where the tie layer is disposed between the first layer and the second layer; the first layer being disposed on a first surface of the tie layer; the second layer being disposed on a second surface of the tie layer; where the second surface is opposedly disposed to the first surface; where the crystalline block composite comprises a crystalline ethylene based polymer, a crystalline alpha-olefin based polymerand a block copolymer comprising a crystalline ethylene block and a crystalline alpha-olefin block; andblowing or casting the multilayer film.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic of the multilayer film;

Figure 2 is a graphical plot showing the heat seal results for Example 1 and for Comparative Examples A, B and C.

DETAILED DESCRIPTION

"Composition" and like terms mean a mixture of two or more materials, such as a polymer which is blended with other polymers or which contains additives, fillers, or the like. Included in compositions are pre-reaction, reaction and post-reaction mixtures the latter of which will include reaction products and by-products as well as unreacted components of the reaction mixture and decomposition products, if any, formed from the one or more components of the pre- reaction or reaction mixture.

"Blend", "polymer blend" and like terms mean a composition 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. Blends are not laminates, but one or more layers of a laminate may contain a blend.

"Polymer" means a compound prepared by polymerizing monomers, whether of the same or a different type. The generic term polymer thus embraces the term homopolymer, usually employed to refer to polymers prepared from only one type of monomer, and the term interpolymer as defined below. It also embraces all forms of interpolymers, e.g., random, block, etc. The terms "ethylene/a-olefin polymer" and "propylene/a-olefin polymer" are indicative of

interpolymers as described below. It is noted that although a polymer is often referred to as being "made of" monomers, "based on" a specified monomer or monomer type, "containing" a specified monomer content, or the like, this is obviously understood to be referring to the polymerized remnant of the specified monomer and not to the unpolymerized species.

"Interpolymer" means a polymer prepared by the polymerization of at least two different monomers. This generic term includes copolymers, usually employed to refer to polymers prepared from two or more different monomers, and includes polymers prepared from more than two different monomers, e.g., terpolymers, tetrapolymers, etc.

"Polyolefin", "polyolefin polymer", "polyolefin resin" and like terms mean a polymer produced from a simple olefin (also called an alkene with the general formula C_nH_{2n}) as a monomer. Polyethylene is produced by polymerizing ethylene with or without one or more comonomers, polypropylene by polymerizing propylene with or without one or more comonomers, etc. Thus, polyolefins include interpolymers such as ethylene-α-olefin copolymers, propylene-α-olefin copolymers, etc.

"Melting Point" as used here (also referred to a melting peak in reference to the shape of the plotted DSC curve) is typically measured by the DSC (Differential Scanning Calorimetry) technique for measuring the melting points or peaks of polyolefins as described in USP 5,783,638. It should be noted that many blends comprising two or more polyolefins will have more than one melting point or peak; many individual polyolefins will comprise only one melting point or peak.

The term 'and/or" includes both "and" as well as "or". For example, the term A and/or B is construed to mean A, B or A and B.

Disclosed herein is a multilayer crystalline polypropylene film structure with an enhanced sealing property. The multilayer film structurescomprise three layers: a first, outer or skin layer that comprises polyethylene; a tie layer that comprises a diblock copolymer; and a second layer that comprises polypropylene. The second layer is bonded to the first layer by the tie layer. Such multilayer films possess excellent seal properties (e.g.,heat seal and hot tack) in comparison with the random copolymer or polypropylene terpolymers as a sealant.

The multilayered film displays good heat seal strength, low heat seal initiation temperature as well as broad hot tack window, which makes them useful in packaging food products. The multilayered film comprises at least 3 layers, one of which is a tie layer that

comprises a crystalline block composite (CBC), optionally a polyolefin based elastomer; optionally a polypropylene and optionally a polyethylene. The tie layer is used to bond a first layer that comprises polyethylene to a second layer (that is opposedly disposed to the first layer) that comprises a polypropylene.

With reference now to the Figure 1, a multilayer film 100 comprises a first layer 102 (also called the outer layer or the skin layer), a tie layer 104 and a second layer 106. The tie layer 104 comprises a first surface 103 and a second surface 105 that are opposedly disposed to each other. The first layer 102 contacts the tie layer 104 at the first surface 103, while the second layer 106 (that is opposedly disposed to the first layer 102) contacts the tie layer 104 at the second surface 105.

As noted above, the tie layer 104 comprises a crystalline block composite (CBC), optionally a polyolefin based elastomer; optionally a polypropylene and optionally a polyethylene.

The term "crystalline block composite" (CBC) refers to polymers having three components: a crystalline ethylene based polymer (CEP) (also referred to herein as a soft polymer), a crystalline alpha-olefin based polymer (CAOP) (also referred to herein as a hard polymer), and a block copolymer comprising a crystalline ethylene block (CEB) and a crystalline alpha-olefin block (CAOB), wherein the CEB of the block copolymer is the same composition as the CEP in the block composite and the CAOB of the block copolymer is the same composition as the CAOP of the block composite. Additionally, 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. When produced in a continuous process, the crystalline block composites desirably have a polydispersity index (PDI) from 1.7 to 15, specifically 1.8 to 10, specifically from 1.8 to 5, more specifically from 1.8 to 3.5. Such crystalline block composites are described in, for example, US Patent Application Publication Nos. 2011/0313106, 2011/0313108 and 2011/0313108, all published on December 22nd, 2011, incorporated herein by reference with respect to descriptions of the crystalline block composites, processes to make them and methods of analyzing them.

The crystalline ethylene polymer (CEP) (i.e., the soft block) comprises blocks of polymerized ethylene units in which any comonomer content is 10 mol% or less, specifically between 0 mol% and 10 mol%, more specifically between 0 mol% and 7 mol% and most

specifically between 0 mol% and 5 mol%. The crystalline ethylene polymer has corresponding melting points that are specifically 75°C and above, specifically 90°C and above, and more specifically 100°C and above.

The crystalline alpha-olefin based polymer (CAOP)comprises highly crystalline blocks of polymerized alpha olefin units in which the monomer is present in an amount greater than 83mol percent, specifically greater than 87mol percent, more specifically greater than 90mol percent, and specifically greater than 95mol percent, based on the total weight of thecrystalline alpha-olefin based polymer. In an exemplary embodiment, the polymerized alpha olefin unit is polypropylene. The comonomer content in the CAOPs is less than 17mol percent, and specifically less than 13mol percent, and more specifically less than 10mol percent, and most specifically less than 5mol%.CAOPs with propylene crystallinity have corresponding melting points that are 80°C and above, specifically 100°C and above, more specifically 115°C and above, and most specifically 120°C and above. In some embodiments, the CAOP comprise all or substantially all propylene units.

Examples of other alpha-olefin units (in addition to the propylene) that may be used in the CAOP contain 4 to 10 carbon atoms. Examples of these are 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene are the most preferred. Preferred diolefins are isoprene, butadiene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 1,7-octadiene, 1, 9-decadiene, dicyclopentadiene, methylene-norbornene, 5-ethylidene-2-norbornene, or the like, or a combination comprising at least one of the foregoing alpha-olefin units.

The block copolymer of the crystalline block composite comprises a crystalline ethylene block (CEB) and a crystalline alpha olefin block (CAOB). In thecrystalline ethylene block (CEB), ethylenemonomer is present in an amount greater than 90 mol%, specifically greater than 93mol percent, more specifically greater than 95mol percent, and specifically greater than 90 mol percent, based on the total weight of the CEB. In an exemplary embodiment, thecrystalline ethylene block (CEB) polymer is polyethylene. The polyethylene is present in an amount greater than 90 mol%, specifically greater than 93mol percent, and more specifically greater than 95mol percent, based on the total weight of the CEB. If any comonomer is present in in the CEB it is present in an amount of less than 10 mole%, specifically less than 5 mole%, based on the total number of moles of the CEB.

The CAOB comprises a polypropylene block that is copolymerized with other alpha-

olefin units that contain 4 to 10 carbon atoms. Examples of the other alpha-olefin units are provided above. The polypropylene is present in the CAOB in an amount of greater than or equal to 83 mole%, specificallygreater than 87 mole%, and more specifically greater than 90 mole%, based on the total number of moles of the CAOB. The comonomer content in the CAOBs is less than 17mol percent, and specifically less than 13mol percent, and more specifically less than 10mol percent, based on the total number of moles in the CAOB.CAOBs with propylene crystallinity have corresponding melting points that are 80°C and above, specifically 100°C and above, more specifically 115°C and above, and most specifically 120°C and above. In some embodiments, the CAOB comprise all or substantially all propylene units.

