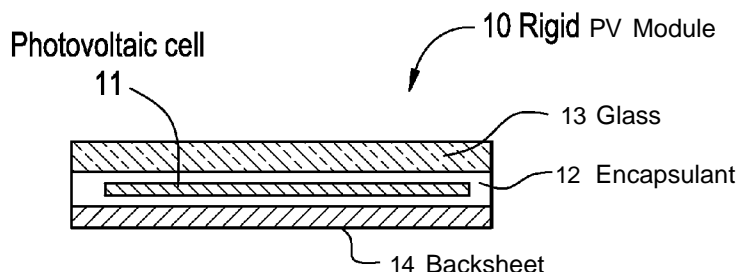




- (51) **International Patent Classification:**  
**B32B 17/10** (2006.01) **H01L 31/048** (2006.01)
- (21) **International Application Number:**  
PCT/US201 1/040492
- (22) **International Filing Date:**  
15 June 201 1 (15.06.201 1)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
61/358,060 24 June 2010 (24.06.2010) US
- (71) **Applicant (for all designated States except US):** **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, MI 48674 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **NAUMOVITZ, John, A.** [US/US]; 5014 Amberwood Court, Midland, MI 48640 (US). **PATEL, Rajen, M.** [US/US]; 220 Arrowhead Drive, Lake Jackson, TX 77566 (US). **WU, Shaofu** [US/US]; 6218 Walston Bend Drive, Sugar Land, TX 77479 (US). **NIEMANN, Debra, H.** [US/US]; 323 Rosemary Lane, Lake Jackson, TX 77566 (US).
- (74) **Agent:** **MORSE, Jonathan, W.;** The Dow Chemical Company, P.O. Box 1967, Intellectual Property, Midland, MI 48641-1967 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— with international search report (Art. 21(3))

(54) **Title:** ELECTRONIC DEVICE MODULE COMPRISING HETEROGENEOUS POLYOLEFIN COPOLYMER AND OPTIONALLY SILANE

**FIG. 1**



(57) **Abstract:** An electronic device module comprising: A. At least one electronic device, e.g., a solar cell, and B. A polymeric material in intimate contact with at least one surface of the electronic device, the polymeric material comprising (1) a polyolefin copolymer characterized as having has an average  $M_v$  and a valley temperature between the interpolymer and high crystalline fraction, The, such that the average  $M_v$  for a fraction above  $Th_C$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $MhC/Mp$ ) is less than about 1.95 and wherein the copolymer has a CDBI of less than 60%, (2) optionally, a vinyl silane, (3) optionally, free radical initiator or a photoinitiator in an amount of at least about 0.05 wt% based on the weight of the copolymer, and (4) optionally, a co-agent in an amount of at least about 0.05 wt% based upon the weight of the copolymer.



## **ELECTRONIC DEVICE MODULE COMPRISING HETEROGENEOUS POLYOLEFIN COPOLYMER AND OPTIONALLY SILANE**

### CROSS REFERENCE TO RELATED APPLICATION

5           This application claims priority from U.S. provisional application serial number 61/358,060, filed June 24, 2010, which is incorporated herein by reference in its entirety. This application is related to US Provisional Application Number 12/750,311 filed March 30, 2010 and US Serial Number 11/857,195 filed on September 18, 2007; the disclosures of which are incorporated herein by reference for U.S. prosecution purposes.

### FIELD OF THE INVENTION

10           This invention relates to electronic device modules. In one aspect, the invention relates to electronic device modules comprising an electronic device, e.g., a solar or photovoltaic (PV) cell, and a protective polymeric material while in another aspect, the invention relates to electronic device modules in which the protective polymeric material is  
15   a polymeric material in intimate contact with at least one surface of the electronic device, wherein the copolymer of ethylene and at least one alpha-olefin is made, characterized wherein the copolymer has an average  $M_v$  and a valley temperature between the interpolymers and high crystalline fraction,  $T_{hc}$ , such that the average  $M_v$  for a fraction above  $T_{hc}$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $M_{hc}/M_p$ ) is  
20   less than about 1.95, preferably less than 1.7, and wherein the copolymer has a CDBI of less than 60%, preferably less than 55%. In yet another aspect, the invention relates to a method of making an electronic device module.

### BACKGROUND OF THE INVENTION

25           Polymeric materials are commonly used in the manufacture of modules comprising one or more electronic devices including, but not limited to, solar cells (also known as photovoltaic cells), liquid crystal panels, electro-luminescent devices and plasma display units. The modules often comprise an electronic device in combination with one or more substrates, e.g., one or more glass cover sheets, often positioned between two substrates in which one or both of the substrates comprise glass, metal, plastic, rubber or another  
30   material. The polymeric materials are typically used as the encapsulant or sealant for the module or depending upon the design of the module, as a skin layer component of the module, e.g., a backskin in a solar cell module. Typical polymeric materials for these

purposes include silicone resins, epoxy resins, polyvinyl butyral resins, cellulose acetate, ethylene-vinyl acetate copolymer (EVA) and ionomers.

United States Patent Application Publication 2001/0045229 A1 identifies a number of properties desirable in any polymeric material that is intended for use in the construction of an electronic device module. These properties include (i) protecting the device from exposure to the outside environment, e.g., moisture and air, particularly over long periods of time (ii) protecting against mechanical shock, (iii) strong adhesion to the electronic device and substrates, (iv) easy processing, including sealing, (v) good transparency, particularly in applications in which light or other electromagnetic radiation is important, e.g., solar cell modules, (vi) short cure times with protection of the electronic device from mechanical stress resulting from polymer shrinkage during cure, (vii) high electrical resistance with little, if any, electrical conductance, and (viii) low cost. No one polymeric material delivers maximum performance on all of these properties in any particular application, and usually trade-offs are made to maximize the performance of properties most important to a particular application, e.g., transparency and protection against the environment, at the expense of properties secondary in importance to the application, e.g., cure time and cost. Combinations of polymeric materials are also employed, either as a blend or as separate components of the module.

EVA copolymers with a high content (28 to 35 wt%) of units derived from the vinyl acetate monomer are commonly used to make encapsulant film for use in photovoltaic (PV) modules. See, for example, WO 95/22844, 99/04971, 99/05206 and 2004/055908. EVA resins are typically stabilized with ultra-violet (UV) light additives, and they are typically crosslinked during the solar cell lamination process using peroxides to improve heat and creep resistance to a temperature between about 80 and 90°C. However, EVA resins are less than ideal PV cell encapsulating film material for several reasons. For example, EVA film progressively darkens in intense sunlight due to the EVA resin chemically degrading under the influence of UV light. This discoloration can result in a greater than 30% loss in power output of the solar module after as little as four years of exposure to the environment. EVA resins also absorb moisture and are subject to decomposition.

Moreover and as noted above, EVA resins are typically stabilized with UV additives and crosslinked during the solar cell lamination and/or encapsulation process using peroxides to improve heat resistance and creep at high temperature, e.g., 80 to 90°C.

However, because of the C=O bonds in the EVA molecular structure that absorbs UV radiation and the presence of residual peroxide crosslinking agent in the system after curing, an additive package is used to stabilize the EVA against UV-induced degradation. The residual peroxide is believed to be the primary oxidizing reagent responsible for the  
5 generation of chromophores (e.g., USP 6,093,757). Additives such as antioxidants, UV-stabilizers, UV-absorbers and others are can stabilize the EVA, but at the same time the additive package can also block UV-wavelengths below 360 nanometers (nm).

Photovoltaic module efficiency depends on photovoltaic cell efficiency and the sun light wavelength passing through the encapsulant. One of the most fundamental limitations  
10 on the efficiency of a solar cell is the band gap of its semi-conducting material, i.e., the energy required to boost an electron from the bound valence band into the mobile conduction band. Photons with less energy than the band gap pass through the module without being absorbed. Photons with energy higher than the band gap are absorbed, but their excess energy is wasted (dissipated as heat). In order to increase the photovoltaic cell  
15 efficiency, "tandem" cells or multi-junction cells are used to broaden the wavelength range for energy conversion. In addition, in many of the thin film technologies such as amorphous silicon, cadmium telluride, or copper indium gallium selenide, the band gap of the semi-conductive materials is different than that of mono-crystalline silicon. These photovoltaic cells will convert light into electricity for wavelength below 360 nm. For these  
20 photovoltaic cells, an encapsulant that can absorb wavelengths below 360 nm is needed to maintain the PV module efficiency.

USP 6,320,116 and 6,586,271 teach another important property of these polymeric materials, particularly those materials used in the construction of solar cell modules. This property is thermal creep resistance, i.e., resistance to the permanent deformation of a  
25 polymer over a period of time as a result of temperature. Thermal creep resistance, generally, is directly proportional to the melting temperature of a polymer. Solar cell modules designed for use in architectural application often need to show excellent resistance to thermal creep at temperatures of 90°C or higher. For materials with low melting temperatures, e.g., EVA, crosslinking the polymeric material is often necessary to  
30 give it higher thermal creep resistance.

Crosslinking, particularly chemical crosslinking, while addressing one problem, e.g., thermal creep, can create other problems. For example, EVA, a common polymeric material used in the construction of solar cell modules and which has a rather low melting

point, is often crosslinked using an organic peroxide initiator. While this addresses the thermal creep problem, it creates a corrosion problem, i.e., total crosslinking is seldom, if ever, fully achieved and this leaves residual peroxide in the EVA. This remaining peroxide can promote oxidation and degradation of the EVA polymer and/or electronic device, e.g.,  
5 through the release of acetic acid over the life of the electronic device module. Moreover, the addition of organic peroxide to EVA requires careful temperature control to avoid premature crosslinking.

Another potential problem with peroxide-initiated crosslinking is the buildup of crosslinked material on the metal surfaces of the process equipment. During extrusion runs,  
10 high residence time is experienced at all metal flow surfaces. Over longer periods of extrusion time, crosslinked material can form at the metal surfaces and require cleaning of the equipment. The current practice to minimize gel formation, i.e., this crosslinking of polymer on the metal surfaces of the processing equipment, is to use low processing temperatures which, in turn, reduces the production rate of the extruded product.

15 One other property that can be important in the selection of a polymeric material for use in the manufacture of an electronic device module is thermoplasticity, i.e., the ability to be softened, molded and formed. For example, if the polymeric material is to be used as a backskin layer in a frameless module, then it should exhibit thermoplasticity during lamination as described in USP 5,741,370. This thermoplasticity, however, must not be  
20 obtained at the expense of effective thermal creep resistance.

### SUMMARY OF THE INVENTION

In one embodiment, the invention is an electronic device module comprising:

- A. At least one electronic device, and
- B. A polymeric material in intimate contact with at least one surface of the  
25 electronic device, an interpolymers of ethylene and at least one alpha-olefin is made, characterized wherein the interpolymers has an average  $M_v$  and a valley temperature between the interpolymers and high crystalline fraction,  $T_{hc}$ , such that the average  $M_v$  for a fraction above  $T_{hc}$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $M_{hc}/M_p$ ) is less than about 1.95, preferably less than 1.7, and wherein the interpolymers has  
30 a CDBI of less than 60%, preferably less than 55%.

In a second embodiment, an interpolymer of ethylene and at least one alpha-olefin is made, wherein the interpolymer is characterized as having a high density (HD) fraction and an overall density such that % HD fraction  $< -2733.3 + 2988.7x + 144111.5 (x - 0.92325)^2$   
5 where x is the density in grams/cubic centimeter.

In either embodiment, the interpolymer is preferably heterogeneously branched. Film can be made from the interpolymers of either embodiment, especially films comprising Dart A of at least 550 grams, or comprising haze of  $< 10\%$ , or comprising 45  
10 degree gloss units of  $> 75$  units, or comprising Normalized MD Tear  $> 400$  grams/mil. The film can comprise at least one layer comprising the interpolymer of either the first or second embodiment.

In either embodiment, the interpolymer can further comprise at least one other  
15 natural or synthetic polymer, preferably low density polyethylene. The interpolymer of either embodiment can comprise a melt index from about 0.1 to about 10 g/10 min., or can comprise an overall density from about 0.9 to about 0.935 g/cm<sup>3</sup>, or can comprise long chain branches of less than 1 per 1000 C atoms, or can comprise a molecular weight distribution,  $M_w/M_n$ , of less than about 5.

