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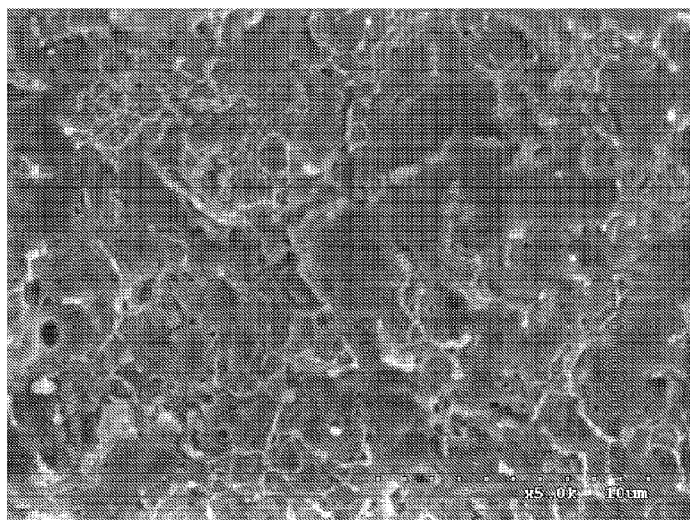


FIG. 2B

(57) Abstract: The present disclosure provides for a polyolefin-based composition made from or comprising (A) a first polymer composition made from, or containing an ethylene polymer grafted with an unsaturated monomer, and (B) a second polymer composition comprising a propylene polymer, wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer. The polymeric composition may be used as a tie-layer adhesive composition.



POLYOLEFIN-BASED COMPOSITIONS, ADHESIVES, AND  
RELATED MULTI-LAYERED STRUCTURES PREPARED THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is filed under the Patent Cooperation Treaty, which claims benefit of priority of U.S. Provisional Application No. 62/278,145, filed on January 13, 2016, the contents of which are incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

[0002] In general, the present disclosure relates to polyolefin-based compositions useful as adhesives, tie-layer adhesives for multi-layered structures, and compatibilizers.

BACKGROUND OF THE INVENTION

[0003] Tie-layer adhesives may be used to bond polyolefins to dissimilar substrates in multi-layer, co-extruded structures for beverage and food containers (*e.g.*, bags, shrink bags, pouches, casings, trays, lidded trays, overwrapped trays, form shrink packages, vacuum skin packages, flow wrap packages, thermoformed packages, packaging inserts or combinations thereof), medicine and makeup containers, shipping packaging, electronic components, synthetic fibers, fiberfill applications (*e.g.*, home insulation, cushions, and pillows), and metal laminate applications (*e.g.*, building and construction products, business and consumer products, containers and packaging products, electrical equipment, machinery and industrial equipment, signs and displays, and transportation products). The adhesives can be used in lamination, extrusion (or coextrusion), sheet extrusion, extrusion coating, injection molding, blow molding, melt thermoforming, and other processes.

[0004] Commercial polypropylene tie layer resins can be produced by let-down of maleic anhydride grafted polypropylene with other polypropylene grades. Those maleated polypropylenes can be produced by grafting the maleic anhydride onto the polypropylene backbone in the presence of relatively high amounts (> 1.5 weight percent) of organic peroxide through high temperature twin screw extrusion.

[0005] Peroxide addition at levels greater than about 1.5 wt. % may result in (a) the formation of waxy species, having molecular weight (Mw) less than about 2000 and (b) an increase of the yellowness index. This level of waxy species can adversely affect the clarity of resulting barrier films.

[0006] To remove the waxy material, a solvent extraction process can be employed. The solvent extraction process can be tedious, time consuming, costly, and detrimental to the environmental.

#### BRIEF SUMMARY OF THE INVENTION

[0007] In general embodiments, the present disclosure provides for a polyolefin-based composition made from or containing:

- (A) a first polymer composition made from or containing an ethylene polymer grafted with an unsaturated monomer, and
  - (B) a second polymer composition comprising a propylene polymer,
- wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer.

[0008] In some embodiments, the present disclosure provides a polyolefin-based composition made from or containing:

- (A) an ethylene polymer grafted with an unsaturated monomer covalently bonded to a propylene polymer yielded from the free-radical reactive blending of;
    - (i) about 20 to about 70 weight percent of a first polymer composition, relative to the total weight of the polyolefin-based composition, made from or containing an ethylene polymer grafted with an unsaturated monomer, and
    - (ii) about 30 to about 80 weight percent of a second polymer composition, relative to the total weight of the polyolefin-based composition, made from or containing a propylene polymer;
- in the presence of
- (iii) about 0.01 to about 3.0 weight percent of a mobile liquid reactant, relative to the total weight of the polyolefin-based composition, made from or containing an organic peroxide.

[0009] In some embodiments, the present disclosure provides for an adhesive made from or containing the polyolefin-based composition.

[0010] In some embodiments, the present disclosure provides a multi-layered structure made from or containing:

- (A) a tie-layer adhesive made from or containing:

- (i) a polyolefin-based composition made from or containing:
  - (a) a first polymer composition made from or containing an ethylene polymer grafted with an unsaturated monomer; and
  - (b) a second polymer composition made from or containing a propylene polymer,

wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer;

- (B) a polymer layer; and
- (C) a substrate layer.

[0011] In some embodiments, the present disclosure provides for a process containing:

- (A) the adding step of combining:
  - (i) a first polymer composition made from or containing an ethylene polymer grafted with an unsaturated monomer,
  - (ii) a second polymer composition made from or containing a propylene polymer, and
  - (iii) a mobile liquid reactant composition made from or containing an organic peroxide;
- (B) the free-radical generation step of decomposing the mobile liquid reactant to form free radicals,
- (C) the treating step of treating at least one of the polymer components with the free radicals to form reactive sites on the polymer components,
- (D) the blending step of agitating the residual non-treated polymer components and the free-radical-treated polymer components,
- (E) the reacting step of covalently bonding the reactive sites of the free-radical-treated polymer components to the residual non-treated polymer components, other free-radical-treated polymer components, or both, and
- (F) the collecting step of collecting the blended, reaction products as the polyolefin-based composition.

[0012] While multiple embodiments are disclosed, still other embodiments will become apparent to those skilled in the art from the following detailed description. As will be apparent,

certain embodiments, as disclosed herein, are capable of modifications in various aspects, all without departing from the spirit and scope of the claims as presented herein. Accordingly, the drawings and detailed description are to be regarded as illustrative in nature and not restrictive.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The following figures illustrate alternative embodiments of the subject matter disclosed herein. The claimed subject matter may be understood by reference to the following description taken in conjunction with the accompanying figures, in which like reference numerals identify like elements, and in which:

[0014] FIG. 1A shows a crystallization curve generated by differential scanning calorimetry (DSC) analysis for a blend of an impact polypropylene and a maleic anhydride-grafted, high-density polyethylene.

[0015] FIG. 1B shows a crystallization curve for a polymeric composition resulting from a reactive blend of (i) the impact polypropylene, (ii) the maleic anhydride-grafted, high-density polyethylene, and (iii) an organic peroxide.

[0016] FIG. 2A shows a micrograph obtained using a Hitachi S-3500 Scanning Electron Microscope (SEM) at an accelerated voltage of 5 kV from an extrudate's surface fractured under liquid nitrogen for a blend of an impact polypropylene and a maleic anhydride-grafted, high-density polyethylene.

[0017] FIG. 2B shows a micrograph for a polymeric composition resulting from a reactive blend of (i) the impact polypropylene, (ii) the maleic anhydride-grafted, high-density polyethylene, and (iii) an organic peroxide.

#### DETAILED DESCRIPTION OF THE INVENTION

[0018] The present disclosure now will be described more fully hereinafter. However, the disclosure can be embodied in many different forms and should not be construed as limited to the embodiments set forth herein. As such, it will be apparent to those skilled in the art that the embodiments can incorporate changes and modifications without departing from the general scope. It is intended to include certain modifications and alterations in so far as the modifications and alterations come within the scope of the appended claims or the equivalents thereof.

[0019] As used in this specification and the claims, the singular forms "a," "an," and "the" include plural referents unless the context dictates otherwise.