In one embodiment, the crystalline block composite polymers comprise propylene, 1-butene or 4-methyl-1-pentene and one or more comonomers. Specifically, the block composites comprise in polymerized form propylene and ethylene and/or one or more C_{4-20} α-olefin comonomers, and/or one or more additional copolymerizable comonomers or they comprise 4-methyl-1-pentene and ethylene and/or one or more C_{4-20} α-olefin comonomers, or they comprise 1-butene and ethylene, propylene and/or one or more C_5-C_{20} α-olefin comonomers and/or one or more additional copolymerizable comonomers. Additional suitable comonomers are selected from diolefins, cyclic olefins, and cyclic diolefins, halogenated vinyl compounds, and vinylidene aromatic compounds. Preferably, the monomer is propylene and the comonomer is ethylene.

Comonomer content in the crystalline block composite polymers may be measured using any suitable technique, with techniques based on nuclear magnetic resonance (NMR) spectroscopy preferred.

The crystalline block composites have a melting point Tm greater than 100°Cspecifically greater than 120°C, and more specifically greater than 125°C. In an embodiment, the Tm is in the range of from 100°C to 250°C, more specifically from 120°C to 220°C and also specifically in the range of from 125°C to 220°C. Specifically the melt flow ratio (MFR) of the block composites and crystalline block composites is from 0.1 to 1000 dg/min, more specifically from 0.1 to 50 dg/min and more specifically from 0.1 to 30 dg/min.

In an embodiment, the crystalline block composites have a weight average molecular weight (Mw) from 10,000 to about 2,500,000 grams per mole (g/mole), specifically from 35000 to about 1,000,000 and more specifically from 50,000 to about 300,000, specifically from 50,000 to about 200,000 g/mole. The sum of the weight percents of soft copolymer, hard polymer and

block copolymer equals 100%.

In an embodiment, the crystalline block composite polymers of the invention comprise from 0.5 to 95 wt % CEP, from 0.5 to 95 wt % CAOP and from 5 to 99 wt % block copolymer. More preferably, the crystalline block composite polymers comprise from 0.5 to 79 wt % CEP, from 0.5 to 79 wt % CAOP and from 20 to 99 wt % block copolymer and more preferably from 0.5 to 49 wt % CEP, from 0.5 to 49 wt % CAOP and from 50 to 99 wt % block copolymer. Weight percents are based on total weight of crystalline block composite. The sum of the weight percents of CEP, CAOP and block copolymer equals 100%.

Preferably, the block copolymers of the invention comprise from 5 to 95 weight percent crystalline ethylene blocks (CEB) and 95 to 5 wt percent crystalline alpha-olefin blocks (CAOB). They may comprise 10 wt% to 90 wt% CEB and 90 wt % to 10 wt% CAOB. More preferably, the block copolymers comprise 25 to 75 wt% CEB and 75 to 25 wt% CAOB, and even more preferably they comprise 30 to 70 wt % CEB and 70 to 30 wt % CAOB.

In some embodiments, the crystalline block composites have a Crystalline Block Composite Index (CBCI) that is greater than zero but less than about 0.4 or from 0.1 to 0.3. In other embodiments, CBCI is greater than 0.4 and up to 1.0. In some embodiments, the CBCI is 0.1 to 0.9, from about 0.1 to about 0.8, from about 0.1 to about 0.7 or from about 0.1 to about 0.6. Additionally, the CBCI can be in the range of from about 0.4 to about 0.7, from about 0.5 to about 0.7, or from about 0.6 to about 0.9. In some embodiments, CBCI is in the range of from about 0.3 to about 0.9, from about 0.3 to about 0.8, or from about 0.3 to about 0.7, from about 0.3 to about 0.6, from about 0.3 to about 0.5, or from about 0.3 to about 0.4. In other embodiments, CBCI is in the range of from about 0.4 to about 1.0, from about 0.5 to about 1.0, or from about 0.6 to about 1.0, from about 0.7 to about 1.0, from about 0.8 to about 1.0, or from about 0.9 to about 1.0.

The crystalline block composite is present in an amount of 30 to 100 weight percent (wt%), specifically 40 to 100 wt%, and more specifically 50 to 100 wt%, based on the total weight of the tie layer 104.

The tie layer 104 may also comprise in addition to the crystalline block composite (CBC) an optional elastomer. The optional elastomer can be an ethylene-α-olefin copolymer (which is already detailed above), homogeneously branched ethylene-α-olefin copolymer, a polyolefin elastomer (e.g., a propylene based elastomer), a vinyl aromatic block copolymer, or the like, or a

combination comprising at least one of the foregoing elastomers.

The polyolefin elastomers may also comprise random or block propylene polymers (i.e., polypropylenes). The random polypropylene elastomer typically comprises 90 or more mole percent units derived from propylene. The remainder of the units in the propylene copolymer is derived from units of at least one α-olefin.

The α-olefin component of the propylene copolymer is preferably ethylene (considered an α-olefin for purposes of this invention) or a C_{4-20} linear, branched or cyclic α-olefin. Examples of C_{4-20}α-olefins include 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The α-olefins also can contain a cyclic structure such as cyclohexane or cyclopentane, resulting in an α-olefin such as 3-cyclohexyl-1-propene (allyl cyclohexane) and vinyl cyclohexane. Although not α-olefins in the classical sense of the term, certain cyclic olefins, such as norbornene and related olefins, particularly 5-ethylidene-2-norbornene, are α-olefins and can be used in place of some or all of the α-olefins described above. Similarly, styrene and its related olefins (for example,α-methylstyrene, and the like) are α-olefins for purposes of this invention. Illustrative random propylene copolymers include but are not limited to propylene/ethylene, propylene/1-butene, propylene/1-hexene, propylene/1-octene, and the like. Illustrative terpolymers include ethylene/propylene/1-octene, ethylene/propylene/1-butene, and ethylene/propylene/diene monomer (EPDM).

In one embodiment the random polypropylene copolymer has a T_m greater than 120°C, and/or a heat of fusion greater than 70 J/g (both measured by DSC) and preferably, but not necessarily, made *via* Ziegler-Natta catalysis.

In another embodiment, the polyolefin elastomer is a propylene-α-olefin interpolymer and is characterized as having substantially isotactic propylene sequences. The propylene-α-olefin interpolymers include propylene-based elastomers (PBE). "Substantially isotactic propylene sequences" means that the sequences have an isotactic triad (mm) measured by ^{13}C 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. Isotactic triads are well-known in the art and are described in, for example, USP 5,504,172 and International Publication No. WO 00/01745, which refers to the isotactic sequence in terms of a triad unit in the copolymer molecular chain determined by ^{13}C NMR spectra.

The propylene-α-olefin copolymer comprises units derived from propylene and polymeric units derived from one or more α-olefin comonomers. Exemplary comonomers utilized to manufacture the propylene-α-olefin copolymer are C_2 and C_4 to C_{10} α-olefins; for example, C_2, C_4, C_6 and C_8 α-olefins.

The propylene-α-olefin interpolymer comprises 1 to 40 percent by weight of one or more alpha-olefin comonomers. The propylene-α-olefin interpolymer may have a melt flow rate in the range of 0.1 to 500 grams per 10 minutes (g/10min), measured in accordance with ASTM D-1238 (at 230°C/2.16 Kg). The propylene-α-olefin interpolymer has 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). The propylene-α-olefin interpolymer has a density of typically less than 0.895 g/cm^3. The propylene-α-olefin interpolymer has a melting temperature (T_m) of less than 120°C and a heat of fusion (H_f) of less than 70 Joules per gram (J/g) as measured by differential scanning calorimetry (DSC) as described in USP 7,199,203. The propylene-α-olefin interpolymer has a molecular weight distribution (MWD), defined as weight average molecular weight divided by number average molecular weight (Mw/Mn) of 3.5 or less; or 3.0 or less; or from 1.8 to 3.0.

Such propylene-α-olefin interpolymers are further described in the USP 6,960,635 and 6,525,157, the entire contents of which are incorporated herein by reference. Such propylene-α-olefin interpolymers are commercially available from The Dow Chemical Company, under the trade name VERSIFY™, or from ExxonMobil Chemical Company, under the trade name VISTAMAXX™.

The tie layer 104 may also optionally comprise homogeneously branched ethylene-α-olefin copolymers. These copolymers are elastomeric and can be made with a single-site catalyst such as a metallocene catalyst or constrained geometry catalyst, and typically have a melting point of less than 105, specifically less than 90, more specifically less than 85, even more specifically less than 80 and still more specifically less than 75°C. The melting point is measured by differential scanning calorimetry (DSC) as described, for example, in USP 5,783,638. The α-olefin is preferably a C_{3-20} linear, branched or cyclic α-olefin. Examples of C_{3-20} α-olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The α-olefins can also contain a

cyclic structure such as cyclohexane or cyclopentane, resulting in an α-olefin such as 3-cyclohexyl-1-propene (allyl cyclohexane) and vinyl cyclohexane.