20

A fabricated article can comprise the interpolymer of either the first or second embodiment. Further the interpolymer of either the first or second embodiment can be at least partially cross-linked to at least 85%, by weight, gel,  
(2) optionally, a vinyl silane, (3) optionally, free radical initiator, e.g., a peroxide or  
25 azo compound, or a photoinitiator, e.g., benzophenone, in an amount of at least about 0.05 wt% based on the weight of the copolymer, and (4) optionally, a co-agent in an amount of at least about 0.05 wt% based upon the weight of the copolymer.

In another embodiment, the invention is an electronic device module comprising:

30

- A. At least one electronic device, and
- B. A polymeric material in intimate contact with at least one surface of the electronic device, the polymeric material comprising an interpolymer characterized wherein the interpolymer has an average  $M_v$  and a valley

temperature between the interpolymer and high crystalline fraction,  $T_{hc}$ , such that the average  $M_v$  for a fraction above  $T_{hc}$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $M_{hc}/M_p$ ) is less than about 1.95, preferably less than 1.7, and wherein the interpolymer has a CDBI of less than 60%, preferably less than 55%, (2) optionally, a vinyl silane, e.g., vinyl tri-ethoxy silane or vinyl tri-methoxy silane, in an amount of at least about 0.1 wt% based on the weight of the copolymer, (3) free radical initiator, e.g., a peroxide or azo compound, or a photoinitiator, e.g., benzophenone, in an amount of at least about 0.05 wt% based on the weight of the copolymer, and (4) optionally, a co-agent in an amount of at least about 0.05 wt% based on the weight of the copolymer.

"In intimate contact" and like terms mean that the polymeric material is in contact with at least one surface of the device or other article in a similar manner as a coating is in contact with a substrate, e.g., little, if any gaps or spaces between the polymeric material and the face of the device and with the material exhibiting good to excellent adhesion to the face of the device. After extrusion or other method of applying the polymeric material to at least one surface of the electronic device, the material typically forms and/or cures to a film that can be either transparent or opaque and either flexible or rigid. If the electronic device is a solar cell or other device that requires unobstructed or minimally obstructed access to sunlight or to allow a user to read information from it, e.g., a plasma display unit, then that part of the material that covers the active or "business" surface of the device is highly transparent.

The module can further comprise one or more other components, such as one or more glass cover sheets, and in these embodiments, the polymeric material usually is located between the electronic device and the glass cover sheet in a sandwich configuration. If the polymeric material is applied as a film to the surface of the glass cover sheet opposite the electronic device, then the surface of the film that is in contact with that surface of the glass cover sheet can be smooth or uneven, e.g., embossed or textured.

Typically, the polyolefin copolymer is an ethylene/a-olefin copolymer. The polymeric material can fully encapsulate the electronic device, or it can be in intimate contact with only a portion of it, e.g., laminated to one face surface of the device. Optionally, the polymeric material can further comprise a scorch inhibitor, and depending upon the application for which the module is intended, the chemical composition of the

copolymer and other factors, the copolymer can remain uncrosslinked or be crosslinked. If crosslinked, then it is crosslinked such that it contains less than about 85 percent xylene soluble extractables as measured by ASTM 2765-95.

In another embodiment, the invention is the electronic device module as described in the two embodiments above except that the polymeric material in intimate contact with at least one surface of the electronic device is a co-extruded material in which at least one outer skin layer (i) does not contain peroxide for crosslinking, and (ii) is the surface which comes into intimate contact with the module. Typically, this outer skin layer exhibits good adhesion to glass. This outer skin of the co-extruded material can comprise any one of a number of different polymers, but is typically the same polymer as the polymer of the peroxide-containing layer but without the peroxide. This embodiment of the invention allows for the use of higher processing temperatures which, in turn, allows for faster production rates without unwanted gel formation in the encapsulating polymer due to extended contact with the metal surfaces of the processing equipment. In another embodiment, the extruded product comprises at least three layers in which the skin layer in contact with the electronic module is without peroxide, and the peroxide-containing layer is a core layer.

In another embodiment, the invention is a method of manufacturing an electronic device module, the method comprising the steps of:

- A. Providing at least one electronic device, and
- B. Contacting at least one surface of the electronic device with a polymeric material comprising an interpolymer characterized wherein the interpolymer has an average  $M_v$  and a valley temperature between the interpolymer and high crystalline fraction,  $T_{hc}$ , such that the average  $M_v$  for a fraction above  $T_{he}$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $M_{hc}/M_p$ ) is less than about 1.95, preferably less than 1.7, and wherein the interpolymer has a CDBI of less than 60%, preferably less than 55%,  
(2) optionally, a vinyl silane; (3) optionally free radical initiator, e.g., a peroxide or azo compound, or a photoinitiator, e.g., benzophenone, in an amount of at least about 0.05 wt% based on the weight of the copolymer, and  
(4) optionally, a co-agent in an amount of at least about 0.05 wt% based upon the weight of the copolymer.



In another embodiment the invention is a method of manufacturing an electronic device, the method comprising the steps of:

- A. Providing at least one electronic device, and
- B. Contacting at least one surface of the electronic device with a polymeric material comprising an interpolymer characterized wherein the interpolymer has an average  $M_v$  and a valley temperature between the interpolymer and high crystalline fraction,  $T_{hc}$ , such that the average  $M_v$  for a fraction above  $T_{he}$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $M_{hc}/M_p$ ) is less than about 1.95, preferably less than 1.7, and wherein the interpolymer has a CDBI of less than 60%, preferably less than 55%, (2) optionally, a vinyl silane, e.g., vinyl tri-ethoxy silane or vinyl tri-methoxy silane, in an amount of at least about 0.1 wt% based on the weight of the copolymer, (3) optionally, free radical initiator, e.g., a peroxide or azo compound, or a photoinitiator, e.g., benzophenone, in an amount of at least about 0.05 wt% based on the weight of the copolymer, and (4) optionally, a co-agent in an amount of at least about 0.05 wt% based on the weight of the copolymer.

In a variant on both of these two method embodiments, the module further comprises at least one translucent cover layer disposed apart from one face surface of the device, and the polymeric material is interposed in a sealing relationship between the electronic device and the cover layer. "In a sealing relationship" and like terms mean that the polymeric material adheres well to both the cover layer and the electronic device, typically to at least one face surface of each, and that it binds the two together with little, if any, gaps or spaces between the two module components (other than any gaps or spaces that may exist between the polymeric material and the cover layer as a result of the polymeric material applied to the cover layer in the form of an embossed or textured film, or the cover layer itself is embossed or textured).

Moreover, in both of these method embodiments, the polymeric material can further comprise a scorch inhibitor, and the method can optionally include a step in which the copolymer is crosslinked, e.g., either contacting the electronic device and/or glass cover sheet with the polymeric material under crosslinking conditions, or exposing the module to crosslinking conditions after the module is formed such that the polyolefin copolymer

contains less than about 85 percent xylene soluble extractables as measured by ASTM 2765-95. Crosslinking conditions include heat (e.g., a temperature of at least about 160°C), radiation (e.g., at least about 15 mega-rad if by E-beam, or 0.05 joules/cm<sup>2</sup> if by UV light), moisture (e.g., a relative humidity of at least about 50%), etc.

5            In another variant on these method embodiments, the electronic device is encapsulated, i.e., fully engulfed or enclosed, within the polymeric material. In another variant on these embodiments, the glass cover sheet is treated with a silane coupling agent, e.g., (-amino propyl tri-ethoxy silane. In yet another variant on these embodiments, the polymeric material further comprises a graft polymer to enhance its adhesive property  
10 relative to the one or both of the electronic device and glass cover sheet. Typically the graft polymer is made *in situ* simply by grafting the polyolefin copolymer with an unsaturated organic compound that contains a carbonyl group, e.g., maleic anhydride.

          In another embodiment, the invention is an ethylene/non-polar  $\alpha$ -olefin polymeric film characterized in that the film has (i) greater than or equal to (>) 92% transmittance over  
15 the wavelength range from 400 to 1100 nanometers (nm), and (ii) a water vapor transmission rate (WVTR) of less than (<) about 50, preferably < about 15, grams per square meter per day (g/m<sup>2</sup>-day) at 38°C and 100% relative humidity (RH).

#### BRIEF DESCRIPTION OF THE DRAWINGS

          Figure 1 is a schematic of one embodiment of an electronic device module of this  
20 invention, i.e., a rigid photovoltaic (PV) module.

          Figure 2 is a schematic of another embodiment of an electronic device module of this invention, i.e., a flexible PV module.

          Figure 3 plots Short Chain Branching Distribution and log M<sub>v</sub> data from ATREF for Inventive Example 1 and Comparative Example 1.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

          The polyolefin copolymers useful in the practice of this invention have a density of greater than or less than or equal to about 0.90, preferably less than about 0.89, more preferably less than about 0.885, even more preferably less than about 0.88 and even more preferably less than about 0.875, g/cc. The polyolefin copolymers typically have a density  
30 greater than about 0.85, and more preferably greater than about 0.86, g/cc. Density is

measured by the procedure of ASTM D-792. Low density polyolefin copolymers are generally characterized as amorphous, flexible and having good optical properties, e.g., high transmission of visible and UV-light and low haze.

The polyolefin copolymers useful in the practice of this invention have a 2% secant  
5 modulus of less than about 150, preferably less than about 140, more preferably less than about 120 and even more preferably less than about 100, mPa as measured by the procedure of ASTM D-882-02. The polyolefin copolymers typically have a 2% secant modulus of greater than zero, but the lower the modulus, the better the copolymer is adapted for use in this invention. The secant modulus is the slope of a line from the origin of a stress-strain  
10 diagram and intersecting the curve at a point of interest, and it is used to describe the stiffness of a material in the inelastic region of the diagram. Low modulus polyolefin copolymers are particularly well adapted for use in this invention because they provide stability under stress, e.g., less prone to crack upon stress or shrinkage.

For polyolefin copolymers made with multi-site catalysts, e.g., Zeigler-Natta and  
15 Phillips catalysts, the melting point is typically less than about 125, preferably less than about 120, more preferably less than about 115 and even more preferably less than about 110, C. The melting point is measured by differential scanning calorimetry (DSC) as described, for example, in USP 5,783,638. Polyolefin copolymers with a low melting point often exhibit desirable flexibility and thermoplasticity properties useful in the fabrication of  
20 the modules of this invention.

The polyolefin copolymers useful in the practice of this invention include ethylene/a-olefin interpolymers having a a-olefin content of between about 15, preferably at least about 20 and even more preferably at least about 25, wt% based on the weight of the interpolymers. These interpolymers typically have an a-olefin content of less than about 50,  
25 preferably less than about 45, more preferably less than about 40 and even more preferably less than about 35, wt% based on the weight of the interpolymers. The a-olefin content is measured by <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy using the procedure described in Randall (*Rev. Macromol. Chem. Phys.*, C29 (2&3)). Generally, the greater the α-olefin content of the interpolymers, the lower the density and the more amorphous the  
30 interpolymers, and this translates into desirable physical and chemical properties for the protective polymer component of the module.

The  $\alpha$ -olefin is preferably a  $C_{3-20}$  linear, branched or cyclic  $\alpha$ -olefin. The term interpolymer refers to a polymer made from at least two monomers. It includes, for example, copolymers, terpolymers and tetrapolymers. Examples of  $C_{3-20}$   $\alpha$ -olefins include propene, 1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 5 1-tetradecene, 1-hexadecene, and 1-octadecene. The  $\alpha$ -olefins can also contain a cyclic structure such as cyclohexane or cyclopentane, resulting in an  $\alpha$ -olefin such as 3-cyclohexyl-1-propene (allyl cyclohexane) and vinyl cyclohexane. Although not  $\alpha$ -olefins in the classical sense of the term, for purposes of this invention certain cyclic olefins, such as norbornene and related olefins, are  $\alpha$ -olefins and can be used in place of some or all of the 10  $\alpha$ -olefins described above. Similarly, styrene and its related olefins (for example,  $\alpha$ -methylstyrene, etc.) are  $\alpha$ -olefins for purposes of this invention. Acrylic and methacrylic acid and their respective ionomers, and acrylates and methacrylates, however, are not  $\alpha$ -olefins for purposes of this invention. Illustrative polyolefin copolymers include ethylene/propylene, ethylene/butene, ethylene/1-hexene, ethylene/1-octene, 15 ethylene/styrene, and the like. Ethylene/acrylic acid (EAA), ethylene/methacrylic acid (EMA), ethylene/acrylate or methacrylate, ethylene/vinyl acetate and the like are not polyolefin copolymers of this invention. Illustrative terpolymers include ethylene/propylene/1-octene, ethylene/propylene/butene, ethylene/butene/1-octene, and ethylene/butene/styrene. The copolymers can be random or blocky.