[0020] As used in this specification and the claims, the terms “comprising,” “containing,” or “including” mean that at least the named compound, element, material, particle, or method step, *etc.*, is present in the composition, the article, or the method, but does not exclude the presence of other compounds, elements, materials, particles, or method steps, *etc.*, even if the other such compounds, elements, materials, particles, or method steps, *etc.*, have the same function as that which is named, unless expressly excluded in the claims. It is also to be understood that the mention of one or more method steps does not preclude the presence of additional method steps before or after the combined recited steps or intervening method steps between those steps expressly identified.

[0021] Moreover, it is also to be understood that the lettering of process steps or ingredients is a means for identifying discrete activities or ingredients and the recited lettering can be arranged in any sequence, unless expressly indicated.

[0022] For the purpose of the present description and of the claims which follow, except where otherwise indicated, numbers expressing amounts, quantities, percentages, and so forth, are to be understood as being modified by the term “about”. Also, ranges include any combination of the maximum and minimum points disclosed and include any intermediate ranges therein, which may or may not be specifically enumerated herein.

[0023] Definitions

[0024] In the present description, the term “additives composition” refers to a composition made from or containing at least one additive.

[0025] In the present description, the terms “adhesive layer” and “tie layer” mean a layer or material placed on one or more substrates to promote the adhesion of that substrate to another layer. Adhesive layers can be positioned between two layers of a multilayer structure to maintain the two layers in position relative to each other and prevent delamination.

[0026] In the present description, the term “ $\alpha$ -olefin” or “alpha-olefin” means an olefin of formula  $\text{CH}_2=\text{CH}-\text{R}$ , wherein R is a linear or branched alkyl containing from 1 to 10 carbon atoms. The  $\alpha$ -olefin can be selected, for example, from propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-dodecene and the like.

[0027] In the present description, the term “first” refers to the order in which a particular species is presented and does not necessarily indicate that a “second” species will be presented. For example, “first polymer composition” refers to the first of at least one polymer composition. The term does not reflect priority, importance, or significance in any other way. Similar terms used that can be used herein include “second,” “third,” “fourth,” etc.

[0028] In the present description, the term “grafted polyolefin” refers to a polyolefin grafted with an unsaturated monomer. The unsaturated monomer can be an unsaturated polar monomer and contain one or more oxygen atoms.

[0029] In the present description, the term “grafted polyolefin composition” refers to a composition made from or containing at least one grafted polyolefin.

[0030] In the present description, the term “homopolymer” as used herein is consistent with its ordinary meaning. To the extent that a homopolymer can contain one or more monomeric units, the incorporation of any additional monomeric units has no measurable effect on the polymer’s primary, secondary or tertiary structure or no effect on the polymer’s physical or chemical properties. In other words, there is no measureable difference between a polymer comprising 100 weight percent of a first monomeric unit, and a co-polymer that includes more than one monomeric units.

[0031] In the present description, the term “interpolymer” means a polymer prepared by the polymerization of at least two types of monomers or comonomers. It includes, but is not limited to, copolymers (which can refer to polymers prepared from two different types of monomers or comonomers, although it can be used interchangeably with “interpolymer” to refer to polymers made from three or more different types of monomers or comonomers), terpolymers (which can refer to polymers prepared from three different types of monomers or comonomers), tetrapolymers (which can refer to polymers prepared from four different types of monomers or comonomers), and the like.

[0032] In the present description, the terms “monomer” and “comonomer” are used interchangeably. The terms mean any compound with a polymerizable moiety that is added to a reactor in order to produce a polymer. In those instances in which a polymer is described as comprising one or more monomers, *e.g.*, a polymer comprising propylene and ethylene, the polymer, of course, comprises units derived from the monomers, *e.g.*,  $\text{---CH}_2\text{---CH}_2\text{---}$ , and not the monomer itself, *e.g.*,  $\text{CH}_2=\text{CH}_2$ .

[0033] In the present description, “plastic film packaging” is of particular concern and discussed throughout this description. To facilitate that discussion, various polymer acronyms are used herein. When referring to blends of polymers, the description can use a colon (:) to indicate that the components to the left and right of the colon are blended. When referring to a multi-layer structure, the description can use a slash "/" to indicate that components to the left and right of the slash are in different layers and the relative position of components in layers can be so indicated by use of the slash to indicate layer boundaries.

- [0034] Acronyms employed herein include:
- EAA: Copolymer of ethylene with acrylic acid
  - EAO: Copolymers of ethylene with at least one alpha-olefin
  - EBA: Copolymer of ethylene with butyl acrylate
  - EEA: Copolymer of ethylene with ethyl acrylate
  - EMA: Copolymer of ethylene with methyl acrylate
  - EMAA: Copolymer of ethylene with methacrylic acid
  - EVA: Copolymer of ethylene with vinyl acetate
  - EVOH: Saponified or hydrolyzed copolymer of ethylene and vinyl acetate
  - PB: Polybutylene-1 (a butylene homopolymer or copolymer of a major portion of butylene-1 with one or more alpha-olefins)
  - PE: Polyethylene (an ethylene homopolymer or copolymer of a major portion of ethylene with one or more alpha-olefins)
  - PP: Polypropylene homopolymer or copolymer
  - PET: Polyethylene terephthalate
  - PETG: Glycol-modified polyethylene terephthalate
  - PLA: Polylactic acid
  - PVDC: Polyvinylidene chloride (also includes copolymers of vinylidene chloride, such as with vinyl chloride or methyl acrylate (MA)).

[0035] In the present description, the term “polymer” means a macromolecular compound prepared by polymerizing monomers of the same or different type. The term “polymer” includes homopolymers, copolymers, terpolymers, interpolymers, and related compositions.

[0036] In the present description, the term “polymer composition” refers to a composition made from or containing at least one polymer.

[0037] In the present description, the term “polyolefin” is used herein to include polymers such as polyethylene, ethylene-alpha olefin copolymers (EAO), polypropylene, polybutene, and ethylene copolymers having at least about 50 percent by weight of ethylene polymerized with a lesser amount of a comonomer such as vinyl acetate, and other polymeric resins within the "olefin" family classification.



[0038] Polyolefins can be made by a variety of processes including batch and continuous processes using single, staged, or sequential reactors, slurry, solution, and fluidized bed processes and one or more catalysts including for example, heterogeneous and homogeneous systems and Ziegler, Phillips, metallocene, single-site, and constrained geometry catalysts to produce polymers having different combinations of properties.

[0039] In the present description, the term “reactive blend” refers to the resulting blend prepared from a mixture of a first polymer component, a second polymer component, and a mobile liquid reactant, wherein (i) under free-radical generation conditions, the mobile liquid reactant decomposes to form free radicals, (ii) at least one of the polymer components is treated with the free radicals, and (iii) the mixture is blended at least partially during the free-radical treatment. For example, the free-radical treatment may cause the polymer components to undergo modifications such as chain scission or hydrogen abstraction.

[0040] In the present description, the term “room temperature” refers to a temperature around 25 degrees Celsius.

[0041] In the present description, the term “thermoplastic polymer” means a polymer that softens when exposed to heat and returns to its original condition when cooled to room temperature.

[0042] In the present description, the term “crystallization point” or “T<sub>c</sub>” means the temperature at which a polymer crystallizes.

[0043] Testing

[0044] ASTM D 792 is entitled “Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement.” The term “ASTM D 792” as used herein refers to the standard test method for determining the specific gravity (relative density) and density of solid plastics in forms such as sheets, rods, tubes, or molded items. The test method includes determining the mass of a specimen of the solid plastic in air, determining the apparent mass of the specimen upon immersion in a liquid, and calculating the specimen’s specific gravity (relative density). This test method was approved on June 15, 2008 and published July 2008, the contents of which are incorporated herein by reference in its entirety.

[0045] ASTM D 1238 is entitled “Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer.” The term “ASTM D 1238” as used herein refers to a test method covering the determination of the rate of extrusion of molten thermoplastic resins using an extrusion plastometer. After a specified preheating time, resin is extruded through a die with a specified length and orifice diameter under prescribed conditions of temperature, load, and piston

position in the barrel. This test method was approved on February 1, 2012 and published March 2012, the contents of which are incorporated herein by reference in its entirety.