Illustrative homogeneously branched ethylene-α-olefin copolymers include ethylene/propylene, ethylene/butene, ethylene/1-hexene, ethylene/1-octene, ethylene/styrene, and the like. Illustrative terpolymers include ethylene/propylene/1-octene, ethylene/propylene/butene, ethylene/butene/1-octene, and ethylene/butene/styrene. The copolymers can be random copolymers or block copolymers.

Examples of commercially available homogeneously branched ethylene-α-olefin interpolymers useful in the tie layer 104 includes homogeneously branched, linear ethylene-α-olefin copolymers (e.g. TAFMER® by Mitsui Petrochemicals Company Limited and EXACT® by Exxon Chemical Company), and the homogeneously branched, substantially linear ethylene-α-olefin polymers (e.g., AFFINITY™ and ENGAGE™ polyethylene available from the Dow Chemical Company). An exemplary ethylene-α-olefin copolymer that may be used in the tie layer 104 is AFFINITY EG 8100G, commercially available from the Dow Chemical Company.

The term vinyl aromatic block copolymer means a polymer having at least one block segment of a vinyl aromatic monomer in combination with at least one saturated or unsaturated elastomeric monomer segment, and more preferably not having a block of polymer that is neither elastomeric nor vinyl aromatic. Examples of vinyl aromatic block copolymers are “styrene block copolymer or styrenic block copolymer”. The term “styrene block copolymer” or “styrenic block copolymer” means a polymer having at least one block segment of a styrenic monomer in combination with at least one saturated or unsaturated elastomer (rubber) monomer segment, and more preferably not having a block of polymer that is neither rubber or styrenic. Suitable styrene block copolymers having unsaturated rubber monomer units include styrene-butadiene (SB), styrene-isoprene (SI), styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), α-methylstyrene-butadiene-α-methylstyrene, α-methylstyrene-isoprene-α-methylstyrene, and the like.

The term “styrene butadiene block copolymer” is used herein inclusive of SB, SBS and higher numbers of blocks of styrene (S) and butadiene (B). Similarly, the term “styrene isoprene block copolymer” is used inclusive of polymers having at least one block of styrene and one of isoprene (I). The structure of the styrene block copolymers can be of the linear or radial type, and of the diblock, triblock or higher block type. In some embodiments, the styrenic block

copolymers having at least four different blocks or a pair of two repeating blocks, for example, repeating styrene/butadiene or styrene/ethylene propylene blocks, are desirable. Styrene block copolymers are commercially available from Dexco Polymers under the trademark VECTOR®, from KRATON Polymers under the trademark KRATON™, from Chevron Phillips Chemical Co. under the trademark SOLPRENE™ and K-Resin, and from BASF Corp. under the trade designation STYROLUX™. The styrene block copolymers are optionally used singly or in combinations of two or more.

The styrenic portion of the block copolymer is preferably a polymer or interpolymer of styrene or its analogs or homologs, including α-methylstyrene, and ring-substituted styrenes, particularly ring-methylated styrenes. Preferred styrenics are styrene and α-methylstyrene, with styrene being especially preferred.

The elastomer portion of the styrenic block copolymer is optionally either unsaturated or saturated. Block copolymers with unsaturated elastomer monomer units may comprise homopolymers of butadiene or isoprene and copolymers of one or both of these two dienes with a minor amount of styrenic monomer. When the monomer employed is butadiene, it is preferred that between about 35 and about 55 mole percent of the condensed butadiene units in the butadiene polymer block have a 1,2-configuration. When such a block is hydrogenated, the resulting product is, or resembles, a regular copolymer block of ethylene and 1-butene (EB). If the conjugated diene employed is isoprene, the resulting hydrogenated product is or resembles a regular copolymer block of ethylene and propylene (EP). Preferred block copolymers have unsaturated elastomer monomer units, more preferably including at least one segment of a styrenic unit and at least one segment of butadiene or isoprene, with SBS and SIS most preferred. Among these, SIS is preferred because it has been found to be particularly effective to compatibilize polypropylene with other polymers in the composition. Furthermore, it is preferred because of a lower tendency to crosslink forming gels during manufacture as compared to SBS. Styrene butadiene block copolymers are alternatively preferred when a cast tenter line is used in manufacturing a film when its higher clarity and lower haze are advantageous.

Elastomeric styrene block copolymers provide toughness and lower stiffness than would be obtained in the absence of the block copolymer. Elastomeric behavior is indicated by a property of tensile percent elongation at break of advantageously at least about 200, specifically at least about 220, more specifically at least about 240, most specifically at least about 260 and

specifically at most about 2000, more specifically at most about 1700, most specifically at most about 1500 percent as measured by the procedures of ASTM D412 and/or ASTM D882. Industrially, most polymers of this type contain 10-80 wt% styrene. Within a specific type and morphology of polymer, as the styrene content increases the elastomeric nature of the block copolymer decreases.

The block copolymers desirably have a melt flow rate (MFR) of at least about 2, specifically at least about 4 grams per 10 minutes (g/10 min), specifically 20 g/10 min, and more specifically 30 g/10 min. Measure MFR according to ASTM method D1238 Condition G.

Preferred styrenic block copolymers include styrene-isoprene-styrene block copolymers ("SIS"), styrene-butadiene-styrene block copolymers ("SBS"), styrene-ethylene-propylene block copolymers ("SEP"), and hydrogenated styrenic block copolymer such as styrene-(ethylene butylene)-styrene block copolymers ("SEBS") (e.g., the SEBS commercially available from Kraton Polymers LLC under the trade designation KRATON™ 1657). Preferably, the styrenic block copolymer used in the tie layer is SBS.

In one embodiment, the styrene butadiene block copolymer has a radial or star block configuration with polybutadiene at the core and polystyrene at the tips of the arms. Such polymers are referred to herein as star styrene butadiene block copolymers and are within the skill in the art and commercially available from Chevron Phillips Chemical Co. under the trade designation K-Resin. These polymers contain about 27% butadiene or more in a star-block form and often feature a bimodal molecular weight distribution of polystyrene. The inner polybutadiene segments are of about the same molecular weight while the outer polystyrene segments are of different molecular weight. This feature facilitates control of polybutadiene segment thickness, to obtain improved clarity. For high clarity, the polybutadiene segment thickness is preferably about one-tenth of the wavelength of visible spectrum or less.

The ethylene-α-olefin copolymer has been described above as has the polyethylene and will not be detailed again. The polypropylene will be detailed below with reference to the layer 106.

If the elastomer is used, it is present in amounts of up to 50 wt%, specifically 5 to 40 wt%, based on the total weight of the tie layer 104.

The tie layer 104 may also optionally comprise polyethylene or polypropylene. The optional polyethylene is selected from ultralow density polyethylene (ULDPE), low density

polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), high melt strength high density polyethylene (HMS-HDPE), ultrahigh density polyethylene (UHDPE), or combinations thereof.

The optional polyethylene and/or the optional polypropylene are present in the tie layer 104 in an amount of up to 50 wt%, specifically 10 to 30 wt%, based on the total weight of the tie layer 104.

The tie layer 104 has a thickness of 1 to 20%, specifically 2 to 15%, and more specifically 3 to 10% of the total thickness of the multilayer film.

The first layer 102 (also called the outer layer or skin layer) comprises polyethylene. The polyethylene is selected from ultralow density polyethylene (ULDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), medium density polyethylene (MDPE), high density polyethylene (HDPE), high melt strength high density polyethylene (HMS-HDPE), ultrahigh density polyethylene (UHDPE), or combinations thereof.

In an exemplary embodiment, the first layer 102 comprises linear low density polyethylene (LLDPE). LLDPE is a copolymer (also referred to as an interpolymer) of ethylene and an α-olefin having 3 to 12 carbon atoms, specifically 4 to 8 carbon atoms (e.g., propene, 1 butene, 4-methyl-1-pentene, 1-hexene, 1 octene, 1-decene, and the like), that has sufficient α-olefin content to reduce the density of the copolymer to that of LDPE. The term "LLDPE", includes both - resin manufactured using the traditional Ziegler-Natta catalyst systems as well as single-site catalysts such as metallocenes (sometimes referred to as "m-LLDPE"). LLDPEs contain less long chain branching than LDPEs and includes the substantially linear ethylene polymers which are further defined in U.S. Patent 5,272,236, U.S. Patent 5,278,272, U.S. Patent 5,582,923 and US Patent 5,733,155; the homogeneously branched linear ethylene polymer compositions such as those in U.S. Patent No. 3,645,992; the heterogeneously branched ethylene polymers such as those prepared according to the processes disclosed in U.S. Patent No. 4,076,698; and/or blends thereof (such as those disclosed in US 3,914,342 or US 5,854,045). The LLDPE can be made by any process such as gas phase polymerization, solution phase polymerization, slurry polymerization or combinations thereof.