20 More specific examples of olefinic interpolymers useful in this invention include very low density polyethylene (VLDPE) (e.g., FLEXOMER<sup>TM</sup> ethylene/1-hexene polyethylene made by Union Carbide Corporation), and DOWLEX<sup>TM</sup> LLDPE (made by The Dow Chemical Company).

The polyolefin copolymers useful in the practice of this invention also include 25 propylene, butene and other alkene-based copolymers, e.g., copolymers comprising a majority of units derived from propylene and a minority of units derived from another  $\alpha$ -olefin (including ethylene). Exemplary polypropylenes useful in the practice of this invention include the VERSIFY<sup>TM</sup> polymers available from The Dow Chemical Company, and the VISTAMAXX<sup>®</sup> polymers available from ExxonMobil Chemical Company.

30 Blends of any of the above olefinic interpolymers can also be used in this invention, and the polyolefin copolymers can be blended or diluted with one or more other polymers to the extent that the polymers are (i) miscible with one another, (ii) the other polymers have little, if any, impact on the desirable properties of the polyolefin copolymer, e.g., optics and

low modulus, and (iii) the polyolefin copolymers of this invention constitute at least about 70, preferably at least about 75 and more preferably at least about 80, weight percent of the blend. Although not favored, EVA copolymer can be one of the diluting polymers.

Typically the polyolefin copolymers used in the practice of this invention also have  
5 a melt index (MI as measured by the procedure of ASTM D-1238 (190C/2.16kg) of less than about 100, preferably less than about 75, more preferably less than about 50 and even more preferably less than about 35, g/10 minutes. The typical minimum MI is about 1, and more typically it is about 5.

The polyolefin copolymers useful in the practice of this invention have an SCBDI  
10 (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) is defined as the weight percent of the polymer molecules having comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as  
15 described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys.Ed., Vol. 20, p. 441 (1982), or as described in USP 4,798,081 and 5,008,204. The SCBDI or CDBI for the polyolefin copolymers used in the practice of this present invention is typically less than about 60, preferably less than about 50.

Due to the low density and modulus of the polyolefin copolymers used in the  
20 practice of this invention, these copolymers are typically cured or crosslinked at the time of contact or after, usually shortly after, the module has been constructed. Crosslinking is important to the performance of the copolymer in its function to protect the electronic device from the environment. Specifically, crosslinking enhances the thermal creep resistance of the copolymer and durability of the module in terms of heat, impact and  
25 solvent resistance. Crosslinking can be effected by any one of a number of different methods, e.g., by the use of thermally activated initiators, e.g., peroxides and azo compounds; photoinitiators, e.g., benzophenone; radiation techniques including sunlight, UV light, E-beam and x-ray; vinyl silane, e.g., vinyl tri-ethoxy or vinyl tri-methoxy silane; and moisture cure.

30 The free radical initiators used in the practice of this invention include any thermally activated compound that is relatively unstable and easily breaks into at least two radicals. Representative of this class of compounds are the peroxides, particularly the organic

peroxides, and the azo initiators. Of the free radical initiators used as crosslinking agents, the dialkyl peroxides and diperoxyketal initiators are preferred. These compounds are described in the Encyclopedia of Chemical Technology, 3rd edition, Vol. 17, pp 27-90. (1982).

5 In the group of dialkyl peroxides, the preferred initiators are: dicumyl peroxide, di-t-butyl peroxide, t-butyl cumyl peroxide, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane, 2,5-dimethyl-2,5-di(t-amylperoxy)-hexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-di(t-amylperoxy)hexyne-3, a, a-di[(t-butylperoxy)-isopropyl]-benzene, di-t-amyl peroxide, 1,3,5-tri-[(t-butylperoxy)-isopropyl]benzene, 1,3-dimethyl-3-  
10 (t-butylperoxy)butanol, 1,3-dimethyl-3-(t-amylperoxy)butanol and mixtures of two or more of these initiators.

In the group of diperoxyketal initiators, the preferred initiators are:  
1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(t-butylperoxy)cyclohexane n-butyl, 4,4-di(t-amylperoxy)valerate, ethyl 3,3-di(t-butylperoxy)butyrate, 2,2-di(t-  
15 amylperoxy)propane, 3,6,6,9,9-pentamethyl-3-ethoxycarbonylmethyl-1, 2,4,5-tetraoxacyclononane, n-butyl-4,4-bis(t-butylperoxy)-valerate, ethyl-3,3-di(t-amylperoxy)-butyrate and mixtures of two or more of these initiators.

Other peroxide initiators, e.g., 00-t-butyl-O-hydrogen-monoperoxysuccinate; 00-t-amyl-O-hydrogen-monoperoxysuccinate and/or azo initiators e.g., 2,2'-azobis-(2-  
20 acetoxypropane), may also be used to provide a crosslinked polymer matrix. Other suitable azo compounds include those described in USP 3,862,107 and 4,129,531. Mixtures of two or more free radical initiators may also be used together as the initiator within the scope of this invention. In addition, free radicals can form from shear energy, heat or radiation.

The amount of peroxide or azo initiator present in the crosslinkable compositions of  
25 this invention can vary widely, but the minimum amount is that sufficient to afford the desired range of crosslinking. The minimum amount of initiator is typically at least about 0.05, preferably at least about 0.1 and more preferably at least about 0.25, wt% based upon the weight of the polymer or polymers to be crosslinked. The maximum amount of initiator used in these compositions can vary widely, and it is typically determined by such factors as  
30 cost, efficiency and degree of desired crosslinking desired. The maximum amount is typically less than about 10, preferably less than about 5 and more preferably less than about 3, wt% based upon the weight of the polymer or polymers to be crosslinked.

Free radical crosslinking initiation *via* electromagnetic radiation, e.g., sunlight, ultraviolet (UV) light, infrared (IR) radiation, electron beam, beta-ray, gamma-ray, x-ray and neutron rays, may also be employed. Radiation is believed to affect crosslinking by generating polymer radicals, which may combine and crosslink. The Handbook of Polymer  
5 Foams and Technology, *supra*, at pp. 198-204, provides additional teachings. Elemental sulfur may be used as a crosslinking agent for diene containing polymers such as EPDM and polybutadiene. The amount of radiation used to cure the copolymer will vary with the chemical composition of the copolymer, the composition and amount of initiator, if any, the nature of the radiation, and the like, but a typical amount of UV light is at least about 0.05,  
10 more typically at about 0.1 and even more typically at least about 0.5, Joules/cm<sup>2</sup>, and a typical amount of E-beam radiation is at least about 0.5, more typically at least about 1 and even more typically at least about 1.5, megarads.

If sunlight or UV light is used to effect cure or crosslinking, then typically and preferably one or more photoinitiators are employed. Such photoinitiators include organic  
15 carbonyl compounds such as benzophenone, benzanthrone, benzoin and alkyl ethers thereof, 2,2-diethoxyacetophenone, 2,2-dimethoxy, 2 phenylacetophenone, p-phenoxy dichloroacetophenone, 2-hydroxycyclohexylphenone, 2-hydroxyisopropylphenone, and 1-phenylpropanedione-2-(ethoxy carboxyl) oxime. These initiators are used in known manners and in known quantities, e.g., typically at least about 0.05, more typically at least  
20 about 0.1 and even more typically about 0.5, wt% based on the weight of the copolymer.

If moisture, i.e., water, is used to effect cure or crosslinking, then typically and preferably one or more hydrolysis/condensation catalysts are employed. Such catalysts include Lewis acids such as dibutyltin dilaurate, dioctyltin dilaurate, stannous octonate, and hydrogen sulfonates such as sulfonic acid.

25 Free radical crosslinking coagents, i.e. promoters or co-initiators, include multifunctional vinyl monomers and polymers, triallyl cyanurate and trimethylolpropane trimethacrylate, divinyl benzene, acrylates and methacrylates of polyols, allyl alcohol derivatives, and low molecular weight polybutadiene. Sulfur crosslinking promoters include benzothiazyl disulfide, 2-mercaptobenzothiazole, copper dimethyldithiocarbamate,  
30 dipentamethylene thiuram tetrasulfide, tetrabutylthiuram disulfide, tetramethylthiuram disulfide and tetramethylthiuram monosulfide.

These coagents are used in known amounts and known ways. The minimum amount of coagent is typically at least about 0.05, preferably at least about 0.1 and more preferably at least about 0.5, wt% based upon the weight of the polymer or polymers to be crosslinked. The maximum amount of coagent used in these compositions can vary widely, and it is typically determined by such factors as cost, efficiency and degree of desired crosslinking desired. The maximum amount is typically less than about 10, preferably less than about 5 and more preferably less than about 3, wt% based upon the weight of the polymer or polymers to be crosslinked.

One difficulty in using thermally activated free radical initiators to promote crosslinking, i.e., curing, of thermoplastic materials is that they may initiate premature crosslinking, i.e., scorch, during compounding and/or processing prior to the actual phase in the overall process in which curing is desired. With conventional methods of compounding, such as milling, Banbury, or extrusion, scorch occurs when the time-temperature relationship results in a condition in which the free radical initiator undergoes thermal decomposition which, in turn, initiates a crosslinking reaction that can create gel particles in the mass of the compounded polymer. These gel particles can adversely impact the homogeneity of the final product. Moreover, excessive scorch can so reduce the plastic properties of the material that it cannot be efficiently processed with the likely possibility that the entire batch will be lost.

One method of minimizing scorch is the incorporation of scorch inhibitors into the compositions. For example, British patent 1,535,039 discloses the use of organic hydroperoxides as scorch inhibitors for peroxide-cured ethylene polymer compositions. USP 3,751,378 discloses the use of N-nitroso diphenylamine or N,N'-dinitroso-para-phenylamine as scorch retardants incorporated into a polyfunctional acrylate crosslinking monomer for providing long Mooney scorch times in various copolymer formulations. USP 3,202,648 discloses the use of nitrites such as isoamyl nitrite, tert-decyl nitrite and others as scorch inhibitors for polyethylene. USP 3,954,907 discloses the use of monomeric vinyl compounds as protection against scorch. USP 3,335,124 describes the use of aromatic amines, phenolic compounds, mercaptothiazole compounds, bis(N,N-disubstituted-thiocarbamoyl) sulfides, hydroquinones and dialkyldithiocarbamate compounds. USP 4,632,950 discloses the use of mixtures of two metal salts of disubstituted dithiocarbamic acid in which one metal salt is based on copper.



One commonly used scorch inhibitor for use in free radical, particularly peroxide, initiator-containing compositions is 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl also known as nitroxyl 2, or NR 1, or 4-oxypiperidol, or tanol, or tempol, or tmpn, or probably most commonly, 4-hydroxy-TEMPO or even more simply, h-TEMPO. The addition of 4-  
5 hydroxy-TEMPO minimizes scorch by "quenching" free radical crosslinking of the crosslinkable polymer at melt processing temperatures.

The preferred amount of scorch inhibitor used in the compositions of this invention will vary with the amount and nature of the other components of the composition, particularly the free radical initiator, but typically the minimum amount of scorch inhibitor  
10 used in a system of polyolefin copolymer with 1.7 weight percent (wt%) peroxide is at least about 0.01, preferably at least about 0.05, more preferably at least about 0.1 and most preferably at least about 0.15, wt% based on the weight of the polymer. The maximum amount of scorch inhibitor can vary widely, and it is more a function of cost and efficiency than anything else. The typical maximum amount of scorch inhibitor used in a system of  
15 polyolefin copolymer with 1.7 wt% peroxide does not exceed about 2, preferably does not exceed about 1.5 and more preferably does not exceed about 1, wt% based on the weight of the copolymer.