[0046] Throughout the present description and claims, the standard melt index values of polyethylene polymers are measured according to ASTM D 1238, using a piston load of 2.16 kg and at a temperature of 190 degrees Celsius.

[0047] Throughout the present description and claims, the standard melt flow rate values of polypropylene polymers are measured according to ASTM D 1238, using a piston load of 2.16 kg and at a temperature of 230 degrees Celsius.

[0048] ASTM D 1505 is entitled "Standard Test Method for Density of Plastics by the Density-Gradient Technique." The term "ASTM D 1505" as used herein refers to a test method based on observing the level to which a test specimen sinks in a liquid column exhibiting a density gradient, in comparison with standards of known density. This test method was approved on July 1, 2010 and published in September 2010, the contents of which are incorporated herein by reference in its entirety.

[0049] ASTM D 1925 (Withdrawn) is entitled "Test Method for Yellowness Index of Plastics." The term "ASTM D 1925" as used herein refers to a measure of the yellowing of a plastic, such as might occur after long-term exposure to light. The deviation in chroma from whiteness or water-whiteness in the dominant wavelength range from 570 to 580 nm as compared to a magnesium oxide standard. This test method was approved in 1988 and withdrawn in 1995, the contents of which are incorporated herein by reference in its entirety.

[0050] ASTM D 3418 is entitled "Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry." The term "ASTM D3418" as used herein refers to determination of transition temperatures and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry and applies to polymers in granular form or to any fabricated shape from which it is possible to cut appropriate specimens. This test method was approved in 2015, the contents of which are incorporated herein by reference in its entirety.

[0051] ASTM D 4440 is entitled "Standard Test Method for Plastics: Dynamic Mechanical Properties Melt Rheology." The term "ASTM D 4440" as used herein refers to a means of characterizing the rheological properties and viscosity of thermoplastic polymers using very small amounts of material (approximately 25 to 50 mm in diameter by 1 to 3 mm in thickness; approximately 3 to 5 g). Viscosity data at low shear (0.0398 rad/sec) and high shear

(100 rad/sec) were determined by parallel plates geometry at 210 degrees Celsius using an ARES rheometer.

[0052] ASTM E 1356 is entitled "Standard Test Method for Assignment of the Glass Transition Temperatures by Differential Scanning Calorimetry." The term "ASTM E1356" as used herein refers to a rapid test method for determining changes in specific heat capacity in a homogeneous material, wherein the glass transition is manifested as a step change in specific heat capacity. This test method is applicable to amorphous materials or to partially crystalline materials containing amorphous regions that are stable and do not undergo decomposition or sublimation in the glass transition region. This test method was approved in 2008, the contents of which are incorporated herein by reference in its entirety.

[0053] For the referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).

[0054] Die Swell: Pellets were extruded through a melt index die having a diameter of  $D_i$ , at 230 degrees Celsius with a weight of 21.6 kg. The extrudates were cooled at room temperature and measured for diameter,  $D_e$ . Die swell was obtained in accordance with the following formula:

$$\% \text{ Die Swell} = ((D_e - D_i)/D_i) * 100.$$

[0055] Incorporated Unsaturated Monomer (Weight Percent): The amount of the unsaturated monomer incorporated into the grafted polyolefin can be measured by wet chemical methods (titration, etc.) or Fourier transform infrared spectroscopy (FTIR).

[0056] Nuclear Magnetic Resonance Measurement of Ethylene and Propylene Content: Pellet samples are dissolved with 1,3,4-trichlorobenzene/*o*-dichlorobenzene- $d_4$  (4:1 ratio). The samples are heated at 125 degrees Celsius until dissolved. The  $^{13}\text{C}$  NMR spectra are obtained on a Bruker Avance 500 spectrometer using an inverse gated decoupling scheme. Triad distributions and C2 and C3 content are calculated based on the integrated peak areas of the spectrum.

[0057] Xylene Solubles for Polymers (percent by weight): 2 g of polymer are dissolved in 200 ml of xylene. Sample is refluxed to dissolve for 1.5 hours to bring to temperature of 140 degrees Celsius and air cooled for 15 minutes. Then, the sample is waterbath cooled at 25 degrees Celsius for 30 minutes. The precipitate is filtered with filter paper and dried in a weighed dish for measurement.

[0058] In general embodiments, the present disclosure provides a polyolefin-based composition made from or containing:

(A) a first polymer composition made from or containing an ethylene polymer grafted with an unsaturated monomer, and

(B) a second polymer composition comprising a propylene polymer,

wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer.

[0059] The First Polymer Composition: Ethylene Polymer Grafted With An Unsaturated Monomer

[0060] In an embodiment, the first polymer composition is present in an amount from about 20 to about 70 weight percent, relative to the total weight of the polyolefin-based composition. The first polymer composition can be present in an amount from about 25 to about 70 weight percent. In some embodiments, the first polymer composition is present in 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, or an intermediate weight percent, relative to the total weight of the polyolefin-based composition.

[0061] The ethylene polymer grafted with an unsaturated monomer for use in making the first grafted polymer composition can be prepared by reacting an ethylene polymer with unsaturated monomers at elevated temperatures, with or without a free-radical initiator, under conditions effective to graft unsaturated monomer units onto the ethylene polymer backbone. Alternatively, the grafting reaction may occur under an inert gas, such as nitrogen.

[0062] Examples of ethylene polymers for making the grafted ethylene polymer for use in the first grafted polymer composition include high-density polyethylenes (HDPE), medium density polyethylenes (MDPE), low density polyethylenes (LDPE), linear low density polyethylenes (LLDPE), and the like, and blends thereof. In some embodiments, the ethylene polymer is an HDPE.

[0063] In some embodiments, the unsaturated monomers are ethylenically unsaturated carboxylic acids and acid derivatives, such as esters, anhydrides, acid salts, and related compounds. Examples include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, maleic anhydride, tetrahydrophthalic anhydride, norborn-5-ene-2,3-dicarboxylic acid anhydride, nadic anhydride, himic anhydride, and mixtures thereof. In various embodiments, maleic anhydride may be used. Other unsaturated monomers are described in U.S. Patent No. 6,385,777 and U.S. Patent Application Publication No. 2007/0054142, the teachings of which are incorporated herein by reference.

[0064] In some embodiments, the ethylene polymer grafted with an unsaturated monomer is a high-density polyethylene (HDPE) grafted with maleic anhydride.

[0065] The relative amounts of ethylene polymer and unsaturated monomer used will vary and depend on factors such as the nature of the ethylene polymer and the unsaturated monomer, the desired tie-layer properties, the reaction conditions, the available equipment, and other factors. In some embodiments, the unsaturated monomer is used in an amount within the range of about 0.1 to about 15 weight percent, based on the total weight of the grafted ethylene polymer. In other embodiments, the unsaturated monomer is used in an amount from about 0.5 to about 6 weight percent. In yet other embodiments, the unsaturated monomer is used in an amount from about 1 to about 3 weight percent. In still other embodiments, the unsaturated monomer is present in 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, or 2.5 weight percent.

[0066] Grafting of the unsaturated monomer(s) to the ethylene polymer can be accomplished by heating a mixture of the unsaturated monomer(s) and the ethylene polymer. The grafted ethylene polymer can be prepared by melt blending the ethylene polymer with the unsaturated monomer in a shear-imparting extruder/reactor. Twin screw extruders such as those marketed by Coperion under the designations ZSK-53, ZSK-83, ZSK-90 and ZSK-92 may be useful for performing the grafting step. A free-radical initiator such as an organic peroxide can be employed.

[0067] Grafting of the unsaturated monomer to the ethylene polymer is performed at elevated temperatures. Shear rates in the extruder can vary over a wide range.

[0068] In some embodiments, the ethylene polymer grafted with an unsaturated monomer has a density in the range of about 0.93 to about 0.98 grams per cubic centimeter. In other embodiments, the density is 0.93, 0.94, 0.95, 0.96, 0.97, or 0.98 grams per cubic centimeter.

[0069] In some embodiments, the ethylene polymer grafted with an unsaturated monomer has a melt index in the range of about 2.0 to about 20.0 grams per 10 minutes, measured according to ASTM D 1238, using a piston load of 2.16 kg and at a temperature of 190 degrees Celsius. In other embodiments, the melt index is 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 grams per 10 minutes.