In one embodiment, the LLDPE used in the first layer 102 comprises the linear low density polyethylene having a melt index I_2 of 0.25 to 20 g/10 minutes when measured as per ASTM D 1238 at 190°C and 2.16 kg, and a density of less than 0.930 grams per square

centimeter (measured as per ASTM D 792). An exemplary LLDPE for use in the outer layer 102 is ELITE™AT 6111, which is an ethylene-octene copolymer with melt index of 3.7 g/10 min (measured as per ASTM D1238 at 190°C and 2.16 kg), density 0.912 g/cc (measured as per ASTM D 792), and commercially available from The Dow Chemical Company. Other exemplary LLDPE's that can be used in the outer layers 102 and 110 are linear ethylene-based polymers such as DOWLEX™ Polyethylene Resins, ELITE™ and ELITE™ ATbrand enhanced polyethylene resin, all available from The Dow Chemical Company, and Exceed™ metallocene polyethylenes, available from ExxonMobil Chemical Company.

Another exemplary polyethylene for use in the outer layers is homogeneously branched ethylene-α-olefin copolymers. These copolymers can be made with a single-site catalyst such as a metallocene catalyst or constrained geometry catalyst, and typically have a melting point of less than 105, specifically less than 90, more specifically less than 85, even more specifically less than 80 and still more specifically less than 75°C. The melting point is measured by differential scanning calorimetry (DSC) as described, for example, in USP 5,783,638. The α-olefin is preferably a C_{3-20} linear, branched or cyclic α-olefin. Examples of C_{3-20} α-olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. The α-olefins can also contain a cyclic structure such as cyclohexane or cyclopentane, resulting in an α-olefin such as 3-cyclohexyl-1-propene (allyl cyclohexane) and vinyl cyclohexane.

Illustrative homogeneously branched ethylene-α-olefin copolymers include ethylene/propylene, ethylene/butene, ethylene/1-hexene, ethylene/1-octene, ethylene/styrene, and the like. Illustrative terpolymers include ethylene/propylene/1-octene, ethylene/propylene/butene, ethylene/butene/1-octene, and ethylene/butene/styrene. The copolymers can be random copolymers or block copolymers.

Examples of commercially available homogeneously branched ethylene-α-olefin interpolymers useful in the outer layers 102 include homogeneously branched, linear ethylene-α-olefin copolymers (e.g. TAFMER® by Mitsui Petrochemicals Company Limited and EXACT® by Exxon Chemical Company), and the homogeneously branched, substantially linear ethylene-α-olefin polymers (e.g., AFFINITY™ and ENGAGE™ polyethylene available from the Dow Chemical Company). Any of these interpolymers or their combinations can also be used in the

first layer 102. An exemplary interpolymeris AFFINITY PL1850G commercially available from The Dow Chemical Company.

Propylene-α-olefin interpolymers can also be used as the first layer 102 (sealant layer) with preferred melting points 90 to 145 °C.

The first layer 102 has a thickness of 5 to 30 %, specifically 10 to 30%, specifically 15 to 25%, of the total thickness of the multilayer film.

The second layer 106 (also called the base layer 106) comprises polypropylene. The polypropylene is selected from random copolymer polypropylene (rcPP), impact copolymer polypropylene (hPP + at least one elastomeric impact modifier) (ICPP) or high impact polypropylene (HIPP), high melt strength polypropylene (HMS-PP), isotactic polypropylene (iPP), syndiotactic polypropylene (sPP), or a combination comprising at least one of the foregoing polypropylenes.

The polypropylene is generally in the isotactic form of homopolymer polypropylene, although other forms of polypropylene can also be used (e.g., syndiotactic or atactic). Polypropylene impact copolymers (e.g., those wherein a secondary copolymerization step reacting ethylene with the propylene is employed) and random copolymers (also reactor modified and usually containing 1.5-7% ethylene copolymerized with the propylene), however, can also be used in the layer 106. A complete 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. The molecular weight and hence the melt flow rate of the polypropylene for use in the present invention varies depending upon the application. The melt flow rate for the polypropylene useful herein is generally from about 0.1 grams/10 minutes (g/10 min, measured as per ASTM D1238 at 230°C and 2.16 kg) to about 100 g/10 min specifically 0.5 g/10 min to about 80 g/10 min, and specifically 4 g/10 min to about 70 g/10 min. The propylene polymer can be a polypropylene homopolymer, or it can be a random copolymer or even an impact copolymer (which already contains a rubber phase). The polypropylene may be produced by using Ziegler-Natta ot metallocene catalysts. Examples of such propylene polymers include ExxonMobil™ hPP 4712E1(made by Exxon Mobil), hPP H03G-05(made by Ineos)and, MOPLENand PROFAX (made by Lyondell).

The second layer 106 may contain polypropylene in an amount of 40 to 100 wt%, specifically 60 to 100 wt%, based on the total weight of the second layer 106.

The second layer 106 may optionally contain an elastomer in an amount of up to 40 wt%, specifically 10 to 35 wt%, based on the total weight of the second layer. The elastomer can be an ethylene-α-olefin copolymer (which is already detailed above), a polyolefin elastomer (e.g., a propylene based elastomer), a vinyl aromatic block copolymer, or a combination thereof (as already detailed above). The second layer 106 may also contain polyethylene in an amount of up to 40 wt%, specifically 10 to 35 wt%, based on the total weight of the second layer. The polyethylenes have been described above, and will not be detailed here again.

The second layer 106 (i.e., the base layer) has a thickness of 50 to 94%, specifically 65 to 90%, and more specifically 70 to 85%, based on the total thickness of the multilayered film 100. In an exemplary embodiment, the second layer has a thickness that is at least 66% of the total thickness of the multilayered film. In another embodiment, the second layer 106 may also be multilayered.

The multilayered film 100 has a total thickness of 10 to 250 micrometers, specifically 20 to 130 micrometers, and more specifically 20 to 75 micrometers.

Each layer of the multilayer film 100 may contain other additives such as waxes, antioxidants, antiozonants, mold release agents, biocides, thermal stabilizers, pigments, dyes, infrared absorption agents, ultraviolet stabilizers, or the like, or a combination comprising at least one of the foregoing additives.

One of more layers of the multilayer film can optionally comprise a wax that may reduce the melt viscosity in addition to reducing costs. Non-limiting examples of suitable waxes include petroleum waxes, polyolefin waxes such as low molecular weight polyethylene or polypropylene, synthetic waxes, paraffin and microcrystalline waxes having melting points from about 55 to about 110°C, Fischer-Tropsch waxes, or a combination comprising at least one of the foregoing waxes. In some embodiments, the wax is a low molecular weight polyethylene homopolymer or interpolymer having a number average molecular weight of about 400 to about 6,000 g/mole.

In further embodiments, each of the layers of the multilayer film can optionally comprise an antioxidant or a stabilizer. Non-limiting examples of suitable antioxidants include amine-based antioxidants such as alkyl diphenylamines, phenyl-α- naphthylamine, alkyl or aralkyl

substituted phenyl-α-naphthylamine, alkylated p-phenylene diamines, tetramethyl-diaminodiphenylamine and the like; and hindered phenol compounds such as 2,6-di-t-butyl-4-methylphenol; 1,3,5-trimethyl-2,4,6-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)benzene; tetrakis[(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)]methane (e.g., IRGANOXTM 1010, from Ciba Geigy, New York); octadecyl-3,5-di-t-butyl-4-hydroxycinnamate (e.g., IRGANOXTM 1076, commercially available from Ciba Geigy) and combinations thereof. Where used, the amount of the antioxidant in the composition can be up to about 1 wt%, specifically 0.05 to 0.75 wt%, and specifically0.1 to 0.5 wt%, based on the total weight of any particular layer.

In further embodiments, the compositions disclosed herein optionally can comprise an UV stabilizer that may prevent or reduce the degradation of the compositions by UV radiation. Non-limiting examples of suitable UV stabilizers include benzophenones, benzotriazoles, aryl esters, oxanilides, acrylic esters, formamidine carbon black, hindered amines, nickel quenchers, hindered amines, phenolic antioxidants, metallic salts, zinc compounds, or the like, or a combination comprising at least one of the foregoing UV stabilizers. Where used, the amount of the UV stabilizer in any particular layer can be from about greater than 0 to about 1 wt%, specifically 0.05 to 0.75 wt%, and specifically 0.1 to 0.5 wt%, based on the total weight of aparticular layer.