Any silane that will effectively graft to and crosslink the polyolefin copolymer can be used in the practice of this invention. Suitable silanes include unsaturated silanes that  
20 comprise an ethylenically unsaturated hydrocarbyl group, such as a vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or -(meth)acryloxy allyl group, and a hydrolyzable group, such as, for example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group. Examples of hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, and alkyl or arylamino groups. Preferred silanes are the unsaturated alkoxy silanes which can  
25 be grafted onto the polymer. These silanes and their method of preparation are more fully described in USP 5,266,627. Vinyl trimethoxy silane, vinyl triethoxy silane, (- (meth)acryloxy propyl trimethoxy silane and mixtures of these silanes are the preferred silane crosslinkers for use in this invention. If filler is present, then preferably the crosslinker includes vinyl triethoxy silane.

30 The amount of silane crosslinker used in the practice of this invention can vary widely depending upon the nature of the polyolefin copolymer, the silane, the processing conditions, the grafting efficiency, the ultimate application, and similar factors, but typically

at least 0.5, preferably at least 0.7, parts per hundred resin wt% is used based on the weight of the copolymer. Considerations of convenience and economy are usually the two principal limitations on the maximum amount of silane crosslinker used in the practice of this invention, and typically the maximum amount of silane crosslinker does not exceed 5,  
5 preferably it does not exceed 2, wt% based on the weight of the copolymer.

The silane crosslinker is grafted to the polyolefin copolymer by any conventional method, typically in the presence of a free radical initiator e.g. peroxides and azo compounds, or by ionizing radiation, etc. Organic initiators are preferred, such as any of those described above, e.g., the peroxide and azo initiators. The amount of initiator can  
10 vary, but it is typically present in the amounts described above for the crosslinking of the polyolefin copolymer.

While any conventional method can be used to graft the silane crosslinker to the polyolefin copolymer, one preferred method is blending the two with the initiator in the first stage of a reactor extruder, such as a Buss kneader. The grafting conditions can vary, but  
15 the melt temperatures are typically between 160 and 260°C, preferably between 190 and 230°C, depending upon the residence time and the half life of the initiator.

In another embodiment of the invention, the polymeric material further comprises a graft polymer to enhance the adhesion to one or more glass cover sheets to the extent that these sheets are components of the electronic device module. While the graft polymer can  
20 be any graft polymer compatible with the polyolefin copolymer of the polymeric material and which does not significantly compromise the performance of the polyolefin copolymer as a component of the module, typically the graft polymer is a graft polyolefin polymer and more typically, a graft polyolefin copolymer that is of the same composition as the polyolefin copolymer of the polymeric material. This graft additive is typically made *in situ*  
25 simply by subjecting the polyolefin copolymer to grafting reagents and grafting conditions such that at least a portion of the polyolefin copolymer is grafted with the grafting material.

Any unsaturated organic compound containing at least one ethylenic unsaturation (e.g., at least one double bond), at least one carbonyl group ( $\text{—C=O}$ ), and that will graft to a polymer, particularly a polyolefin polymer and more particularly to a polyolefin copolymer,  
30 can be used as the grafting material in this embodiment of the invention. Representative of compounds that contain at least one carbonyl group are the carboxylic acids, anhydrides, esters and their salts, both metallic and nonmetallic. Preferably, the organic compound

contains ethylenic unsaturation conjugated with a carbonyl group. Representative compounds include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, V-methyl crotonic, and cinnamic acid and their anhydride, ester and salt derivatives, if any. Maleic anhydride is the preferred unsaturated organic compound containing at least one ethylenic  
5 unsaturation and at least one carbonyl group.

The unsaturated organic compound content of the graft polymer is at least about 0.01 wt %, and preferably at least about 0.05 wt %, based on the combined weight of the polymer and the organic compound. The maximum amount of unsaturated organic compound content can vary to convenience, but typically it does not exceed about 10 wt%,  
10 preferably it does not exceed about 5 wt%, and more preferably it does not exceed about 2 wt%.

The unsaturated organic compound can be grafted to the polymer by any known technique, such as those taught in USP 3,236,917 and 5,194,509. For example, in the '917 patent the polymer is introduced into a two-roll mixer and mixed at a temperature of 60°C.  
15 The unsaturated organic compound is then added along with a free radical initiator, such as, for example, benzoyl peroxide, and the components are mixed at 30°C until the grafting is completed. In the '509 patent, the procedure is similar except that the reaction temperature is higher, e.g., 210 to 300°C, and a free radical initiator is not used or is used at a reduced concentration.

20 An alternative and preferred method of grafting is taught in USP 4,950,541 by using a twin-screw devolatilizing extruder as the mixing apparatus. The polymer and unsaturated organic compound are mixed and reacted within the extruder at temperatures at which the reactants are molten and in the presence of a free radical initiator. Preferably, the unsaturated organic compound is injected into a zone maintained under pressure within the  
25 extruder.

The polymeric materials of this invention can comprise other additives as well. For example, such other additives include UV-stabilizers and processing stabilizers such as trivalent phosphorus compounds. The UV-stabilizers are useful in lowering the wavelength of electromagnetic radiation that can be absorbed by a PV module (e.g., to less than 360  
30 nm), and include hindered phenols such as Cyasorb UV2908 and hindered amines such as Cyasorb UV 3529, Hostavin N30, Univil 4050, Univin 5050, Chimassorb UV 119, Chimassorb 944 LD, Tinuvin 622 LD and the like. The phosphorus compounds include

phosphonites (PEPQ) and phosphites (Weston 399, TNPP, P-168 and Doverphos 9228).

The amount of UV-stabilizer is typically from about 0.1 to 0.8%, and preferably from about 0.2 to 0.5%. The amount of processing stabilizer is typically from about 0.02 to 0.5%, and preferably from about 0.05 to 0.15%.

5            Still other additives include, but are not limited to, antioxidants (e.g., hindered phenolics (e.g., Irganox® 1010 made by Ciba Geigy Corp.), cling additives, e.g., PIB, anti-blocks, anti-slips, pigments, anti-stats, and fillers (clear if transparency is important to the application). In-process additives, e.g. calcium stearate, water, etc., may also be used. These and other potential additives are used in the manner and amount as is commonly  
10        known in the art.

             The polymeric materials of this invention are used to construct electronic device modules in the same manner and using the same amounts as the encapsulant materials known in the art, e.g., such as those taught in USP 6,586,271, US Patent Application Publication US2001/0045229 A1, WO 99/05206 and WO 99/04971. These materials can  
15        be used as "skins" for the electronic device, i.e., applied to one or both face surfaces of the device, or as an encapsulant in which the device is totally enclosed within the material. Typically, the polymeric material is applied to the device by one or more lamination techniques in which a layer of film formed from the polymeric material is applied first to one face surface of the device, and then to the other face surface of the device. In an  
20        alternative embodiment, the polymeric material can be extruded in molten form onto the device and allowed to congeal on the device. The polymeric materials of this invention exhibit good adhesion for the face surfaces of the device.

             In one embodiment, the electronic device module comprises (i) at least one electronic device, typically a plurality of such devices arrayed in a linear or planar pattern,  
25        (ii) at least one glass cover sheet, typically a glass cover sheet over both face surfaces of the device, and (iii) at least one polymeric material. The polymeric material is typically disposed between the glass cover sheet and the device, and the polymeric material exhibits good adhesion to both the device and the sheet. If the device requires access to specific forms of electromagnetic radiation, e.g., sunlight, infrared, ultra-violet, etc., then the  
30        polymeric material exhibits good, typically excellent, transparency for that radiation, e.g., transmission rates in excess of 90, preferably in excess of 95 and even more preferably in excess of 97, percent as measured by UV-vis spectroscopy (measuring absorbance in the wavelength range of about 250-1200 nanometers. An alternative measure of transparency is

the internal haze method of ASTM D-1003-00. If transparency is not a requirement for operation of the electronic device, then the polymeric material can contain opaque filler and/or pigment.

In Figure 1, rigid PV module 10 comprises photovoltaic cell 11 surrounded or  
5 encapsulated by transparent protective layer or encapsulant 12 comprising a polyolefin copolymer used in the practice of this invention. Glass cover sheet 13 covers a front surface of the portion of the transparent protective layer disposed over PV cell 11. Backskin or back sheet 14, e.g., a second glass cover sheet or another substrate of any kind, supports a rear surface of the portion of transparent protective layer 12 disposed on a rear surface of  
10 PV cell 11. Backskin layer 14 need not be transparent if the surface of the PV cell to which it is opposed is not reactive to sunlight. In this embodiment, protective layer 12 encapsulates PV cell 11. The thicknesses of these layers, both in an absolute context and relative to one another, are not critical to this invention and as such, can vary widely depending upon the overall design and purpose of the module. Typical thicknesses for  
15 protective layer 12 are in the range of about 0.125 to about 2 millimeters (mm), and for the glass cover sheet and backskin layers in the range of about 0.125 to about 1.25 mm. The thickness of the electronic device can also vary widely.

In Figure 2, flexible PV module 20 comprises thin film photovoltaic 21 over-lain by transparent protective layer or encapsulant 22 comprising a polyolefin copolymer used in  
20 the practice of this invention. Glazing/top layer 23 covers a front surface of the portion of the transparent protective layer disposed over thin film PV 21. Flexible backskin or back sheet 24, e.g., a second protective layer or another flexible substrate of any kind, supports the bottom surface of thin film PV 21. Backskin layer 24 need not be transparent if the surface of the thin film cell which it is supporting is not reactive to sunlight. In this  
25 embodiment, protective layer 21 does not encapsulate thin film PV 21. The overall thickness of a typical rigid or flexible PV cell module will typically be in the range of about 5 to about 50 mm.

The modules described in Figures 1 and 2 can be constructed by any number of different methods, typically a film or sheet co-extrusion method such as blown-film,  
30 modified blown-film, calendaring and casting. In one method and referring to Figure 1, protective layer 14 is formed by first extruding a polyolefin copolymer over and onto the top surface of the PV cell and either simultaneously with or subsequent to the extrusion of this first extrusion, extruding the same, or different, polyolefin copolymer over and onto the

back surface of the cell. Once the protective film is attached the PV cell, the glass cover sheet and backskin layer can be attached in any convenient manner, e.g., extrusion, lamination, etc., to the protective layer, with or without an adhesive. Either or both external surfaces, i.e., the surfaces opposite the surfaces in contact with the PV cell, of the protective layer can be embossed or otherwise treated to enhance adhesion to the glass and backskin layers. The module of Figure 2 can be constructed in a similar manner, except that the backskin layer is attached to the PV cell directly, with or without an adhesive, either prior or subsequent to the attachment of the protective layer to the PV cell.

Balance of processability, dart, tear and optical properties was achieved by making a unique combination of resin molecular weight distribution and high crystalline and copolymer fraction content. Resin characteristics and film property details are listed in Table 1, Figure 1 and Table 2. High density fraction content was significantly dropped and that of the copolymer fraction was increased. Ratio of viscosity average molecular weight of the high crystalline fraction to that of the whole polymer was lowered, indicating lower molecular weight of the high crystalline fraction. Ratio of viscosity average molecular weight of the copolymer fraction to that of the whole polymer was increased indicating higher molecular weight of the copolymer fraction. These differences in the resin characteristics were achieved by reducing the reactor temperature from about 160°C to about 180°C, especially 175°C and reducing the Al/Ti molar ratio from about 1:1 to about 5:1, especially 1:1 to about 2.5:1.

Low reactor temperature is useful for narrowing the molecular weight distribution. Reactor temperature of 175°C yielded a product with narrow molecular weight distribution without significantly reducing the production output (lb/hr). Significant further reduction in temperature could further narrow the molecular weight distribution but significantly lower the output and also make the product hurt the processability (film fabrication) of the resin.

Low Al/Ti ratio is useful for narrowing the molecular weight distribution and also for reducing the high crystalline fraction and increasing the copolymer fraction. For a HEC-3 catalyst with 3.0 Ti/40 Mg ratio, an Al/Ti ratio of 1.5 yielded a product with narrow molecular weight distribution, less high crystalline fraction and more copolymer fraction without significantly affecting reactor stability.