[0070] The Second Polymer Composition: Propylene Polymer

[0071] In an embodiment, the second polymer composition is present in an amount from about 30 to about 80 weight percent, relative to the total weight of the polyolefin-based composition. The second polymer composition can be present in an amount from about 30 to about 75 weight percent. In some embodiments, the second polymer composition is present in

30, 35, 40, 45, 50, 55, 60, 65, 70, 75, or an intermediate weight percent, relative to the total weight of the polyolefin-based composition.

[0072] The propylene polymer is a propylene-ethylene impact copolymer.

[0073] In particular embodiments, the impact copolymers of propylene and ethylene are produced using gas-phase, stirred-bed polymerization processes. Propylene-ethylene impact copolymers may be reactor-made intimate mixtures of propylene homopolymer and propylene-ethylene copolymer. More specifically, propylene-ethylene impact copolymers may be produced in two reactors connected in series using high activity supported transition metal catalysts. Propylene homopolymer may be produced in the first reactor and then introduced to the second reactor where additional propylene, ethylene, hydrogen and catalyst, as desired, are metered to produce the intimate physical mixtures which comprise the propylene-ethylene impact copolymers utilized in various embodiments of the present disclosure. Gas phase polymerizations of this type are described in the article by Ross, et al., entitled "An Improved Gas-Phase Polypropylene Process" in *Ind. Eng. Chem. Prod. Res. Dev.* 1985, 24, 149-154, which is incorporated herein by reference.

[0074] Propylene-ethylene impact copolymers produced in gas-phase polymerizations of the above types are comprised of crystalline (propylene homopolymer) and amorphous or rubber (ethylene-propylene copolymer) phases.

[0075] In some embodiments, the propylene polymer has propylene content in the range of about 70 to about 95 weight percent propylene-derived units, relative to the total weight of the propylene polymer. In other embodiments, the propylene content is 70, 75, 80, 85, 90, 95, or an intermediate weight percent propylene-derived units, relative to the total weight of the propylene polymer.

[0076] In some embodiments, the propylene polymer has ethylene content in the range of about 5 to about 30 weight percent ethylene-derived units, relative to the total weight of the propylene polymer. In other embodiments, the ethylene content is 5, 10, 15, 20, 25, or 30, or an intermediate weight percent ethylene-derived units, relative to the total weight of the propylene polymer.

[0077] In some embodiments, the propylene polymer has a density in the range of about 0.87 to about 0.92 grams per cubic centimeter. In other embodiments, the density is 0.87, 0.88, 0.89, 0.90, 0.91, or 0.92 grams per cubic centimeter.

[0078] In some embodiments, the propylene polymer has a melt flow rate in the range of about 1.0 to about 10.0 grams per 10 minutes, measured according to ASTM D 1238, using a

piston load of 2.16 kg and at a temperature of 230 degrees Celsius. In other embodiments, the melt flow rate is 1, 2, 3, 4, 5, 6, 7, 8, 9, or 10 grams per 10 minutes.

[0079] In some embodiments, the propylene polymer has a xylene soluble content in the range of about 10 to about 20 weight percent, relative to the total weight of the propylene polymer. In other embodiments, the xylene soluble content is 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20 weight percent, relative to the total weight of the propylene polymer.

[0080] The Covalent Bond: Formation In The Presence of Mobile Liquid Reactant

[0081] In an embodiment, the covalent bond between the ethylene polymer grafted with an unsaturated monomer and the propylene polymer is formed in the presence of a mobile liquid reactant. In some embodiments, the mobile liquid reactant is present in an amount from about 0.01 to about 3.0 weight percent, relative to the total weight of the polyolefin-based composition. In other embodiments, the mobile liquid reactant is present in 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, or an intermediate weight percent, relative to the total weight of the polyolefin-based composition.

[0082] In some embodiments, the mobile liquid reactant is an organic peroxide.

[0083] The covalently bonded products may be prepared by melt blending the grafted ethylene polymer and the propylene impact copolymer with the mobile liquid reactant (*i.e.*, the free radical generating catalyst) in a shear-imparting reactor, such as an extruder/reactor. Twin screw extruder/reactors such as those marketed by Coperion under the designations ZSK-53 and ZSK-83 can be used.

[0084] In one embodiment, the organic peroxide is introduced to the molten polymeric composition. The free-radical reaction is carried at a temperature selected to minimize or avoid rapid vaporization and organic peroxide loss.

[0085] In an embodiment, the temperature profile where the temperature of the polymer melt can increase gradually through the length of the extruder/reactor up to a maximum in the grafting reaction zone and then decrease toward the reactor exit. The maximum temperature within the reactor should be such that vaporization losses, premature decomposition, or both of the organic peroxide are avoided or minimized. For example, with di-*t*-butyl peroxide and 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane, maximum temperatures within the reactor should be maintained at or below about 220 degrees Celsius. The maximum useful temperature varies with the selection of catalyst. Examples of useful peroxide catalysts include 1,1-bis(*tert*-butylperoxy)cyclohexane; *n*-butyl-4,4-bis(*tert*-butylperoxyvalerate); 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane; 2,2-bis(*tert*-butylperoxy)butane; dicumylperoxide; *tert*-

butylcumylperoxide;  $\alpha\alpha'$ -bis(tert-butylperoxypropoxy-isopropyl)benzene; di-tert-butylperoxide (DTBP); 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane; and related compounds.

[0086] The Formulated Composition

[0087] In some embodiments, the present disclosure provides a polyolefin-based composition made from or containing

(A) an ethylene polymer grafted with an unsaturated monomer covalently bonded to a propylene polymer yielded from the free-radical reactive blending of

(i) about 20 to about 70 weight percent of a first polymer composition, relative to the total weight of the polyolefin-based composition, made from or containing an ethylene polymer grafted with an unsaturated monomer, and

(ii) about 30 to about 80 weight percent of a second polymer composition, relative to the total weight of the polyolefin-based composition, made from or containing a propylene polymer,

in the presence of

(iii) about 0.01 to about 3.0 weight percent of a mobile liquid reactant, relative to the total weight of the polyolefin-based composition, made from or containing an organic peroxide.

[0088] In some embodiments, the polyolefin-based composition has a melt flow rate in the range of about 1.0 to about 5.0 grams per 10 minutes, measured according to ASTM D 1238, using a piston load of 2.16 kg and at a temperature of 230 degrees Celsius. In other embodiments, the melt flow rate is 1, 2, 3, 4, or 5 grams per 10 minutes.

[0089] In some embodiments, the polyolefin-based composition has a xylene soluble content in the range of about 3 to about 10 weight percent, relative to the total weight of the polyolefin-based composition. In other embodiments, the xylene soluble content is in the range of about 5 to about 7 weight percent, relative to the total weight of the polyolefin-based composition. In other embodiments, the xylene soluble content is 5, 5.5, 6.0, 6.5, or 7.0 weight percent, relative to the total weight of the polyolefin-based composition.

[0090] In some embodiments, the polyolefin-based composition has a shear rate (*i.e.*, low shear rate) from about 500,000 to about 800,000 poise, measured at 0.0398 rad/sec.

[0091] In some embodiments, the polyolefin-based composition has a shear rate (*i.e.*, high shear rate) from about 4,000 to about 7,000 poise, measured at 100 rad/sec.



[0092] In some embodiments, the polyolefin-based composition has a ratio of low shear viscosity to high shear viscosity of about 70:1 to about 200:1.

[0093] In some embodiments, the polyolefin-based composition has a percent die swell in the range of about 20 to about 50 percent change in diameter. In other embodiments, the percent die swell is in the range of about 30 to about 35. In other embodiments, the percent die swell is 30, 31, 32, 33, 34, or 35.

[0094] In some embodiments, the polyolefin-based composition has propylene content in the range of about 30 to about 60 weight percent propylene-derived units, relative to the total weight of the polyolefin-based composition. In other embodiments, the propylene content is 30, 35, 40, 45, 50, 55, 60, or an intermediate weight percent propylene-derived units, relative to the total weight of the polyolefin-based composition.

[0095] In some embodiments, the polyolefin-based composition has an ethylene content in the range of about 40 to about 70 weight percent ethylene-derived units, relative to the total weight of the polyolefin-based composition. In other embodiments, the ethylene content is 40, 45, 50, 55, 60, 65, or 70, or an intermediate weight percent ethylene-derived units, relative to the total weight of the polyolefin-based composition.