In further embodiments, the compositions disclosed herein optionally can comprise a colorant or pigment. Any colorant or pigment known to a person of ordinary skill in the art may be used in the adhesion composition disclosed herein. Non-limiting examples of suitable colorants or pigments include inorganic pigments such as titanium dioxide and carbon black, phthalocyanine pigments, and other organic pigments such as IRGAZIN®, CROMOPHTAL®, MONASTRAL®, CINQUASIA®, IRGALITE®, ORASOL®, all of which are available from Ciba Specialty Chemicals, Tarrytown, NY. Where used, the amount of the colorant or pigment in any particular layer can be present in an amount of up to 10 wt%, specifically 0.1 to 5 wt%, and more specifically 0.5 to 2 wt%, based on the total weight of any particular layer of the multilayered film.

In further embodiments, the compositions disclosed herein optionally can comprise polymeric processing aids (such as Dynamar™ 5911 from Dyneon Corporation), antiblocks and

slip additives. These additives may advantageously be used to reduce stickiness and modify coefficient of friction to desired levels for ease of handling.

In one embodiment, in one method of manufacturing the film 100, the respective compositions for each of the layers 102, 104, and 106 of the multilayered film 100 is fed to a separate device in which it is subjected to shear, extensional and elongational forces. The device that exerts the foregoing forces on the composition can be conducted in an extruder (single screw or twin screw), a Henschel mixer, a Waring blender, a Buss Kneader, a Banbury, a roll mill (two or more rolls), high shear impeller disperser, dough mixer, or the like. The ingredients for any layer in the multilayered film may be dry mixed or solution blended in either a Henschel mixer, a Waring blender, a high shear impeller disperser, or the like, prior to being extruded.

In an exemplary embodiment, the composition for each of the respective layers are fed to separate extruders. The composition for the first layer 102 is fed to a first extruder, the composition for the tie layer 104 is fed to a second extruder, and the composition for the third layer 106 is fed to a third extruder. The compositions from the respective extruders are fed to a single die and are coextruded to form the multilayered film. The coextruded film is then blown to form a multilayered film of the desired thickness. In an embodiment, the multilayered film after being coextruded is laminated in a roll mill having two or more rolls.

In another embodiment, in another method of manufacturing the multilayered film, each layer may be extruded separately, and the extruded layers may then be formed into a laminate (such as extrusion lamination, thermal lamination, compression moldng, adhesive lamination). The compression molding or lamination can be conducted in a roll mill, or in a compression molding press.

In one embodiment, the multilayered film may be cast, i.e., extruded from the extruder into a stream of fluid that quenches the film. In an embodiment, each layer of the multilayer film may be cast, and the respective films are then laminated together in a roll mill, if desired.

As detailed above, a plurality of multilayered films may be laminated together to form a single multilayered film. When two or more multilayered films are laminated together, at least one of the common layers may be omitted if desired. For example, if two multilayered films are laminated together, then at least one of the second layers 106 may be omitted. Thus while a single multilayered film contains 3 layers, two multilayered films laminated together will contain 5 layers, and three multilayered films will contain 7 layers.

Additionally, the multilayered film 100 can be adhesive laminated to the surface of the press sheet or other substrate,typically polypropylene, polyester, or nylon. Typically the bonding agent, dissolved into a liquid (water or a solvent), is applied to one of the webs, before being evaporated in the drying oven. The adhesive coated web is laminated to the other under strong pressure and using heated rollers, which improves the bond strength of the laminate.

The multilayered films disclosed herein exhibit a high heat seal strength, preferably greater than 3.5 lb/in (9.2 N/15mm) for a total film thickness of 30μm, 5.7 lb/in (15 N/15mm) for a total film thickness of 50μm and 10 lb/in (26.3 N/15mm) for a total film thickness of 125μm. The seal strength of laminated film is preferably greater than 8 lb/in (21.0 N/15mm), and more preferably greater than 10 lb/in (26.3 N/15mm). The preferred films of the present invention also exhibit low heat initiation temperature, such as less than or equal to 110°C, and more preferably less than or equal to 100°C.Additionally, the preferred films of the present invention possess good optical clarity and mechanical properties. Accordingly, the preferred films of the present invention can meet the heat seal and other performance requirements for food packaging market.

The multilayered films disclosed herein and the method of manufacturing the films are exemplified in the following examples.

EXAMPLE

This example was conducted to demonstrate the method of manufacturing the multilayer films disclosed herein as well as the properties of these films. A variety of different films were manufactured and tested to determine their properties. The compositions for these materials are shown in the Table 1. Tables 2 and 3 show the different properties for the crystalline block composites. Table 3 shows the crystalline block composite Index estimation, while Table 2 shows physical properties for the crystalline block composite.

Table 1

Material	MI (190°C, g/10min)	MFR (230°C, g/10min)	Density (g/cm3)	Supplier
CBC 1		6.7	0.902	50/50 EP/iPP Diblock, 90wt% C2 in EP
CBC 2		10.1	0.906	50/50 EP/iPP Diblock, 90wt% C2 in EP
CBC 3		6.6	0.895	40/60 EP/iPP Diblock, 90wt% C2 in EP, 9% C2 in iPP
hPP DX5E66 (PP1)		8.7	0.9	Braskem
hPP D115 (PP2)		11	0.9	Braskem
ELITE AT 6111(PE1)	3.7		0.912	The Dow Chemical Company
ELITE5230 (PE2)	4.0		0.916	The Dow Chemical Company
Dowlex 2247 (PE3)	2.3		0.917	The Dow Chemical Company
VERSIFY 3200 (PBE1)		8	0.878	The Dow Chemical Company
Cosmoplene FL7641L (ter-PP)		7	0.9	The Polyolefin Company (TPC), Singapore

Table 2

Example	MFR (230°C/ 2.16 kg)	Wt% PP from HTLC Separation	Mw Kg/mol	Mw/ Mn	Total Wt% C_2	Tm (°C) Peak 1 (Peak 2)	Melt Enthalpy (J/g)
CBC1	6.7	19.6	114	2.90	48.3	131 (105)	90
CBC2	10.1	20.3	92	3.50	48.1	130 (105)	103
CBC3	6.6	not determined	119	3.08	42.9	107	87

Table 3

Sample	wt% iPP	wt% EP	Wt% C_2 in EP	Wt% C_2 in iPP	Crystalline Block Composite Index
CBC1	50	50	90	Minimum	0.579
CBC2	50	50	90	Minimum	0.566
CBC3	40	60	90	9	not determined

*C_2 is ethylene.

The multilayer films were tested using the following test standards.

Haze, Clarity and Gloss:

Haze is the percentage of transmitted light scattered by the film more than 2.5° from the normal incident beam and was measured according to ASTM D 1003. Determination of the direct transmittance of the specimen has been frequently used to assess clarity. Film transmittance was measured according to ASTM D1746. Gloss is concerned not with the visibility of a body viewed through a sample, but rather with the quality of the image formed by a reflection on its surface. Gloss was measured according to ASTM D2457 at 45°.

Hot Tack

Hot tack measurements on the film were performed using an Enepay commercial testing machine according to ASTM F-1921 (Method B). Prior to testing, the samples were conditioned for a minimum of 40 hours at 23°C and 50% relative humidity (R.H.) per ASTM D-618 (Procedure A). The hot tack test simulates the filling of material into a pouch or bag before the seal has had a chance to cool completely. Sheets of dimensions 8.5" by 14" are cut from the film, with the longest dimension in the machine direction. Strips 1" wide and 14" long are cut from the film [samples need only be of sufficient length for clamping]. Tests are performed on these samples over a range of temperatures and the results reported as the maximum load as a function of temperature. Typical temperature steps are 5°C or 10°C with 6 replicates performed at each temperature. The Enepay machines make 0.5 inch seals. The data are reported as a hot tack curve where Average Hot Tack Force (N) is plotted as a function of temperature. The parameters used in the test are as follows:

- Specimen Width: 25.4 mm (1.0 in)
- Sealing Pressure: 0.275 N/mm^2
- Sealing Dwell Time: 0.5 s
- Delay time: 0.1 s
- Peel speed: 200 mm/s

Heat Seal

Heat seal measurements on the film are performed on a commercial tensile testing machine according to ASTM F-88 (Technique A). The heat seal test is a gauge of the strength of seals (seal strength) in flexible barrier materials. It does this by measuring the force required to separate a test strip of material containing the seal and identifies the mode of specimen failure. Seal strength is relevant to the opening force and package integrity. Prior to cutting, the films are conditioned for a minimum of 40 hours at 23°C (± 2°C) and 50% (± 5%) R.H. per ASTM D-618 (Procedure A). Sheets are then cut from the film in the machine direction to a length of approximately 11 inches and a width of approximately 8.5 inches. The sheets are heat sealed across the machine direction on a Kopp Heat Sealer over a range of temperatures under the following conditions:

- Sealing Pressure: 0.275 N/mm^2
- Sealing Dwell Time: 0.5 s

The temperature range is approximately given by the Hot Tack Range (i.e. the temperature range over which at least a minimum hot tack seal is achieved and prior to the burn-through temperature). The sealed sheets are conditioned for a minimum of 3 hours at 23°C (± 2°C) and 50% R.H (± 5%) prior to cutting into one inch wide strips. These strips are then further conditioned for a minimum of 24 hours at 23° (± 2°C) and 50% R.H (± 5%) prior to testing. For testing, the strips are loaded into the grips of a tensile testing machine at an initial separation of 2 inches and pulled at a grip separation rate of 10 inches/min at 23°C (± 2°C) and 50% R.H (± 5%). The strips are tested unsupported. Six replicate tests are performed for each sealing temperature.Heat seal initiation temperature is determined as the minimum temperature at which a seal of 1.0 lb/inch or2.6 N/15 mmis obtained.