Preferably the reactor temperature is from about 160°C to about 180°C.

Preferably the ratio of aluminum to metal atom, preferably Al/Ti, is from about 1:1 to about 5:1.

The melt index of the disclosed ethylenic polymer can be from about 0.01 to about 1000 g/ 10 minutes, as measured by ASTM 1238-04 (2.16 kg and 190 °C).

## 5        **Ethylene-based Polymers**

Suitable ethylene-based polymers can be prepared with Ziegler-Natta catalysts. Examples of linear ethylene-based polymers include high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). Suitable polyolefins include, but are not limited to, ethylene/diene interpolymers, ethylene/ $\alpha$ -olefin interpolymers, ethylene homopolymers, and blends thereof.

Suitable heterogeneous linear ethylene-based polymers include linear low density polyethylene (LLDPE), ultra low density polyethylene (ULDPE), and very low density polyethylene (VLDPE). For example, some interpolymers produced using a Ziegler-Natta catalyst have a density of about 0.89 to about 0.94 g/cm<sup>3</sup> and have a melt index ( $I_2$ ) from about 0.01 to about 1,000 g/10 minutes, as measured by ASTM 1238-04 (2.16 kg and 190°C). Preferably, the melt index ( $I_2$ ) can be from about 0.1 to about 50 g/ 10 minutes. Heterogeneous linear ethylene-based polymers may have a molecular weight distribution,  $M_w/M_n$ , from about 3.5 to about 5.

The linear ethylene-based polymer may comprise units derived from one or more  $\alpha$ -olefin copolymers as long as there is at least 50 mole percent polymerized ethylene monomer in the polymer.

High density polyethylene (HDPE) may have a density in the range of about 0.94 to about 0.97 g/cm<sup>3</sup>. HDPE is typically a homopolymer of ethylene or an interpolymers of ethylene and low levels of one or more  $\alpha$ -olefin copolymers. HDPE contains relatively few branch chains relative to the various copolymers of ethylene and one or more  $\alpha$ -olefin copolymers. HDPE can be comprised of less than 5 mole % of the units derived from one or more  $\alpha$ -olefin comonomers

Linear ethylene-based polymers such as linear low density polyethylene and ultra low density polyethylene (ULDPE) are characterized by an absence of long chain branching, in contrast to conventional low crystallinity, highly branched ethylene-based

polymers such as LDPE. Heterogeneous linear ethylene-based polymers such as LLDPE can be prepared via solution, slurry, or gas phase polymerization of ethylene and one or more  $\alpha$ -olefin comonomers in the presence of a Ziegler-Natta catalyst, by processes such as are disclosed in U.S. Patent No. 4,076,698 (Anderson, et al.). Relevant discussions of both  
5 of these classes of materials, and their methods of preparation are found in U.S. Patent No. 4,950,541 (Tabor, et al.). Other patents and publications to make LLDPE include WO 2008/0287634, US 41983 15, US 5487938, EP 089138 1, and US 597725 1.

An  $\alpha$ -olefin comonomer may have, for example, from 3 to 20 carbon atoms. Preferably, the  $\alpha$ -olefin comonomer may have 3 to 8 carbon atoms. Exemplary  $\alpha$ -olefin  
10 comonomers include, but are not limited to, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene, 4,4-dimethyl-1-pentene, 3-ethyl-1-pentene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. Commercial examples of linear ethylene-based polymers that are interpolymers include ATTANE<sup>TM</sup> Ultra Low Density Linear  
15 Polyethylene Copolymer, DOWLEX<sup>TM</sup> Polyethylene Resins, and FLEXOMER<sup>TM</sup> Very Low Density Polyethylene.

In a further aspect, when used in reference to an ethylene homopolymer (that is, a high density ethylene homopolymer not containing any comonomer and thus no short chain branches), the terms "homogeneous ethylene polymer" or "homogeneous linear ethylene  
20 polymer" may be used to describe such a polymer.

The presence of long chain branching can be determined in ethylene homopolymers by using <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method described by Randall (Rev. *Macromol Chem. Phys.*, C29, V. 2&3, 285-297). There are other known techniques useful for determining the presence of long chain branches in  
25 ethylene polymers, including ethylene/1-octene interpolymers. Two such exemplary methods are gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) and gel permeation chromatography coupled with a differential viscometer detector (GPC-DV). The use of these techniques for long chain branch detection and the underlying theories have been well documented in the literature. See, for  
30 example, Zimm, G. H. and Stockmayer, W. H., *J. Chem. Phys.*, 17, 1301 (1949), and Rudin, A., *Modern Methods of Polymer Characterization*, John Wiley & Sons, New York (1991) 103-112.



The terms "heterogeneous" and "heterogeneously branched" mean that the ethylene polymer can be characterized as a mixture of interpolymer molecules having various ethylene to comonomer molar ratios. Heterogeneously branched linear ethylene polymers are available from The Dow Chemical Company as DOWLEX™ linear low density polyethylene and as ATTANE™ ultra-low density polyethylene resins. Heterogeneously branched linear ethylene polymers can be prepared via the solution, slurry or gas phase polymerization of ethylene and one or more optional  $\alpha$ -olefin comonomers in the presence of a Ziegler Natta catalyst, by processes such as are disclosed in U.S. Pat. No. 4,076,698 (Anderson, et al.). Heterogeneously branched ethylene polymers are typically characterized as having molecular weight distributions,  $M_w/M_n$ , from about 3 to about 5 and, as such, are distinct from substantially linear ethylene polymers and homogeneously branched linear ethylene polymers in regards to both compositional short chain branching distribution and molecular weight distribution.

### **Highly Long Chain Branched Ethylene-based Polymers**

Highly long chain branched ethylene-based polymers, such as low density polyethylene (LDPE), which can be blended with the novel heterogeneous ethylene polymers herein, can be made using a high-pressure process using free-radical chemistry to polymerize ethylene monomer. Typical LDPE polymer density is from about 0.91 to about 0.94 g/cm<sup>3</sup>. The low density polyethylene may have a melt index ( $I_2$ ) from about 0.01 to about 150 g/10 minutes. Highly long chain branched ethylene-based polymers such as LDPE may also be referred to as "high pressure ethylene polymers", meaning that the polymer is partly or entirely homopolymerized or copolymerized in autoclave or tubular reactors at pressures above 13,000 psig with the use of free-radical initiators, such as peroxides (see, for example, U.S. Patent No. 4,599,392 (McKinney, et al.)). The process creates a polymer with significant branches, including long chain branches.

Highly long chain branched ethylene-based polymers are typically homopolymers of ethylene; however, the polymer may comprise units derived from one or more  $\alpha$ -olefin copolymers as long as there is at least 50 mole percent polymerized ethylene monomer in the polymer.

Comonomers that may be used in forming highly branched ethylene-based polymer include, but are not limited to,  $\alpha$ -olefin comonomers, typically having no more than 20 carbon atoms. For example, the  $\alpha$ -olefin comonomers, for example, may have 3 to 10

carbon atoms; or in the alternative, the  $\alpha$ -olefin comonomers, for example, may have 3 to 8 carbon atoms. Exemplary  $\alpha$ -olefin comonomers include, but are not limited to, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, and 4-methyl-1-pentene. In the alternative, exemplary comonomers include, but are not limited to  $\alpha$ ,  $\beta$ -unsaturated C<sub>3</sub>-C<sub>8</sub>-carboxylic acids, in particular maleic acid, fumaric acid, itaconic acid, acrylic acid, methacrylic acid and crotonic acid derivatives of the  $\alpha$ ,  $\beta$ -unsaturated C<sub>3</sub>-C<sub>8</sub>-carboxylic acids, for example unsaturated C<sub>3</sub>-Cis-carboxylic acid esters, in particular ester of C<sub>1</sub>-C<sub>6</sub>-alkanols, or anhydrides, in particular methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, ter-butyl methacrylate, methyl acrylate, ethyl acrylate n-butyl acrylate, 2-ethylhexyl acrylate, tert-butyl acrylate, methacrylic anhydride, maleic anhydride, and itaconic anhydride. In another alternative, the exemplary comonomers include, but are not limited to, vinyl carboxylates, for example vinyl acetate. In another alternative, exemplary comonomers include, but are not limited to, n-butyl acrylate, acrylic acid and methacrylic acid.

## 15            **Process**

For producing the ethylene-based polymer of the invention, a solution-phase polymerization process may be used. Typically such a process occurs in a well-stirred reactor such as a loop reactor or a sphere reactor at temperature from about 150 to about 300°C, preferably from about 160 to about 180°C, and at pressures from about 30 to about 1000 psi, preferably from about 30 to about 750 psi. The residence time in such a process is from about 2 to about 20 minutes, preferably from about 10 to about 20 minutes. Ethylene, solvent, catalyst, and optionally one or more comonomers are fed continuously to the reactor. Exemplary catalysts in these embodiments include, but are not limited to, Ziegler-Natta catalysts. Exemplary solvents include, but are not limited to, isoparaffins. For example, such solvents are commercially available under the name ISOPAR E (ExxonMobil Chemical Co., Houston, Texas). The resultant mixture of ethylene-based polymer and solvent is then removed from the reactor and the polymer is isolated. Solvent is typically recovered via a solvent recovery unit, that is, heat exchangers and vapor liquid separator drum, and is recycled back into the polymerization system.

30            Suitable catalysts for use in embodiment processes include any compound or combination of compounds that is adapted for preparing polymers of the desired composition or type, either the ethylene-based polymers or the highly long chain branched ethylene-based polymers. Heterogeneous catalysts may be employed. In some embodiment

processes, heterogeneous catalysts, including the well known Ziegler-Natta compositions, especially Group 4 metal halides supported on Group 2 metal halides or mixed halides and alkoxides and the well known chromium or vanadium based catalysts, may be used. In some embodiment processes, the catalysts for use may be homogeneous catalysts

5 comprising a relatively pure organometallic compound or metal complex, especially compounds or complexes based on metals selected from Groups 3-10 or the Lanthanide series. If more than one catalyst is used in a system, it is preferred that any catalyst employed not significantly detrimentally affect the performance of another catalyst under the conditions of polymerization. Desirably, no catalyst is reduced in activity by greater

10 than 25 percent, more preferably greater than 10 percent under the conditions of the polymerization.

In embodiment processes employing a complex metal catalyst, such a catalyst may be activated to form an active catalyst composition by combination with a cocatalyst, preferably a cation forming cocatalyst, a strong Lewis acid, or a combination thereof.

15 Suitable cocatalysts for use include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. So-called modified methyl aluminoxane (MMAO) or triethyl aluminum (TEA) is also suitable for use as a cocatalyst. One technique for preparing such modified aluminoxane is disclosed in U.S. Patent No. 5,041,584 (Crapo, et al.). Aluminoxanes can

20 also be made as disclosed in U.S. Patent Nos. 5,542,199 (Lai, et al.); 4,544,762 (Kaminsky, et al.); 5,015,749 (Schmidt, et al.); and 5,041,585 (Deavenport, et al.).

In some embodiment processes, processing aids, such as plasticizers, can also be included in the embodiment ethylenic polymer product. These aids include, but are not limited to, the phthalates, such as dioctyl phthalate and diisobutyl phthalate, natural oils

25 such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining, and liquid resins from rosin or petroleum feedstocks. Exemplary classes of oils useful as processing aids include white mineral oil such as KAYDOL oil (Chemtura Corp.; Middlebury, Conn.) and SHELLFLEX 371 naphthenic oil (Shell Lubricants; Houston, Tex.). Another suitable oil is TUFFLO oil (Lyondell Lubricants; Houston, Tex).

30 In some embodiment processes, embodiment ethylenic polymers are treated with one or more stabilizers, for example, antioxidants, such as IRGANOX 1010 and IRGAFOS 168 (Ciba Specialty Chemicals; Glattbrugg, Switzerland). In general, polymers are treated with one or more stabilizers before an extrusion or other melt processes. In other

embodiment processes, other polymeric additives include, but are not limited to, ultraviolet light absorbers, antistatic agents, pigments, dyes, nucleating agents, fillers, slip agents, fire retardants, plasticizers, processing aids, lubricants, stabilizers, smoke inhibitors, viscosity control agents and anti-blocking agents. The embodiment ethylenic polymer composition  
5 may, for example, comprise less than 10 percent by the combined weight of one or more additives, based on the weight of the embodiment ethylenic polymer.