[0096] In some embodiments, the polyolefin-based composition has a yellowness index of less than about 35. In other embodiments, the yellowness index is in the range of about 0.01 to about 35.

[0097] In some embodiments, the polyolefin-based composition has polyolefins with molecular weights (Mw) of less than about 2000 in an amount of less than about 5 weight percent, relative to the total weight of the polyolefin-based composition. In other embodiments, the amount is in the range of about 0.01 to about 5 weight percent, relative to the total weight of the polyolefin-based composition.

[0098] In some embodiments, the polyolefin-based composition may be made from or contain a maleated polyolefin having a waxy material content of less than about 5 weight percent, a yellowness index of less than about 35, and may be useful as an adhesive, a tie-layer adhesive for multi-layered structures, and a compatibilizer.

[0099] Additives

[00100] In some embodiments, the polyolefin-based composition can include an additives composition made from or containing one or more additives. Examples of additives are adhesion promoters, elastomeric polymers, UV inhibitors, antioxidants, thermal stabilizers, and the like.

[00101] Adhesive

[00102] In some embodiments, the present disclosure provides for an adhesive made from or containing a polyolefin-based composition.

[00103] The adhesive composition can take any form, *e.g.*, hot-melt, pressure sensitive, solvent-based, *etc.*, and may comprise tie-layer and laminate adhesive compositions.

[00104] Tie-Layer Structure

[00105] In some embodiments, the present disclosure provides for adhesives that are useful as tie-layers for making multi-layer structures such as films and sheets, including barrier films. A film can have a thickness of less than about 10 mils while a sheet has a thickness of at least about 10 mils. The multi-layer structures have at least two layers in addition to the adhesive layer, which bonds the other layers together. In some embodiments, at least one layer serves as a barrier layer.

[00106] Tie-layer adhesives of the present disclosure can be used in numerous multi-layer structures, including structures having from 2 to 11 polymer-based layers.

[00107] Multi-Layered Structure

[00108] In some embodiments, the present disclosure provides a multi-layered structure made from or containing

(A) a tie-layer adhesive made from or containing

(i) a polyolefin-based composition made from or containing:

(a) a first polymer composition made from or containing an ethylene polymer grafted with an unsaturated monomer, and

(b) a second polymer composition made from or containing a propylene polymer,

wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer;

(B) a polymer layer; and

(C) a substrate layer.

[00109] Multi-layer films may be made by coextrusion and may include a polyolefin layer such as LDPE, LLDPE, HDPE, EVA, ethylene-acrylic acid copolymers, ethylene-methacrylic acid copolymers, ethylene-acrylic acid ester copolymers, ethylene-methacrylic acid ester

copolymers, ionomers, and similar compounds. Barrier resins for use in the present disclosure may be polar polymers such as ethylene-vinyl alcohol (EVOH) or polyamide resins such as nylon. Other layers may be made from and/or contain a polyester.

[00110] Tie-layer adhesives of the present disclosure can be used in numerous multi-layer barrier film constructions. Generic illustrative multi-layer constructions include the following:

- PE/tie-layer/barrier/tie-layer/PP/tie-layer/PE
- PE/tie-layer/barrier/tie-layer/PE/tie-layer/PP
- PP/tie-layer/barrier/tie-layer/PE/tie-layer/PP
- PE/tie-layer/barrier/tie-layer/PE/tie-layer/PE
- PP/tie-layer/barrier/tie-layer/PP/tie-layer/PP
- PE/tie-layer/barrier/tie-layer/PE
- PE/tie-layer/barrier/tie-layer/PP
- PP/tie-layer/barrier/tie-layer/PP
- PET/tie-layer/barrier/tie-layer/PP/tie-layer/PET
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- PET/tie-layer/barrier/tie-layer/PET/tie-layer/PET
- PP/tie-layer/barrier/tie-layer/PP/tie-layer/PP
- PET/tie-layer/barrier/tie-layer/PET
- PET/tie-layer/barrier/tie-layer/PP
- PP/tie-layer/barrier/tie-layer/PP

[00111] Additional examples, where “FCL” represents a food contact layer, include:

- HDPE/tie-layer/EVOH/tie-layer/HDPE
- HDPE/tie-layer/polyamide/tie-layer/HDPE
- EVOH/tie-layer/HDPE/tie-layer/EVOH
- LDPE/tie-layer/polyamide/tie-layer/FCL
- LDPE/tie-layer/EVOH/tie-layer/FCL
- LLDPE/tie-layer/EVOH/tie-layer/FCL

- LLDPE/tie-layer/polyamide/tie-layer/FCL
- HDPE/tie-layer/EVOH/tie-layer/FCL
- HDPE/tie-layer/polyamide/tie-layer/FCL
- HDPE/tie-layer/polyamide/EVOH/polyamide/tie-layer/FCL

[00112] In some embodiments, the multi-layered structure can have three layers, having a first polymer layer, a tie-layer, and a second polymer layer. The first polymer layer can have a thickness in the range of about 20 to about 50 percent, based upon the total thickness of the structure. The tie-layer can have a thickness in the range of about 3 to about 12 percent, based upon the total thickness of the structure. The second polymer layer can have a thickness in the range of about 20 to about 50 percent, based upon the total thickness of the structure.

[00113] In some embodiments, the multi-layered structure can have five layers, having a first polymer layer, a first tie-layer, a second polymer layer, a second tie-layer, and a third polymer layer. The first polymer layer can have a thickness in the range of about 20 to about 50 percent, based upon the total thickness of the structure. The first tie-layer can have a thickness in the range of about 3 to about 12 percent, based upon the total thickness of the structure. The second polymer layer can have a thickness in the range of about 3 to about 15 percent, based upon the total thickness of the structure. The second tie-layer can have a thickness in the range of about 3 to about 12 percent, based upon the total thickness of the structure. The third polymer layer can have a thickness in the range of about 20 to about 50 percent, based upon the total thickness of the structure.

[00114] Process for Preparing Polyolefin-Based Compositions

[00115] In some embodiments, the present disclosure provides a process containing:

(A) the adding step of combining:

- (i) a first polymer composition made from or containing an ethylene polymer grafted with an unsaturated monomer,
- (ii) a second polymer composition made from or containing a propylene polymer, and
- (iii) a mobile liquid reactant composition made from or containing an organic peroxide;

(B) the free-radical generation step of decomposing the mobile liquid reactant to form free radicals,

- (C) the treating step of treating at least one of the polymer components with the free radicals to form reactive sites on the polymer components,
- (D) the blending step of agitating the residual non-treated polymer components and the free-radical-treated polymer components,
- (E) the reacting step of covalently binding the reactive sites of the free-radical-treated polymer components to the residual non-treated polymer components, other free-radical-treated polymer components, or both, and
- (F) the collecting step of collecting the blended, reaction products as the polyolefin-based composition.

[00116] Some Other Embodiments

[00117] In some embodiments, the present disclosure provides a compatibilizer made from or containing a polyolefin-based composition.

#### EXAMPLES

[00118] The following examples are included to demonstrate some embodiments of the present disclosure. It should be appreciated by those of skill in the art that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of this disclosure.

[00119] The Ethylene Polymer Grafted with an Unsaturated Monomer (1.9%): Equistar Chemicals's PMG 2300 maleated high-density polyethylene having a melt index at 190 degrees Celsius, 2.16 kg (ASTM D1238) of 9.0 grams per 10 minutes; a density of 0.956 grams per cubic centimeter; and a maleic anhydride content (weight percent) of 1.9.

[00120] The Ethylene Polymer Grafted with an Unsaturated Monomer (1.2%): Equistar Chemicals's PMG 2572 maleated high-density polyethylene having a melt index at 190 degrees Celsius, 2.16 kg (ASTM D1238) of 3.0 grams per 10 minutes; a density of 0.930 grams per cubic centimeter; and a maleic anhydride content (weight percent) of 1.2.

[00121] Control Polypropylene: LyondellBasell's PRO-FAX™ SR257M random copolymer polypropylene, having ethylene as the comonomer, a specific gravity of 0.90, a melt flow rate of 2.0 grams per 10 minutes, and a polydispersity index of 3.3.