Example 1 and Comparative Examples A and B

Inventive Example 1 is a three layer cast film having a thickness of approximately 5mills prepared via co-extrusion cast film process prepared on a Dr. Collin co-extrusion cast film line equipped with three single screw extruders under the conditions reported in Table 4, based on the formulation components reported in Table 5. Layer C is the substrate layer, which is approximately 60% of total film thickness. Layer B is the tie layer, which is approximately 20% of the total thickness. Layer A is sealant layer, which is approximately 20% of the total thickness.

Comparative Examples A, B and C are two layer cast films having a thickness of approximately 5mills prepared via co-extrusion cast film process prepared on a Dr. Collin co-extrusion cast film line equipped with three single screw extruders under the conditions reported in Table 4A, based on the formulation components reported in Table 5. Layer C is the substrate layer, which is approximately 80% of total film thickness. Layer A is sealant layer, which is approximately 20% of the total thickness.

Inventive Example 1 and Comparative Examples A, B and C were tested for their properties, and the results are reported in Figures 2 and Table 6.

Table 4 shows the process conditions for the inventive Example 1. Table 4A shows process conditions of Collin cast film line for Comparative Examples A and B. Table 5 shows the layer structure of Example 1, Comp A and B (2 mil or 50.8 μm thickness).

Table 4

Die Total Gap, mils	20		
Air Gap, in	0.75		
Film Width, in	8		
Film Thickness, mils	1.2 / 2 / 5		
Total Throughput, Kg/h	6		
	Extruder A	Extruder B	Extruder C
Material	PE1 (Sealant layer)	CBC1 (Tie layer)	PP1 (Substrate)
L/D	25	30	25
Melt Temperature, °C	234-238	234-236	234-237
Throughput for 1.2 / 2 / 5 mil film, Kg/h	1.0 – 1.2	1.0 - 1.2	3
Screw speed, rpm	26/ 24 / 20	45 / 40 / 15	74 / 45 / 14

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Table 4A

Die Total Gap, mils	20		
Air Gap, in	0.75		
Film Width, in	8		
Film Thickness, mils	5		
Total Throughput, Kg/h	6		
	Extruder A	Extruder B	Extruder C
Material	PE1 or ter-PP (Sealant layer)	PP1 (Substrate)	PP1 (Substrate)
L/D	25	30	25
Melt Temperature, °C	234-238	234-236	234-237
Throughput for 1.2 / 2 / 5 mil film, Kg/h	1.0 – 1.2	1.0 - 1.2	3
Screw speed, rpm	26/ 24 / 20	45 / 40 / 15	74 / 45 / 14

Table 5

Example	Layer C	Layer B	Layer A	C/B/A Thickness ratio
Inventive Example 1	PP1	CBC 1	PE1	60/20/20
Inventive Example 2	PP1	CBC 2	PE2	60/20/20
Inventive Example 3	PP1	CBC 2	PE3	60/20/20
Inventive Example 4	PP1	CBC 3	PE2	60/20/20
Comp A	PP1	--	PE1	80/0/20
Comp B	PP1	--	ter-PP	80/0/20
Comp C	PP1	--	80% ter-PP + 20% PBE1	80/0/20

Figure 2 compares the heat seal results for Example 1 and Comparative Example A, B and C. Inventive Example 1 exhibits a plateau seal strength of 15 lb/in and a seal initiation temperature (SIT) around between 80 and 90°C. The advantage of Inventive Ex. 1 over Comparative Example A is the higher seal strength. When PE1 is used as sealant layer without tie layer, the seal delaminates during the peel test, which results in low heat seal strength. The advantage of Inventive Ex. 1 over Comparative ExamplesB and Cis the lower SIT.The SIT is between 80 to 90°Cfor Inventive Ex. 1, whereas between 100 to 110°C for Comparative Examples B and C.

Table 6summarizesheat seal strength and haze of Examples 1 to 4 and Comparative Examples A-C. Ex. 1-4 have a plateau strength in the range of 15 lb/in. The SIT for Examples 1 to 4 is below 100°C, and SIT for Ex. 1 to 2 is below 90°C. The total haze of Examples 1 to 4 is 1.7% vs Comp A-C, which show total haze of 3-7%.

Table 6

		Seal strength (lb/in)								
Example	Thickness (mil)	80°C	90°C	100°C	110°C	120°C	130°C	140°C	150°C	Total haze (%)
1	5.0	0.03	5.47	8.66	9.40	13.78	15.16	14.99	14.65	1.7
2	5.0	0.02	3.31	6.21	6.02	13.54	14.59	17.39	14.76	1.7
3	5.0	0.03	0.07	4.05	6.58	10.36	16.01	15.38	14.98	1.7
4	5.0		0.05	11.94	14.63	15.81	15.33	16.02	16.01	1.6
Comp A	5.0	0.70	1.11	1.44	3.59	4.94	8.70	5.10	3.24	6.5
Comp B	5.0	0.00	0.00	0.00	6.49	16.84	16.82	17.50	16.96	3.7
Comp C	5.0	0.00	0.00	0.20	4.82	13.78	15.30	15.80	16.40	3.6

Examples 5-8

Inventive Examples 5-8 are three layer cast films (having a thickness of approximately 1.2 mil (30.4 μm) prepared via co-extrusion cast film process on a Dr. Collin co-extrusion cast film line equipped with three single screw extruders under the conditions reported in Table 7, based on the formulation components reported in Table 8. Layer C is the substrate layer, which is approximately 60% of total film thickness. Layer B is the tie layer, which is approximately 20% of the total thickness. Layer A is sealant layer, which is approximately 20% of the total thickness.

Table 7shows process conditions of Collin cast film line for Inventive Example 1, while Table 8shows the layer structure of inventive examples 5– 8. Table 9 shows the heat seal properties of the inventive examples 5 –8, while Table 10 shows optical properties for these samples.

Table 7

Die Total Gap, mils	20		
Air Gap, in	0.75		
Film Width, in	8		
Film Thickness, mils	1.2		
Total Throughput, Kg/h	6		
	Extruder A	Extruder B	Extruder C
Material	PE1-PE3(Sealant layer)	CBC2-CBC3 (Tie layer)	PP1 (Substrate)
L/D	25	30	25
Melt Temperature, °C	234-238	234-236	234-237
Throughput for 1.2/2/5 mil film, Kg/h	1.0 – 1.2	1.0 - 1.2	3
Screw speed, rpm	26/24/20	45/40/15	74/45/14

Table 8

Example	Layer C	Layer B	Layer A	C/B/A Thickness ratio	Film thickness (mil)
5	PP1	CBC 2	PE1	60/20/20	1.2
6	PP1	CBC 2	PE2	60/20/20	1.2
7	PP1	CBC 2	PE3	60/20/20	1.2
8	PP1	CBC 3	PE2	60/20/20	1.2

The heat seal properties of Examples 5 to 8 are shown in Table 9. These inventive samples using different PE as sealant show a plateau seal strength in the range of 3.5 to 5.2 lb/in. The SIT for Examples 5 to 8 is below 100°C, and Examples 5 to 6 are below 90°C.

Table 9

		Seal strength (lb/in)							
Example	Thickness (mil)	80°C	90°C	100°C	110°C	120°C	130°C	140°C	150°C
5	1.2	0.29	2.52	2.43	3.84	4.76	4.20	4.38	5.23
6	1.2	0.07	1.84	2.69	4.06	4.93	5.11	5.06	4.35
7	1.2		0.22	2.58	2.79	3.52	4.25	3.53	3.72
8	1.2		0.02	3.94	4.14	4.16	5.09	4.41	4.69

Table 10below shows the optical properties of Ex. 5-8. The clarity ofEx. 5-8 is around 97% and total haze around 0.6 to 0.9%.