The embodiment ethylenic polymer may further be compounded. In some embodiment ethylenic polymer compositions, one or more antioxidants may further be compounded into the polymer and the compounded polymer pelletized. The compounded  
10 ethylenic polymer may contain any amount of one or more antioxidants. For example, the compounded ethylenic polymer may comprise from about 200 to about 600 parts of one or more phenolic antioxidants per one million parts of the polymer. In addition, the compounded ethylenic polymer may comprise from about 800 to about 1200 parts of a phosphite-based antioxidant per one million parts of polymer. The compounded disclosed  
15 ethylenic polymer may further comprise from about 300 to about 1250 parts of calcium stearate per one million parts of polymer.

### **Cross-linking Agents**

Some suitable cross-linking agents have been disclosed in Zweifel Hans et al., "Plastics Additives Handbook," Hanser Gardner Publications, Cincinnati, Ohio, 5th edition,  
20 Chapter 14, pages 725-812 (2001); Encyclopedia of Chemical Technology, Vol. 17, 2nd edition, Interscience Publishers (1968); and Daniel Seern, "Organic Peroxides," Vol. 1, Wiley-Interscience, (1970), all of which are incorporated herein by reference.

Non-limiting examples of suitable cross-linking agents include peroxides, phenols, azides, aldehyde-amine reaction products, substituted ureas, substituted guanidines;  
25 substituted xanthates; substituted dithiocarbamates; sulfur-containing compounds, such as thiazoles, sulfenamides, thiuramidisulfides, paraquinonedioxime, dibenzoparaquinonedioxime, sulfur; imidazoles; silanes and combinations thereof.

Non-limiting examples of suitable organic peroxide cross-linking agents include alkyl peroxides, aryl peroxides, peroxyesters, peroxyarbonates, diacylperoxides,  
30 peroxyketals, cyclic peroxides and combinations thereof. In some embodiments, the organic peroxide is dicumyl peroxide, t-butylisopropylidene peroxybenzene, 1,1-di-t-butyl

peroxy-3,3,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di(t-butyl peroxy) hexane, t-butyl-cumyl peroxide, di-t-butyl peroxide, 2,5-dimethyl-2,5-di-(t-butyl peroxy) hexyne or a combination thereof. In one embodiment, the organic peroxide is dicumyl peroxide.

Additional teachings regarding organic peroxide cross-linking agents are disclosed in C. P.

- 5 Park, "*Polyolefin Foam*", Chapter 9 of *Handbook of Polymer Foams and Technology*, edited by D. Klemperer and K. C. Frisch, Hanser Publishers, pp. 198-204, Munich (1991), which is incorporated herein by reference.

Non-limiting examples of suitable azide cross-linking agents include azidoformates, such as tetramethylenebis(azidoformate); aromatic polyazides, such as 4,4'-

- 10 diphenylmethane diazide; and sulfonazides, such as p,p'-oxybis(benzene sulfonyl azide).

The disclosure of azide cross-linking agents can be found in U.S. Patent Nos. 3,284,421 and 3,297,674, both of which are incorporated herein by reference.

The poly(sulfonyl azide) is any compound having at least two sulfonyl azide groups (*i.e.*,  $-\text{SO}_2\text{N}_3$ ) that are reactive towards the ethylene/a-olefin interpolymer disclosed herein.

- 15 In some embodiments, the poly(sulfonyl azide)s have a structure of X-R-X wherein each X is  $-\text{SO}_2\text{N}_3$  and R represents an unsubstituted or inertly substituted hydrocarbyl, hydrocarbyl ether or silicon-containing group. In some embodiments, the R group has sufficient carbon, oxygen or silicon, preferably carbon, atoms to separate the sulfonyl azide groups sufficiently to permit a facile reaction between the ethylene/a-olefin interpolymer and the
- 20 sulfonyl azide groups. In other embodiments, the R group has at least 1, at least 2, or at least 3 carbon, oxygen or silicon, preferably carbon, atoms between the sulfonyl azide groups. The term "inertly substituted" refers to substitution with atoms or groups which do not undesirably interfere with the desired reaction(s) or desired properties of the resulting cross-linked polymers. Such groups include fluorine, aliphatic or aromatic ethers, siloxanes and the like. Non-limiting examples of suitable structures of R include aryl, alkyl, alkaryl,
- 25 arylalkyl, silanyl, heterocyclyl, and other inert groups. In some embodiments, the R group includes at least one aryl group between the sulfonyl groups. In other embodiments, the R group includes at least two aryl groups (such as when R is 4,4' diphenylether or 4,4'-biphenyl). When R is one aryl group, it is preferred that the group have more than one ring,
- 30 as in the case of naphthylene bis(sulfonyl azides). In some embodiments, the poly(sulfonyl)azides include 1,5-pentane bis(sulfonylazide), 1,8-octane bis(sulfonyl azide), 1,10-decane bis(sulfonyl azide), 1,10-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis(4'-

sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), and mixed sulfonyl azides of chlorinated aliphatic hydrocarbons containing an average of from 1 to 8 chlorine atoms and from about 2 to 5 sulfonyl azide groups per molecule, and combinations thereof. In other embodiments, the poly(sulfonyl azide)s include oxy-bis(4-sulfonylazidobenzene), 2,7-  
5 naphthalene bis(sulfonyl azido), 4,4'-bis(sulfonyl azido)biphenyl, 4,4'-diphenyl ether bis(sulfonyl azide) and bis(4-sulfonyl azidophenyl)methane, and combinations thereof.

Non-limiting examples of suitable aldehyde-amine reaction products include formaldehyde-ammonia, formaldehyde-ethylchloride-ammonia, acetaldehyde-ammonia, formaldehyde-aniline, butyraldehyde-aniline, heptaldehyde-aniline, and combinations  
10 thereof.

Non-limiting examples of suitable substituted ureas include trimethylthiourea, diethylthiourea, dibutylthiourea, tripropylthiourea, 1,3-bis(2-benzothiazolylmercaptomethyl)urea, N,N-diphenylthiourea, and combinations thereof.

Non-limiting examples of suitable substituted guanidines include diphenylguanidine, di-o-tolylguanidine, diphenylguanidine phthalate, the di-o-tolylguanidine salt of dicatchol  
15 borate, and combinations thereof.

Non-limiting examples of suitable substituted xanthates include zinc ethylxanthate, sodium isopropylxanthate, butylxanthic disulfide, potassium isopropylxanthate, zinc butylxanthate, and combinations thereof.

Non-limiting examples of suitable dithiocarbamates include copper dimethyl-, zinc  
20 dimethyl-, tellurium diethyl-, cadmium dicyclohexyl-, lead dimethyl-, lead dimethyl-, selenium dibutyl-, zinc pentamethylene-, zinc didecyl-, zinc isopropyloctyl-dithiocarbamate, and combinations thereof.

Non-limiting examples of suitable thiazoles include 2-mercaptobenzothiazole, zinc  
25 mercaptothiazolyl mercaptide, 2-benzothiazolyl-N,N-diethylthiocarbamyl sulfide, 2,2'-dithiobis(benzothiazole), and combinations thereof.

Non-limiting examples of suitable imidazoles include 2-mercaptoimidazoline 2-mercapto-4,4,6-trimethyldihydropyrimidine, and combinations thereof.

Non-limiting examples of suitable sulfenamides include N-t-butyl-2-benzothiazole-, N-cyclohexylbenzothiazole-, N,N-diisopropylbenzothiazole-, N-(2,6-dimethylmorpholino)-2-benzothiazole-, N,N-diethylbenzothiazole-sulfenamide, and combinations thereof.

Non-limiting examples of suitable thiuramidisulfides include N,N'-diethyl-,  
5 tetrabutyl-, N,N'-diisopropyldioctyl-, tetramethyl-, N,N'-dicyclohexyl-, N,N'-tetraurylthiuramidisulfide, and combinations thereof.

In some embodiments, the cross-linking agents are silanes. Any silane that can effectively graft to and/or cross-link the ethylene/a-olefin interpolymers or the polymer blend disclosed herein can be used. Non-limiting examples of suitable silane cross-linking  
10 agents include unsaturated silanes that comprise an ethylenically unsaturated hydrocarbyl group, such as a vinyl, allyl, isopropenyl, butenyl, cyclohexenyl or gamma-(meth)acryloxy allyl group, and a hydrolyzable group such as a hydrocarbyloxy, hydrocarbonyloxy, and hydrocarbylamino group. Non-limiting examples of suitable hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy, propionyloxy, alkyl and arylamino groups. In other  
15 embodiments, the silanes are the unsaturated alkoxy silanes which can be grafted onto the interpolymers. Some of these silanes and their preparation methods are more fully described in U.S. Pat. No. 5,266,627, which is incorporated herein by reference. In further embodiments, the silane cross-linking agents are vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(2-methoxyethoxy)silane, vinyltriacetoxysilane,  
20 vinylmethyldimethoxysilane, 3-methacryloyloxypropyltrimethoxysilane, and combinations thereof.

The amount of the silane cross-linking agent can vary widely, depending upon the nature of the ethylene/a-olefin interpolymers or the polymer blend, the silane employed, the processing conditions, the amount of grafting initiator, the ultimate application, and other  
25 factors. When vinyltrimethoxysilane (VTMOS) is used, the amount of VTMOS is generally at least about 0.1 weight percent, at least about 0.5 weight percent, or at least about 1 weight percent, based on the combined weight of the silane cross-linking agent and the interpolymers or the polymer blend.

### Uses

30 The embodiment ethylenic polymer may be employed in a variety of conventional thermoplastic fabrication processes to produce useful articles, including objects comprising

at least one film layer, such as a monolayer film, or at least one layer in a multilayer film prepared by cast, blown, calendared, or extrusion coating processes. Thermoplastic compositions comprising the embodiment ethylenic polymer include blends with other natural or synthetic materials, polymers, additives, reinforcing agents, ignition resistant  
5 additives, antioxidants, stabilizers, colorants, extenders, crosslinkers, blowing agents, anti-stats, and plasticizers.

The embodiment ethylenic polymer may also be crosslinked by any known means, such as the use of peroxide, electron beam, silane, azide, or other cross-linking technique. The embodiment ethylenic polymer can also be chemically modified, such as by grafting  
10 (for example by use of maleic anhydride (MAH), silanes, or other grafting agent), halogenation, amination, sulfonation, or other chemical modification.

Additives and adjuvants may be added to the embodiment ethylenic polymer post-formation. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, titanium dioxide, zeolites, powdered metals, organic or inorganic  
15 fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders, including paraffinic or naphthelenic oils; and other natural and synthetic polymers, including other polymers that are or can be made according to the embodiment methods.

Blends and mixtures of the embodiment ethylenic polymer with other polyolefins  
20 may be performed. Suitable polymers for blending with the embodiment ethylenic polymer include thermoplastic and non-thermoplastic polymers including natural and synthetic polymers. Exemplary polymers for blending include polypropylene, (both impact modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of polyethylene, including high pressure,  
25 free-radical LDPE, Ziegler-Natta LLDPE, metallocene PE, including multiple reactor PE ("in reactor" blends of Ziegler-Natta PE and metallocene PE, such as products disclosed in U.S. Patent Nos. 6,545,088 (Kolthammer, et al.); 6,538,070 (Cardwell, et al.); 6,566,446 (Parikh, et al.); 5,844,045 (Kolthammer, et al.); 5,869,575 (Kolthammer, et al.); and 6,448,341 (Kolthammer, et al.)), ethylene-vinyl acetate (EVA), ethylene/vinyl alcohol  
30 copolymers, polystyrene, impact modified polystyrene, ABS, styrene/butadiene block copolymers and hydrogenated derivatives thereof (SBS and SEBS), and thermoplastic polyurethanes. Homogeneous polymers such as olefin plastomers and elastomers, ethylene and propylene-based copolymers (for example, polymers available under the trade



designation VERSIFY™ Plastomers & Elastomers (The Dow Chemical Company) and VISTAMAXX™ (ExxonMobil Chemical Co.) can also be useful as components in blends comprising the embodiment ethylenic polymer.