[00122] Impact Propylene Polymer: LyondellBasell's PROFAX™ PP 8623 very high impact polypropylene copolymer, having a melt flow rate at 230 degrees Celsius, 2.16 kg (ASTM D1238) of 1.5 grams per 10 minutes; a density of 0.902 grams per cubic centimeter; an

ethylene content (weight percent) of 19.5%; and a percentage of xylenes solubles (weight percent) of 14.4%.

[00123] Mobile Liquid Reactant: A masterbatch of 1.5 weight percent of LUPEROX™ 101 2,5-bis(tert-butyl peroxide)-2,5-dimethylhexane in Equistar Chemicals's PMG 2300 maleated high-density polyethylene, prepared by rotating 1 gallon glass jar containing 1800 g of PMG 2300 pellets with 1.5 weight percent of the organic peroxide under a heat lamp, was used.

[00124] An additive package comprising the following components was also used:

- (a) 530 ppm of IRGANOX™ 1010 sterically-hindered phenolic antioxidant,
- (b) 440 ppm of calcium stearate lubricant, and
- (c) 2100 ppm of DSTDP (dioctadecyl 3,3'-thiodipropionate) thioester antioxidant.

[00125] For the comparative example (Comparative Example 1), the 1.9% maleated polyethylene and the control polypropylene were dry blended in a 50:50 weight percent ratio with a Lestriz-18 twin screw extrusion with 250 rpm at 230 degrees Celsius at die temperature, followed by pelletization, with a strand cut through water bath. No further additives were added during compounding.

[00126] For the exemplified product (Example 2), the 1.9% maleated polyethylene, the impact polypropylene copolymer, and the organic peroxide master batch were dry blended in a 40:50:10 weight percent ratio with a Lestriz-18 twin screw extrusion with 250 rpm at 230 degrees Celsius at die temperature followed by pelletization with strand cut through water bath. No further additives were added during compounding.

Table I

Test	Comparative Example 1	Example 2
Shear Rate measured at 0.0398 rad/sec, Poise	50,400	673,000
Shear Rate measured at 100 rad/sec, Poise	5,830	5,880
Ratio of Low Shear Rate to High Shear Rate	8.6	114.4
Melt Flow Rate (230 degrees Celsius, 2.16 kg), Grams per 10 minutes	3.6	2.2
Xylene Solubles, percentage	7.5	5.7

Die Swell, percentage	116	34
Yellowness Index	10.0	14.2
DSC Crystallization	Double peak	Single peak

[00127] The exemplified composition shows a ratio of low shear rate to high shear rate more than ten times greater than the comparative example. Yet, the exemplified composition has a die swell that less than one third of the die swell of the comparative example.

[00128] FIG. 1 shows crystallization curves generated by differential scanning calorimetry (DSC) analysis of (1A) a blend of an impact polypropylene and a maleic anhydride-grafted, high-density polyethylene and (1B) a polymeric composition resulting from a reactive blend of (i) the impact polypropylene, (ii) the maleic anhydride-grafted, high-density polyethylene, and (iii) an organic peroxide. Crystallization curve 1A corresponds to Comparative Example 1 and shows a double peak. Crystallization curve 1B corresponds to Example 2 and shows a single peak for a covalently-bonded polyolefin-based composition. The curves were obtained from a 10 degrees per minute cooling rate from 170 degrees Celsius down to 25 degrees Celsius using a TA DSCII-1000 unit.

[00129] FIG. 2 shows two micrographs obtained using a Hitachi S-3500 Scanning Electron Microscope (SEM) at an accelerated voltage of 5 kV from an extrudate's surface fractured under liquid nitrogen, wherein (2A) is a blend of an impact polypropylene and a maleic anhydride-grafted high density polyethylene and (2B) is a polymeric composition resulting from a reactive blend of (i) the impact polypropylene, (ii) the maleic anhydride-grafted, high-density polyethylene, and (iii) an organic peroxide. Micrograph 2A shows phase boundaries and corresponds to Comparative Example 1. Micrograph 2B shows less defined boundaries and corresponds to Example 2.

[00130] For comparative examples and examples comprising some embodiments of the present disclosure, various compounds were formulated and then evaluated to determine the crystallization profile of a compound by Differential Scanning Calorimetry (DSC). The materials were admixed in the weight percents shown in Table II.

Table II

Component* /Test	C.Ex. 3	Ex. 4	C.Ex. 5	Ex. 6	C.Ex. 7	C.Ex. 8	Ex. 9	Ex. 10	C.Ex. 11
PMG 2300	49.8	49.8		69.8	49.7	49.7	49.7		
PMG 2572			49.8					49.7	49.7
SR 257M			49.8		24.8	49.7			49.7
PP 8623	49.8	49.8		29.8	24.8		49.7	49.7	
Luperox 101	0.00	0.15	0.15	0.15	0.30	0.30	0.30	0.30	0.30
Irganox 1010	0.053	0.053	0.053	0.053	0.053	0.053	0.053	0.053	0.053
CaStearate	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044	0.044
DSTDP	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Total	100	100	100	100	100	100	100	100	100
DSC Curve, Number Peaks	Double	Single	Double	Single	Double	Double	Single	Single	Double

[00131] It should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of this disclosure as defined by the appended claims. As one of the ordinary skill in the art will readily appreciate from the disclosure, processes, machines, manufacture, compositions of matter, means, methods, or steps, presently existing or later to be developed that may produce the same or similar results as the corresponding embodiments described herein. Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.



## CLAIMS

What is claimed is:

1. A polyolefin-based composition comprising:
  - (A) a first polymer composition comprising an ethylene polymer grafted with an unsaturated monomer, and
  - (B) a second polymer composition comprising a propylene polymer,wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer.
2. The polyolefin-based composition of claim 1, wherein the ethylene polymer is a high-density polyethylene.
3. The polyolefin-based composition of claim 1, wherein the unsaturated monomer is maleic anhydride.
4. The polyolefin-based composition of claim 1, wherein the ethylene polymer grafted with an unsaturated monomer is a high-density polyethylene (HDPE) grafted with maleic anhydride.
5. The polyolefin-based composition of claim 1, wherein the ethylene polymer grafted with an unsaturated monomer comprises:
  - (A) a melt index from about 2.0 to about 20.0 grams per 10 minutes; and
  - (B) a density in a range from about 0.930 to about 0.980 grams per cubic centimeter.
6. The polyolefin-based composition of claim 1, wherein the propylene polymer is an impact polypropylene copolymer.
7. The polyolefin-based composition of claim 6, wherein the impact polypropylene copolymer comprises:
  - (A) a melt flow rate from about 1.0 to about 10.0 grams per 10 minutes;
  - (B) a total content of ethylene-derived units in an amount from about 5 to about 30 weight percent, based upon the total weight of the impact polypropylene copolymer; and
  - (C) a total content of propylene-derived units in an amount from about 70 to about 95 weight percent, based upon the total weight of the impact polypropylene copolymer.

8. The polyolefin-based composition of claim 1, further comprising an additives composition having one or more additives.
9. The polyolefin-based composition of claim 1, comprising:
  - (A) a melt flow rate from about 1.0 to about 5.0 grams per 10 minutes;
  - (B) a xylene soluble fraction from about 3.0 to about 10.0 weight percent, based upon the total weight of the polyolefin-based composition;
  - (C) a shear rate from about 500,000 to about 800,000 poise, measured at 0.0398 rad/sec;
  - (D) a shear rate from about 4,000 to about 7,000 poise, measured at 100 rad/sec;
  - (E) a total content of ethylene-derived units of about 40 to about 70 weight percent, based upon the total weight of the polyolefin-based composition; and
  - (F) a total content of propylene-derived units of about 30 to about 60 weight percent, based upon the total weight of the polyolefin-based composition.
10. The polyolefin-based composition of claim 1, comprising a yellowness index of less than about 35.
11. The polyolefin-based composition of claim 1, comprising less than about 5 weight percent of polyolefins having a molecular weight (Mw) less than about 2000, relative to the total weight of the polyolefin-based composition.
12. A multi-layered structure comprising:
  - (A) a tie-layer adhesive comprising:
    - (i) a polyolefin-based composition comprising:
      - (a) a first polymer composition comprising an ethylene polymer grafted with an unsaturated monomer, and
      - (b) a second polymer composition comprising a propylene polymer, wherein the ethylene polymer grafted with an unsaturated monomer is covalently bonded to the propylene polymer;
  - (B) a polymer layer; and
  - (C) a substrate layer.
13. A process comprising:
  - (A) combining:
    - (i) a first polymer composition comprising an ethylene polymer grafted with an unsaturated monomer,

- (ii) a second polymer composition comprising a propylene polymer, and
- (iii) a mobile liquid reactant,
- (B) decomposing the mobile liquid reactant to form free radicals,
- (C) treating at least one of the polymer components with the free radicals to form reactive sites on the polymer components,
- (D) agitating the residual non-treated polymer components and the free-radical-treated polymer components,
- (E) covalently binding the reactive sites of the free-radical-treated polymer components to the residual non-treated polymer components, other free-radical-treated polymer components, or both, and
- (F) collecting the blended, reaction products as the polyolefin-based composition.