Table 10

Example	Thickness (mil)	Clarity (%)	45° Gloss (%)	Total haze (%)
5	1.2	97.5	91.0	0.6
6	1.2	97.2	91.5	0.6
7	1.2	96.3	89.5	0.9
8	1.2	97.2	91.7	0.6

Examples 9and D

Inventive Example 9is a three layer cast films having a thickness of approximately 2 mils (50.8 μm) prepared via co-extrusion cast film process an Egan co-ex cast film line (Margot Machinery, Inc.) equipped with three single screw extruders and conditions detail in Table 11, based on the formulation components reported in Table 12. Layer C is the substrate layer, which is approximately 60% of total film thickness. The layer C is a multilayer substrate comprising three layers (layers C, D and E). Layer B is the tie layer, which is approximately 10% of the total thickness. Layer A is sealant layer, which is approximately 20% of the total thickness.

Comparative Example Dis a two layer cast films having a thickness of approximately 2 mils prepared via co-extrusion cast film process an Egan co-ex cast film line (Margot Machinery, Inc.) equipped with three single screw extruders and conditions detail in Table 11A, based on the formulation components reported in Table 12. Layer C is the substrate layer, which is approximately 80% of total film thickness. Layer A is sealant layer, which is approximately 20% of the total thickness.

The cast films are laminated to PET using an Egan Pilot Laminator using a solvent based lamination. Prior to lamination, corona treatment is performed on the sealant side, bringing the surface tension up to 42 dynes. The adhesive used are Adcote 577A (70% solids) and Adcote 577B (71% solids). Adcote 577A and Adcote 577B after supplied by The Dow Chemical Company. The adhesive system was diluted down to 32 wt% solids with Ethyl Acetate.

Table 13compares the optical properties of Example9and comparative Example D. The clarity of the inventive Example9is slightly higher than comparative Example Dand the haze of Example9is slightly lower than comparative Example D. Overall, both examples have high clarity and low haze.

As shown in Table 14, the heat seal property of inventive Example 9after lamination shows lower SIT (<90°C) as compared to comparative Example D.

Table 11

Die Total Gap, mils	36				
Film Width, in	23				
Film Thickness, mils	2				
Total Throughput, Kg/h	160 - 164				
	Extruder A	Extruder B	Extruder C	Extruder D	Extruder E
Material	PE3 (Sealant layer)	Tie layer	PP2 (Substrate layer)		
% Thickness, Target	20%	10%	24%	23%	23%

Melt Temperature, °C	237-239	232-233	226-228	214-220	228-231
Throughput, Kg/h	30 - 32	17 – 18	37 – 38	37 - 38	35 - 36
Screw speed, rpm	50 - 53	18 - 20	46 - 48	46 - 47	46 - 48

Table 11A showsprocess conditions of Egan cast film line for Comparative Example D.

Table 11A

Die Total Gap, mils	36				
Film Width, in	23				
Film Thickness, mils	2				
Total Throughput, Kg/h	160 - 164				
	Extruder A	Extruder B	Extruder C	Extruder D	Extruder E
Material	Ter-PP (Sealant layer)	PP2 (Substrate layer)	PP2 (Substrate layer)		
% Thickness, Target	20%	10%	24%	23%	23%
Melt Temperature, °C	237-239	232-233	226-228	214-220	228-231
Throughput, Kg/h	30 - 32	17 – 18	37 – 38	37 - 38	35 - 36
Screw speed, rpm	50 - 53	18 - 20	46 - 48	46 - 47	46 - 48

Table 12shows the layer structure of Examples 10 and comparative Example D.

Table 12

Example	Layer C	Layer B	Layer A	C/B/A Thickness ratio	Film thickness (mil)
9	PP2	CBC 2 + 20% PBE1	PE1	70/10/20	2
D	PP2		Ter-PP	80/0/20	2

Table 13shows theoptical properties of Examples 9and comparative Example Dbefore lamination.

Table 13

Example	Thickness (mil)	Clarity (%)	45 Gloss (%)	Total haze (%)
9	2	99.0	89.3	0.8
D	2	97.9	86.9	1.7

Table 14shows the heat seal property of Examples 9and Dafter lamination.

Table 14

		Seal strength (lb/in)							
Example	Thickness (mil)	80°C	90°C	100°C	110°C	120°C	130°C	140°C	150°C
9	2	0.00	2.94	5.25	5.51	8.45	9.93	11.97	12.77
D	2			0.15	1.88	2.88	13.97	15.13	15.15

Examples E-F

ComparativeExamples E and Fare three layer cast films (having a thickness of approximately 2 mils (50.8 μm)) prepared via co-extrusion cast film process on a Dr. Collin co-ex cast film line equipped with three single screw extruders under the conditions reported in Table 15, based on the formulation components reported in Table 16. Layer C is the substrate layer, which is approximately 60% of total film thickness. Layer B is the tie layer, which is approximately 20% of the total thickness. Layer A is sealant layer, which is approximately 20% of the total thickness.

The heat seal properties of ComparativeExamples Eand Fare shown in Table 17. The 2 mil thick film samples using terpolymer-PP as sealant show a plateau seal strength in the range of 6.4 to 8.0 lb/in, and no delamination is observed during the peel test. However, the SIT is >100°C.

Table 15shows process conditions of Collin cast film line for ComparativeExamplesEand F.

Table 15

Die Total Gap, mils	20		
Air Gap, in	0.75		
Film Width, in	8		
Film Thickness, mils	2		
Total Throughput, Kg/h	6		
	Extruder A	Extruder B	Extruder C
Material	Ter-PP (Sealant layer)	CBC2-CBC3 (Tie layer)	PP2 (Substrate)
L/D	25	30	25
Melt Temperature, °C	234-238	234-236	234-237
Throughput for 1.2 / 2 / 5 mil film, Kg/h	1.0 – 1.2	1.0 - 1.2	3
Screw speed, rpm	26/ 24 / 20	45 / 40 / 15	74 / 45 / 14

Table 16 shows the layer structure of Examples E and F.

Table 16

Example	Layer C	Layer B	Layer A	C/B/A Thickness ratio	Film thickness (mil)
E	PP2	CBC 2	Ter-PP	60/20/20	2
F	PP2	CBC 3	Ter-PP	60/20/20	2

Table 17shows heat seal properties of Examples Eand F.

Table 17

		Seal strength (lb/in)							
Example	Thickness (mil)	80°C	90°C	100°C	110°C	120°C	130°C	140°C	150°C
E	2	0.02	0.02	0.26	6.86	7.51	7.91	7.74	7.97
F	2	0.02	0.02	0.34	6.35	7.09	6.86	7.39	7.10

From the forgoing examples, it may be seen that the inventive samples display high plateau heat seal strength, preferably greater than 3.5 lb/in (9.2 N/15mm) for a total film thickness of 30 μm, 5.7 lb/in (15 N/15mm) for a total film thickness of 50 μm and 10 lb/in (26.3 N/15mm) for a total film thickness of 125μm. After lamination, the seal strength of laminated film is preferably greater than 8 lb/in (21.0 N/15mm), and more preferably greater than 10 lb/in (26.3 N/15mm). The preferred films of the present invention also exhibit low heat initiation temperature, specifically less than or equal to 100°C. The inventive films also showclarity (transparency) that is greater than those of the comparative samples. The inventive samples show a transparency of greater than 80%, specifically greater than 85%, and more specifically greater than 90%. The inventive samples also show a haze less than 1% when total film thickness is less than or equal to 50 μm.

CLAIMS

What is claimed is:

1. A multilayer film comprising:

a first layer and a second layer; and

a tie layer; where the tie layer comprises a crystalline block composite and where the tie layer is disposed between the first layer and the second layer; the first layer being disposed on a first surface of the tie layer; the second layer being disposed on a second surface of the tie layer; where the second surface is opposedly disposed to the first surface;where the crystalline block composite comprises a crystalline ethylene based polymer, a crystalline alpha-olefin based polymerand a block copolymer comprising a crystalline ethylene block and a crystalline alpha-olefin block.

2. The multilayer film of Claim 1, where the crystalline block composite has a melt flow ratio 0.1 to 30 dg/min, when measured as per ASTM D 1238 at 230°C and 2.16 kilograms.

3. The multilayer film of Claim 1, where the crystalline block composite comprises 5 to 95 weight percent crystalline ethylene blocks and 95 to 5 wt percent crystalline alpha-olefin blocks.

4. The multilayer film of Claim 1, where the crystalline block composite has a Crystalline Block Composite Index 0.3 to 1.0.

5. The multilayer film of claim 1, where the tie layer further comprises an elastomer; and where the elastomer is a homogeneously branched ethylene-α-olefin copolymer, a polyolefin elastomer, a vinyl aromatic block copolymer, or a combination comprising at least one of the foregoing elastomers.

6. The multilayer film of claim 1, where the tie layer further comprises an elastomer; and where the elastomer is a homogeneously branched ethylene-α-olefin copolymer, a polyolefin elastomer, a vinyl aromatic block copolymer, or a combination comprising at least one of the foregoing elastomers.