Blends and mixtures of the embodiment ethylenic polymer may include thermoplastic polyolefin blends (TPO), thermoplastic elastomer blends (TPE), thermoplastic vulcanizates (TPV) and styrenic polymer blends. TPE and TPV blends may be prepared by combining embodiment ethylenic polymers, including functionalized or unsaturated derivatives thereof, with an optional rubber, including conventional block copolymers, especially an SBS block copolymer, and optionally a crosslinking or vulcanizing agent. TPO blends are generally prepared by blending the embodiment polymers with a polyolefin, and optionally a crosslinking or vulcanizing agent. The foregoing blends may be used in forming a molded object, and optionally crosslinking the resulting molded article. A similar procedure using different components has been previously disclosed in U.S. Patent No. 6,797,779 (Ajmani, et al.).

## Definitions

The term "composition," as used, includes a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

The terms "blend" or "polymer blend," as used, mean an intimate physical mixture (that is, without reaction) of two or more polymers. A blend may or may not be miscible (not phase separated at molecular level). A blend may or may not be phase separated. A blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art. The blend may be effected by physically mixing the two or more polymers on the macro level (for example, melt blending resins or compounding) or the micro level (for example, simultaneous forming within the same reactor).

The term "linear" refers to polymers where the polymer backbone of the polymer lacks measurable or demonstrable long chain branches; for example, the polymer is substituted with an average of less than 0.01 long branch per 1000 carbons.

The term "polymer" refers to a polymeric 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. The terms "ethylene/a-olefin polymer" is indicative of interpolymers as described.

5 The term "interpolymer" refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different types of monomers.

10 The term "ethylene-based polymer" refers to a polymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers) and, optionally, may contain at least one comonomer.

The term "ethylene/a-olefin interpolymer" refers to an interpolymer that contains more than 50 mole percent polymerized ethylene monomer (based on the total amount of polymerizable monomers) and at least one a-olefin.

15 The term "ethylenic polymer" refers to a polymer resulting from the bonding of an ethylene-based polymer and at least one highly long chain branched ethylene-based polymer.

## TEST METHODS

### Density

20 Density ( $\text{g/cm}^3$ ) is measured according to ASTM-D 792-03, Method B, in isopropanol. Specimens are measured within 1 hour of molding after conditioning in the isopropanol bath at 23° C for 8 min to achieve thermal equilibrium prior to measurement. The specimens are compression molded according to ASTM D-4703-00 Annex A with a 5 min initial heating period at about 190° C and a 15° C/min cooling rate per Procedure C. The specimen is cooled to 45° C in the press with continued cooling until "cool to the  
25 touch."

### Melt Index

Melt index, or  $I_2$ , is measured in accordance with ASTM D 1238, Condition 190°C/2.16 kg, and is reported in grams eluted per 10 minutes.  $I_{10}$  is measured in

accordance with ASTM D 1238, Condition 190°C/10 kg, and is reported in grams eluted per 10 minutes.

### DSC Crystallinity

Differential Scanning Calorimetry (DSC) can be used to measure the melting and crystallization behavior of a polymer over a wide range of temperature. For example, the TA Instruments Q1000 DSC, equipped with an RCS (refrigerated cooling system) and an autosampler is used to perform this analysis. During testing, a nitrogen purge gas flow of 50 ml/min is used. Each sample is melt pressed into a thin film at about 175°C; the melted sample is then air-cooled to room temperature (~25°C). A 3-10 mg, 6 mm diameter specimen is extracted from the cooled polymer, weighed, placed in a light aluminum pan (ca 50 mg), and crimped shut. Analysis is then performed to determine its thermal properties.

The thermal behavior of the sample is determined by ramping the sample temperature up and down to create a heat flow versus temperature profile. First, the sample is rapidly heated to 180°C and held isothermal for 3 minutes in order to remove its thermal history. Next, the sample is cooled to -40°C at a 10°C/minute cooling rate and held isothermal at -40°C for 3 minutes. The sample is then heated to 150°C (this is the "second heat" ramp) at a 10°C/minute heating rate. The cooling and second heating curves are recorded. The cool curve is analyzed by setting baseline endpoints from the beginning of crystallization to -20°C. The heat curve is analyzed by setting baseline endpoints from -20°C to the end of melt. The values determined are peak melting temperature ( $T_m$ ), peak crystallization temperature ( $T_c$ ), heat of fusion ( $H_f$ ) (in Joules per gram), and the calculated % crystallinity for polyethylene samples using:

$$\% \text{ Crystallinity} = ((H_f)/(292 \text{ J/g})) \times 100.$$

The heat of fusion ( $H_f$ ) and the peak melting temperature are reported from the second heat curve. Peak crystallization temperature is determined from the cooling curve.

### Gel Permeation Chromatography (GPC)

The GPC system consists of a Waters (Milford, MA) 150C high temperature chromatograph (other suitable high temperatures GPC instruments include Polymer Laboratories (Shropshire, UK) Model 210 and Model 220) equipped with an on-board

differential refractometer (RI). Additional detectors can include an IR4 infra-red detector from Polymer ChAR (Valencia, Spain), Precision Detectors (Amherst, MA) 2-angle laser light scattering detector Model 2040, and a Viscotek (Houston, TX) 150R 4-capillary solution viscometer. A GPC with the last two independent detectors and at least one of the first detectors is sometimes referred to as "3D-GPC", while the term "GPC" alone generally refers to conventional GPC. Depending on the sample, either the 15-degree angle or the 90-degree angle of the light scattering detector is used for calculation purposes. Data collection is performed using Viscotek TriSEC software, Version 3, and a 4-channel Viscotek Data Manager DM400. The system is also equipped with an on-line solvent degassing device from Polymer Laboratories (Shropshire, UK). Suitable high temperature GPC columns can be used such as four 30 cm long Shodex HT803 13 micron columns or four 30 cm Polymer Labs columns of 20-micron mixed-pore-size packing (MixA LS, Polymer Labs). The sample carousel compartment is operated at 140°C and the column compartment is operated at 150°C. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent. The chromatographic solvent and the sample preparation solvent contain 200 ppm of butylated hydroxytoluene (BHT). Both solvents are sparged with nitrogen. The polyethylene samples are gently stirred at 160°C for four hours. The injection volume is 200 microliters. The flow rate through the GPC is set at 1 ml/minute.

The GPC column set is calibrated before running the Examples by running twenty-one narrow molecular weight distribution polystyrene standards. The molecular weight (MW) of the standards ranges from 580 to 8,400,000 grams per mole, and the standards are contained in 6 "cocktail" mixtures. Each standard mixture has at least a decade of separation between individual molecular weights. The standard mixtures are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 g in 50 mL of solvent for molecular weights equal to or greater than 1,000,000 grams per mole and 0.05 g in 50 ml of solvent for molecular weights less than 1,000,000 grams per mole. The polystyrene standards were dissolved at 80°C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene  $M_w$  using the Mark-Houwink K and a (sometimes referred to as a) values mentioned later for polystyrene and polyethylene. See the Examples section for a demonstration of this procedure.

With 3D-GPC absolute weight average molecular weight (" $M_{w\text{Abs}}$ ") and intrinsic viscosity are also obtained independently from suitable narrow polyethylene standards using the same conditions mentioned previously. These narrow linear polyethylene standards may be obtained from Polymer Laboratories (Shropshire, UK; Part No.'s PL2650-0101 and  
5 PL2650-0102).

The systematic approach for the determination of multi-detector offsets is performed in a manner consistent with that published by Balke, Mourey, et al. (Mourey and Balke, *Chromatography Polym.*, Chapter 12, (1992)) (Balke, Thitiratsakul, Lew, Cheung, Mourey, *Chromatography Polym.*, Chapter 13, (1992)), optimizing triple detector log ( $M_w$  and  
10 intrinsic viscosity) results from Dow 1683 broad polystyrene (American Polymer Standards Corp.; Mentor, OH) or its equivalent to the narrow standard column calibration results from the narrow polystyrene standards calibration curve. The molecular weight data, accounting for detector volume off-set determination, are obtained in a manner consistent with that published by Zimm (Zimm, B.H., *J. Chem. Phys.*, 16, 1099 (1948)) and Kratochvil  
15 (Kratochvil, P., *Classical Light Scattering from Polymer Solutions*, Elsevier, Oxford, NY (1987)). The overall injected concentration used in the determination of the molecular weight is obtained from the mass detector area and the mass detector constant derived from a suitable linear polyethylene homopolymer, or one of the polyethylene standards. The calculated molecular weights are obtained using a light scattering constant derived from one  
20 or more of the polyethylene standards mentioned and a refractive index concentration coefficient,  $dn/dc$ , of 0.104. Generally, the mass detector response and the light scattering constant should be determined from a linear standard with a molecular weight in excess of about 50,000 daltons. The viscometer calibration can be accomplished using the methods described by the manufacturer or alternatively by using the published values of suitable  
25 linear standards such as Standard Reference Materials (SRM) 1475a, 1482a, 1483, or 1484a. The chromatographic concentrations are assumed low enough to eliminate addressing 2<sup>nd</sup> virial coefficient effects (concentration effects on molecular weight).

### **Analytical Temperature Rising Elution Fractionation (ATREF)**

High Density Fraction (percent) is measured via analytical temperature rising elution  
30 fractionation analysis (ATREF). ATREF analysis is conducted according to the method described in U.S. Patent No. 4,798,081 and Wilde, L.; Ryle, T.R.; Knobloch, D.C.; Peat, I.R.; Determination of Branching Distributions in Polyethylene and Ethylene Copolymers, *Journal of Polymer Science*, 20, 441-455 (1982). The composition to be analyzed is

dissolved in trichlorobenzene and allowed to crystallize in a column containing an inert support (stainless steel shot) by slowly reducing the temperature to 20°C at a cooling rate of 0.1°C/min. The column is equipped with an infrared detector. An ATREF chromatogram curve is then generated by eluting the crystallized polymer sample from the column by

5 slowly increasing the temperature of the eluting solvent (trichlorobenzene) from 20 to 120°C at a rate of 1.5°C/min. Viscosity average molecular weight ( $M_v$ ) of the eluting polymer is measured and reported. An ATREF plot has the short chain branching distribution (SCBD) plot and a molecular weight plot. The SCBD plot has 3 peaks, one for the high crystalline fraction (typically above 90°C), one for copolymer fraction (typically in

10 between 30-90°C) and one for purge fraction (typically below 30°C). The curve also has a valley in between the copolymer and the high crystalline fraction. The is the lowest temperature in this valley. % High density (HD) fraction is the area under the curve above The.  $M_v$  is the viscosity average molecular weight from ATREF.  $M_{hc}$  is the average  $M_v$  for fraction above The.  $M_c$  is the average  $M_v$  of copolymer between 60-90°C.  $M_p$  is the

15 average  $M_v$  of whole polymer.

#### **Fast Temperature Rising Elution Fractionation (F-TREF)**

The fast-TREF can be performed with a Crystex instrument by Polymer ChAR (Valencia, Spain) in orthodichlorobenzene (ODCB) with IR-4 infrared detector in compositional mode (Polymer ChAR, Spain) and light scattering (LS) detector (Precision

20 Detector Inc., Amherst, MA).

When testing F-TREF, 120 mg of the sample is added into a Crystex reactor vessel with 40 ml of ODCB held at 160°C for 60 minutes with mechanical stirring to achieve sample dissolution. The sample is loaded onto TREF column. The sample solution is then cooled down in two stages: (1) from 160°C to 100°C at 40°C/minute, and (2) the polymer

25 crystallization process started from 100°C to 30°C at 0.4°C/minute. Next, the sample solution is held isothermally at 30°C for 30 minutes. The temperature-rising elution process starts from 30°C to 160°C at 1.5°C /minute with flow rate of 0.6 ml/minute. The sample loading volume is 0.8 ml. Sample molecular weight ( $M_{3/4}$ ) is calculated as the ratio of the 15° or 90° LS signal over the signal from measuring sensor of IR-4 detector. The LS-MW

30 calibration constant is obtained by using polyethylene national bureau of standards SRM 1484a. The elution temperature is reported as the actual oven temperature. The tubing delay volume between the TREF and detector is accounted for in the reported TREF elution temperature.