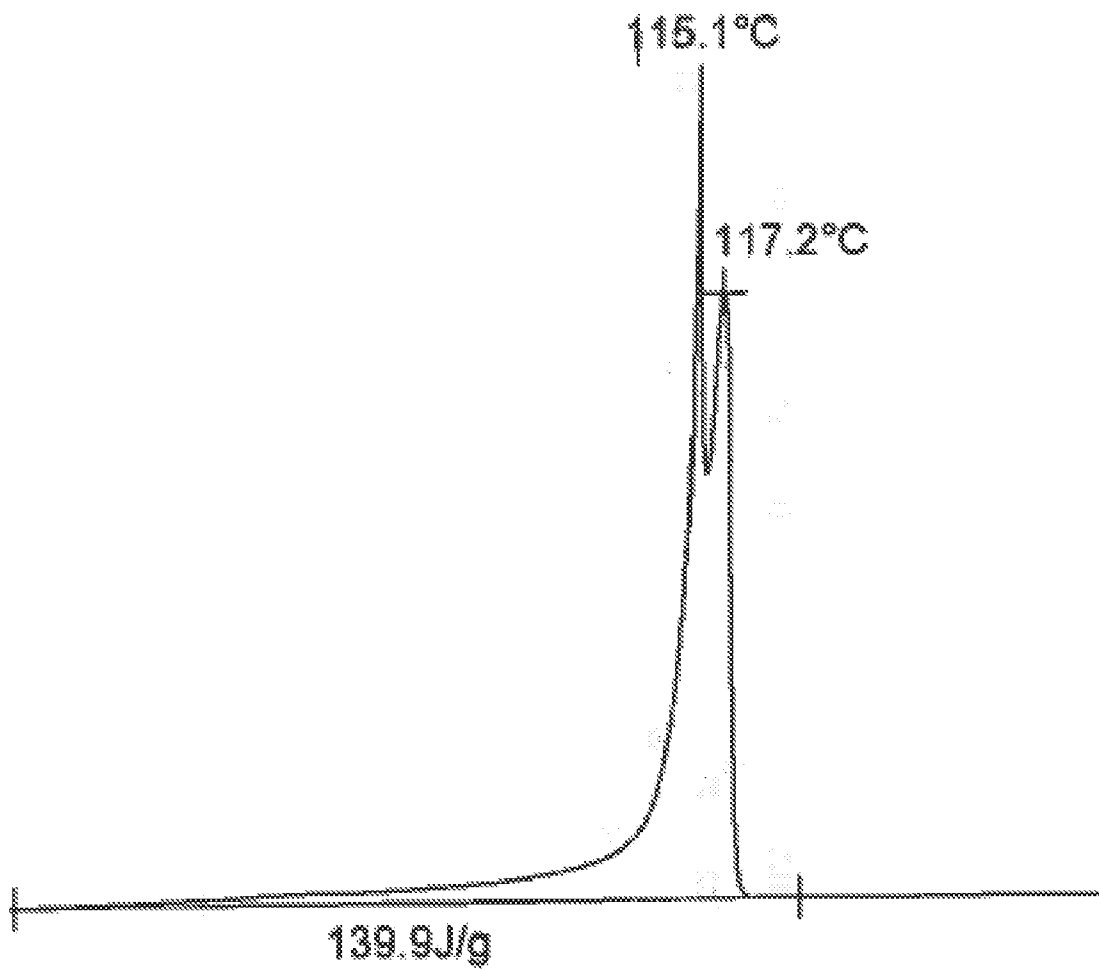


FIG. 1A

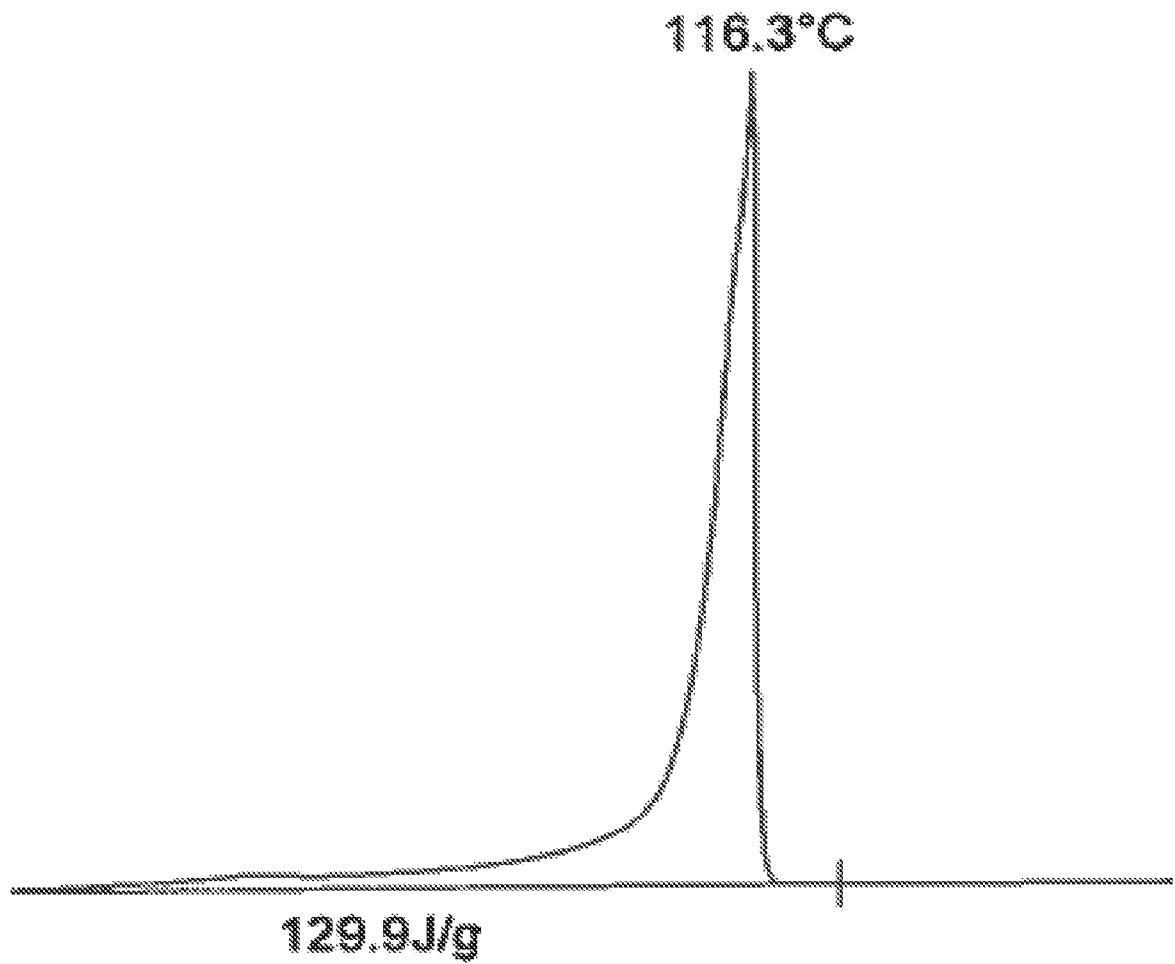


FIG. 1B

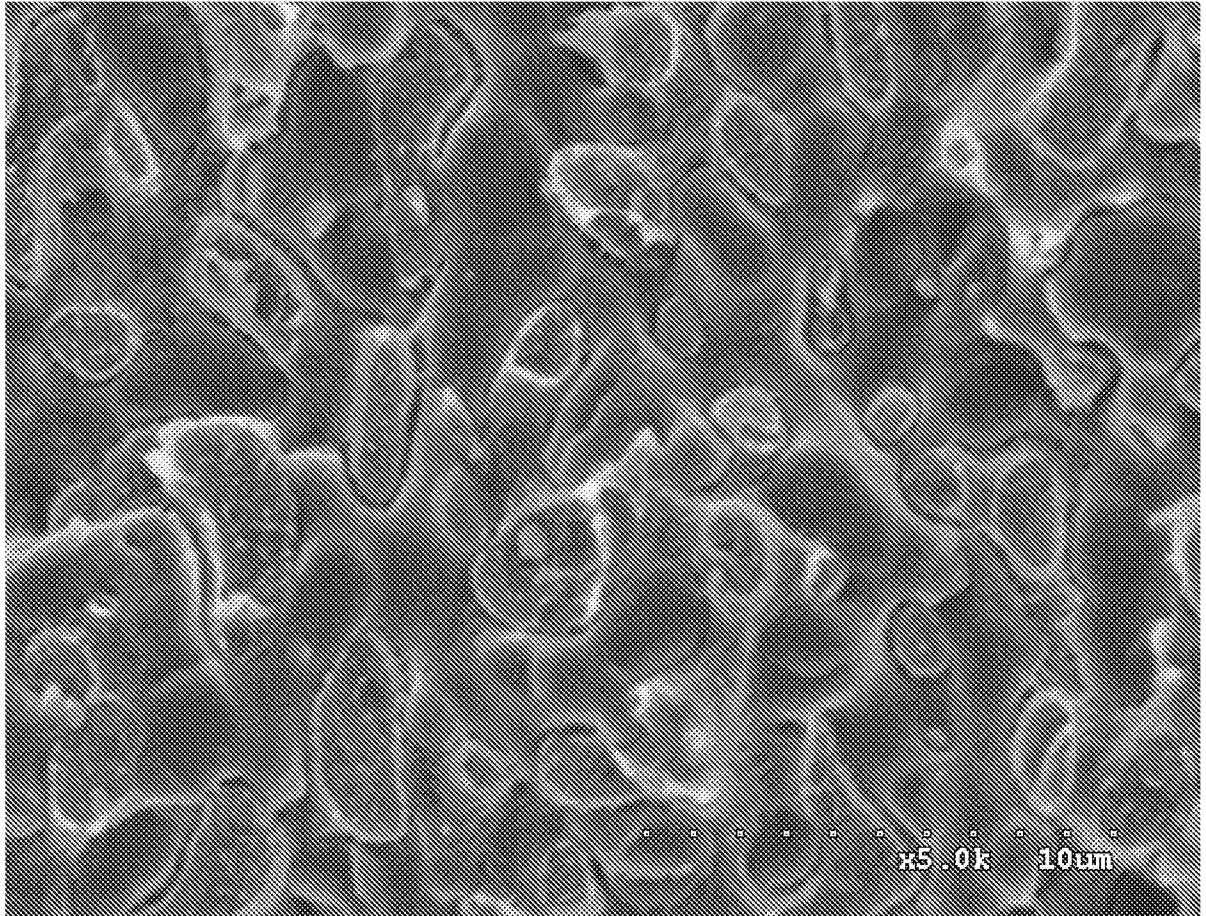


FIG. 2A

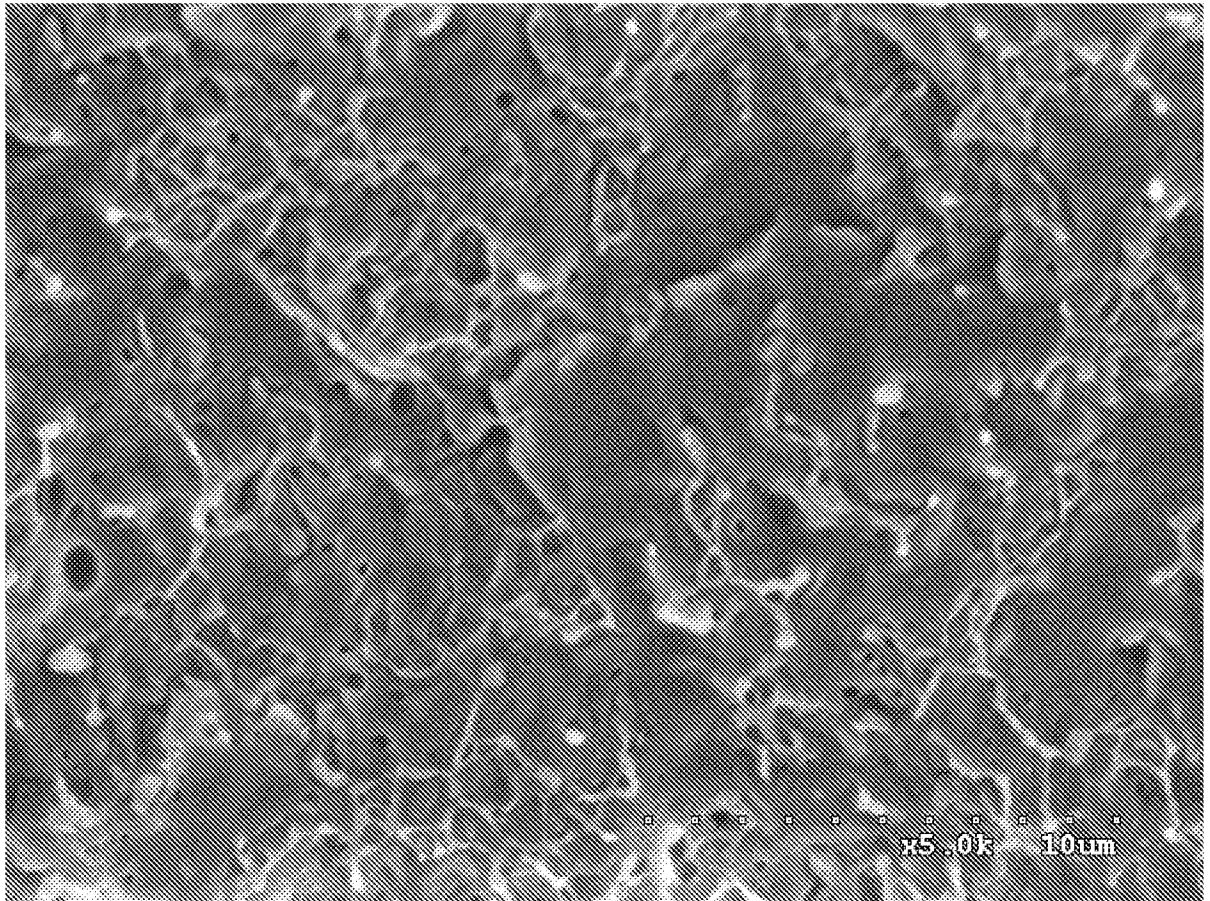


FIG. 2B

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/US2017/013220

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C08L23/12 C08L23/16 C08L51/06 B32B27/32 C09J151/06  
 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 C09J B32B

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 A	US 2012/329929 A1 (MILLER RICHARD A [US] ET AL) 27 December 2012 (2012-12-27) claims 1,8,14,17 tables 1,2	1-5,8-13 6,7
X	----- US 2003/050401 A1 (JACKSON PETER [CA] ET AL) 13 March 2003 (2003-03-13) claim 1 examples 4,5 table 3	1-3,5,8
A	----- WO 2015/142602 A1 (EQUISTAR CHEM LP [US]; BASELL POLIOLEFINE SRL [IT]) 24 September 2015 (2015-09-24) claims 1,2,4 paragraphs [0001], [0054] - paragraph [0059] -----	1-13

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  8 March 2017	Date of mailing of the international search report  16/03/2017
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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  van Bergen, Marc
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2017/013220

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
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			CN 103649258 A	19-03-2014
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