7. The multilayer film of claim 1, where the first layer comprises polyethylene.

8. The multilayer film of claim 7, where the polyethylene is selected from the group consisting of ultralow density polyethylene, low density polyethylene, linear low density polyethylene, medium density polyethylene, high density polyethylene, high melt strength high density polyethylene, ultrahigh density polyethylene, or combinations thereof.

9. The multilayer film of claim 7, where the polyethylene comprises linear low density polyethylene.

10. The multilayer film of claim 1, where the second layer comprises polypropylene.

11. The multilayer film of claim 1, where the polypropylene is selected from the groups consisting of random copolymer polypropylene, impact copolymer polypropylene, high impact polypropylene, high melt strength polypropylene, isotactic polypropylene, syndiotactic polypropylene, or a combination comprising at least one of the foregoing polypropylenes.

12. The multilayer film of claim 1, where the second layer comprises a polypropylene homopolymer.

13. The multilayer film of claim 1, where the first layer has a thickness of 5 to 30%, the tie layer has a thickness of 1 to 20% and the second layer has a thickness of 50 to 94%, based on the total thickness of the multilayer film.

14. The multilayer film of claim 1, where the multilayer film has a total film thickness of 10 to 250 micrometers.

15. The multilayer film of claim 1, where the multilayer film has a plateau heat seal strength greater than 3.5 lb/in (9.2 N/15mm) for a total film thickness of 30 μm, 5.7 lb/in (15 N/15mm) for a total film thickness of 50 μm and 10 lb/in (26.3 N/15mm) for a total film thickness of 125μm.

16. The multilayer film of claim 1, where the multilayer film has a plateau seal strength greater than 8 lb/in (21.0 N/15mm) after lamination.

17. The multilayer film of claim 1, where the multilayer film has a heat initiation temperature less than or equal to 100°C.

18. The multilayer film of claim 1, where the multilayer film has a transparency of greater than 80% when tested as per ASTM D1746, and a haze of less than 3%, when tested as per ASTM D 1003.

19. An article comprising the multilayer film of claim 1.

20. A method of manufacturing a multilayer film comprising:

coextruding a multilayer film comprising:

a first layer and a second layer; and

a tie layer; where the tie layer comprises a crystalline block composite and where the tie layer is disposed between the first layer and the second layer; the first layer being disposed on a first surface of the tie layer; the second layer being disposed on a second surface of the tie layer; where the second surface is opposedly disposed to the first surface; where the crystalline block composite comprises a crystalline ethylene based polymer, a crystalline alpha-olefin based polymerand a block copolymer comprising a crystalline ethylene block and a crystalline alpha-olefin block;and

blowing or casting the multilayer film.

21. The method of claim 20, further comprising laminating the multilayer film in a roll mill.

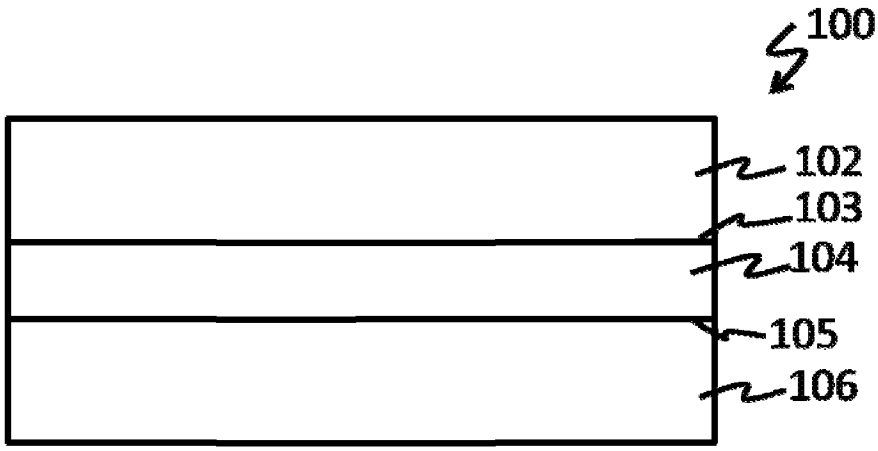


Figure 1

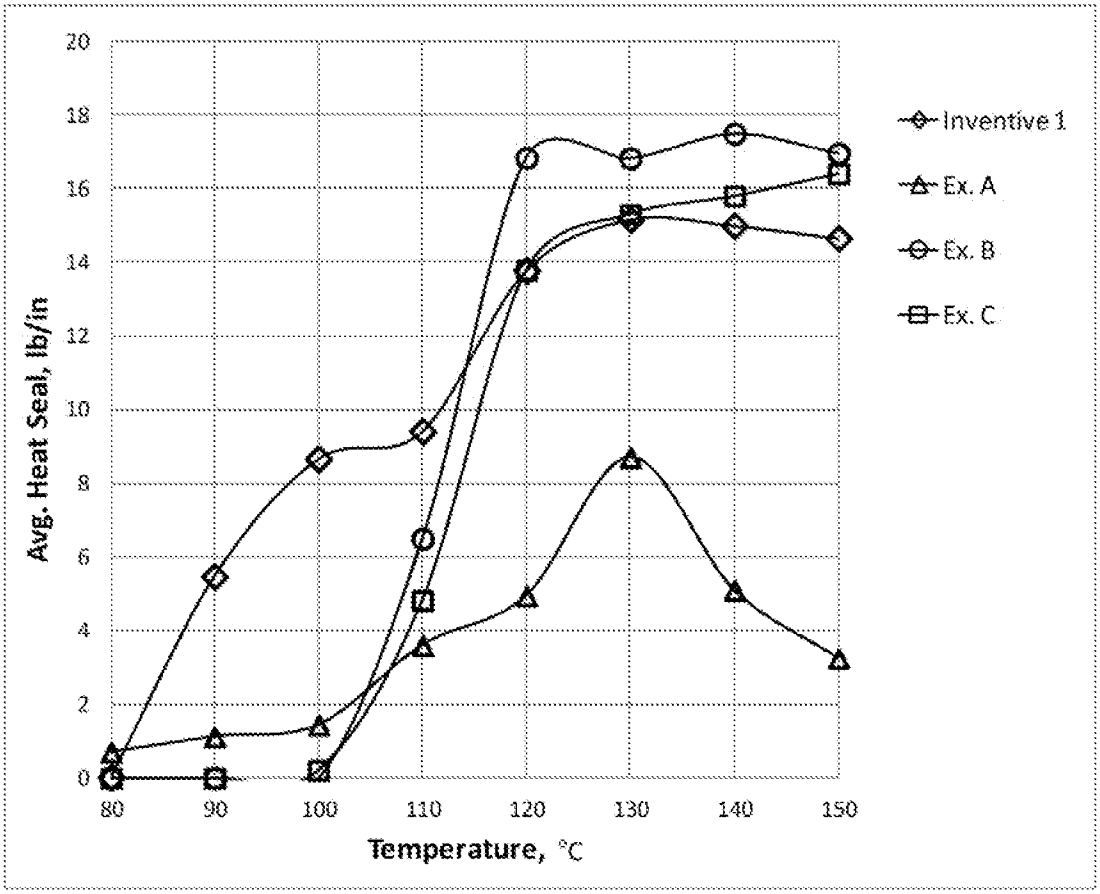

Avg. Heat Seal, lb/in
Temperature, °C
Inventive 1
Ex. A
Ex. B
Ex. C
0
2
4
6
8
10
12
14
16
18
20
80
90
100
110
120
130
140
150

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2014/072265

A. CLASSIFICATION OF SUBJECT MATTER

B32B 27/32 (2006.01) i

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)

B32B27/-

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)

WPI;EPODOC,CNPAT;CNKI:multilayer film,tie layer,crystalline,block,ethylene,alpha-olefin,polymer,copolymer,melt flow ratio,weight,elastomer,polyethylene,thickness,plateau heat seal strength,heat initiation temperature,transparency,haze,article, blowing,casting,laminating,roll mill

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013003543 A1 (DOW GLOBAL TECHNOLOGIES LLC.) 03 January 2013 (2013-01-03) claims 6, 9, 17; paragraphs [0013], [0040], [0057], [00109], [00157], [00161], table 2 and fig. 1	1-21
X	WO 2013003541 A1 (DOW GLOBAL TECHNOLOGIES LLC.) 03 January 2013 (2013-01-03) claims 3, 6, 12-13; paragraphs [0013], [0041], [0058], [00150], [00154] and fig. 1	1-21
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☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 November 2014	**28 November 2014**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA(ISA/CN) **6,Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088 China**	**HE,Chu**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)61648546**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	CN 102470633 A (RENOLIT BELGIUM N. V.) 23 May 2012 (2012-05-23) the whole document	1-21

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2014/072265

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