### Preparative Temperature Rising Elution Fractionation (P-TREF)

The temperature rising elution fractionation method (TREF) can be used to preparatively fractionate the polymers (P-TREF) and is derived from Wilde, L.; Ryle, T.R.; Knobeloch, D.C.; Peat, I.R.; "Determination of Branching Distributions in Polyethylene and Ethylene Copolymers", *J. Polym. Sci.*, 20, 441-455 (1982), including column dimensions, solvent, flow and temperature program. An infrared (IR) absorbance detector is used to monitor the elution of the polymer from the column. Separate temperature programmed liquid baths - one for column loading and one for column elution - are also used.

Samples are prepared by dissolution in trichlorobenzene (TCB) containing approximately 0.5% 2,6-di-tert-butyl-4-methylphenol at 160°C with a magnetic stir bar providing agitation. Sample load is approximately 150 mg per column. After loading at 125°C, the column and sample are cooled to 25°C over approximately 72 hours. The cooled sample and column are then transferred to the second temperature programmable bath and equilibrated at 25°C with a 4 ml/minute constant flow of TCB. A linear temperature program is initiated to raise the temperature approximately 0.33°C/minute, achieving a maximum temperature of 102°C in approximately 4 hours.

Fractions are collected manually by placing a collection bottle at the outlet of the IR detector. Based upon earlier ATREF analysis, the first fraction is collected from 56 to 60°C. Subsequent small fractions, called subfractions, are collected every 4°C up to 92°C, and then every 2°C up to 102°C. Subfractions are referred to by the midpoint elution temperature at which the subfraction is collected.

Subfractions are often aggregated into larger fractions by ranges of midpoint temperature to perform testing. Fractions may be further combined into larger fractions for testing purposes.

A weight-average elution temperature is determined for each Fraction based upon the average of the elution temperature range for each subfraction and the weight of the subfraction versus the total weight of the sample. Weight average temperature is defined as:

$$T_w = \frac{\sum T(f) * A(f)}{\sum A(f)} ,$$

where  $T(f)$  is the mid-point temperature of a narrow slice or segment and  $A(f)$  is the area of the segment, proportional to the amount of polymer, in the segment.

Data are stored digitally and processed using an EXCEL (Microsoft Corp.; Redmond, WA) spreadsheet. The TREF plot, peak maximum temperatures, fraction weight percentages, and fraction weight average temperatures were calculated with the spreadsheet program.

Haze is determined according to ASTM-D 1003.

Gloss 45° is determined according to ASTM-2457.

Elmendorf Tear Resistance is measured according to ASTM-D 1922.

10 Dart Impact Strength is measured according to ASTM-D 1709-04, Method A.

### **C13 NMR Comonomer Content**

It is well known to use NMR spectroscopic methods for determining polymer composition. ASTM D 5017-96, J. C. Randall et al., in "NMR and Macromolecules" ACS Symposium series 247, J. C. Randall, Ed., Am. Chem. Soc, Washington, D.C., 1984, Ch. 9, and J. C. Randall in "Polymer Sequence Determination", Academic Press, New York (1977) provide general methods of polymer analysis by NMR spectroscopy.

### **Gel Content Measurement**

When the ethylene interpolymers, either alone or contained in a composition is at least partially crosslinked, the degree of crosslinking may be measured by dissolving the composition in a solvent for specified duration, and calculating the percent gel or unextractable component. The percent gel normally increases with increasing crosslinking levels. For cured articles according to the invention, the percent gel content is desirably in the range from at least about 5 to 100 percent as measured according to ASTM D-2765.

## **EXAMPLES**

### **25 Preparation of Ethylene-Based Polymers**



### Multi-Constituent Catalyst

An exemplary multi-constituent catalyst system includes a Ziegler-Natta catalyst composition including a magnesium and titanium containing procatalyst and a cocatalyst. The procatalyst is a titanium supported  $\text{MgCl}_2$  Ziegler Natta catalyst characterized by a  
 5 Mg:Ti molar ratio of 40:1.0. The cocatalyst is a triethylaluminum. The procatalyst may have a Ti:Mg ratio between 1.0:40 to 5.0:40, preferably 3.0:40. The procatalyst and the cocatalyst components can be contacted either before entering the reactor or in the reactor. The procatalyst may, for example, be any other titanium based Ziegler Natta catalyst. The Al:Ti molar ratio of cocatalyst component to procatalyst component can be from about 1:1  
 10 to about 5:1.

### General Description of the Multi-Constituent Catalyst System

The multi-constituent catalyst system, as used herein, refers to a Ziegler-Natta catalyst composition including a magnesium and titanium containing procatalyst and a cocatalyst. The procatalyst may, for example, comprise the reaction product of magnesium  
 15 dichloride, an alkylaluminum dihalide, and a titanium alkoxide.

The olefin polymerization procatalyst precursors comprise the product which results from combining:

(A) a magnesium halide prepared by contacting:

(1) at least one hydrocarbon soluble magnesium component  
 20 represented by the general formula  $\text{R}'' \text{R}'\text{Mg}_x\text{AlR}'_3$  wherein each  $\text{R}''$  and  $\text{R}'$  are alkyl groups

(2) at least one non-metallic or metallic halide source under conditions such that the reaction temperature does not exceed about  $60^\circ \text{C}$ , preferably does not exceed about  $40^\circ \text{C}$ , and most preferably does not exceed  
 25 about  $35^\circ \text{C}$ ;

(B) at least one transition metal compound represented by the formula  $\text{Tm}(\text{OR})_y \text{X}_{y-x}$  wherein  $\text{Tm}$  is a metal of Groups IVB, VB, VIB, VIIB or VIII of the Periodic Table;  $\text{R}$  is a hydrocarbyl group having from 1 to about 20, preferably from 1 to about 10 carbon atoms.

(C) an additional halide source if an insufficient quantity of component (A-2) is present to provide the desired excess X:Mg ratio;

Particularly suitable transition metal compounds include, for example, titanium tetrachloride, titanium trichloride, vanadium tetrachloride, zirconium tetrachloride, 5 tetra(isopropoxy)-titanium, tetrabutoxytitanium, diethoxytitanium dibromide, dibutoxytitanium dichloride, tetraphenoxytitanium, tri-isopropoxy vanadium oxide, zirconium tetra-n-propoxide, mixtures thereof and the like.

Other suitable titanium compounds which can be employed as the transition metal component herein include those titanium complexes and/or compounds resulting from 10 reacting:

(A) at least one titanium compound represented by the formula  $Ti(OR)_x X_{4-x}$  wherein each R is independently a hydrocarbyl group having from 1 to about 20, preferably from about 1 to about 10, most preferably from about 2 to about 4 carbon atoms; X is a halogen and x has a value from zero to 4; with

15 (B) at least one compound containing at least one aromatic hydroxyl group.

The foregoing procatalyst components are combined in proportions sufficient to provide atomic ratios as previously mentioned.

The foregoing pro-catalytic reaction product is preferably prepared in the presence of an inert diluent. The concentrations of catalyst components are preferably such that when 20 the essential components of the catalytic reaction product are combined, the resultant slurry is from about 0.005 to about 1.0 molar (moles/liter) with respect to magnesium. By way of an example of suitable inert organic diluents can be mentioned liquified ethane, propane, isobutane, n-butane, n-hexane, the various isomeric hexanes, isooctane, paraffinic mixtures of alkanes having from 8 to 12 carbon atoms, cyclohexane, methylcyclopentane, 25 dimethylcyclohexane, dodecane, industrial solvents composed of saturated or aromatic hydrocarbons such as kerosene, naphthas, etc., especially when freed of any olefin compounds and other impurities, and especially those having boiling points in the range from about -50°C to about 200°C. Mixing of the procatalyst components to provide the desired catalytic reaction product is advantageously prepared under an inert atmosphere 30 such as nitrogen, argon or other inert gas at temperatures in the range from about -100°C to about 200°C, preferably from about -20°C to about 100°C, provided that the magnesium halide support is prepared such that the reaction temperature does not exceed about 60°C. In the preparation of the catalytic reaction product, it is not necessary to separate

hydrocarbon soluble components from hydrocarbon insoluble components of the reaction product.

The procatalyst composition serves as one component of a Ziegler-Natta catalyst composition, in combination with a cocatalyst. The cocatalyst is preferably employed in a molar ratio based on titanium in the procatalyst of from 1:1 to 100: 1, but more preferably in a molar ratio of from 1:1 to 5:1.

#### Inventive Example 1

Inventive Example 1 is made according to the following procedures: A heterogeneously branched ethylene/a-olefin copolymer is prepared using a multi-constituent catalyst system, as described hereinabove, suitable for (co)polymerizing ethylene and one or more a-olefin comonomers, e.g. 1-octene, in two adiabatic spherical reactors, linked together in series, operating under a solution condition. The ethylene monomer, 1-octene comonomer, and hydrogen were combined with a solvent, e.g. Isopar® E, commercially available from ExxonMobil. The feed streams are purified from polar impurities such as water, carbon monoxide, sulfurous compounds, and unsaturated compounds such as acetylene and cooled to 13°C before entering the reactor. The majority (85-90%) of the reaction occurs in the first sphere reactor that is 10-foot diameter. The mixing is achieved via circulating the polymer/catalyst/cocatalyst/solvent/ethylene/co-monomer/hydrogen solution with agitator equipped with mixing blades. The feed (ethylene/comonomer/solvent/hydrogen) enters the reactor from the bottom and the catalyst/cocatalyst enters the reactor separately from the feed and also from the bottom. The first reactor temperature is about 175°C, and the reactor pressure is about 500 psi. The temperature of the second reactor, in series with the first, increases to 202°C with approximately 10-15% of the remaining reaction occurring and no additional streams added. Catalyst/Co-catalyst Al/Ti molar feed ratio is set at 1.5. The average reactor residence time is about 8 minutes per sphere reactor prior to termination post-reactor by a fluid specially designed for that purpose. After the polymer solution leaves the reactor, the solvent with unconverted ethylene monomer and 1-octene comonomer is removed from the polymer solution via a two stage devolatilizer system, and then recycled. The recycled stream is purified before entering the reactor again. The polymer melt is pumped through a die specially designed for underwater pelletization. The pellets are transferred to classifier screens to remove over and undersize particles. The finished pellets are then transferred to

rail cars. The properties of the heterogeneously branched ethylene/a-olefin copolymer are listed in Table 1. Figure 3 is an ATREF of Inventive Example 1.

The heterogeneously branched ethylene/a-olefin copolymer is further processed via blown film extrusion process on Gloucester line with a 6-inch diameter Sano die. The die has a gap of 70 mils. The film is blown with a blow up ratio of about 2.5 and a frost-line height of about 30 inches. The layflat width of the film is about 23.5 inches, while the thickness of the films is about 2 mils. The heterogeneously branched ethylene/a-olefin copolymer is melt extruded through an annular circular die. The hot melt emerges from the die thereby forming a tube. The tube is expanded by air, and at the same time, the cooled air chills the web to a solid state. The film tube is then collapsed within a V-shaped frame of rollers and is nipped at the end of the frame to trap the air within the bubble. The nip rolls also draw the film away from the die. The tube is slit and wound as a single-film layer onto a roll. The properties of the inventive film 1 are listed in Table 2.

#### Comparative Example 1

Comparative Example 1, a linear low density polyethylene, is made at 190°C reactor temperature and 3.5:1 Al/Ti ratio. All other conditions remain the same as the Inventive Example 1. The properties of Comparative Example 1 are listed in Table 1. Figure 3 is an ATREF of Comparative Example 1. The Comparative Example 1 is processed via blown film extrusion process, as described above. The Comparative Example 1 is melt extruded through an annular circular die. The hot melt emerges from the die thereby forming a tube. The tube is expanded by air, and at the same time, the cooled air chills the web to a solid state. The film tube is then collapsed within a V-shaped frame of rollers and is nipped at the end of the frame to trap the air within the bubble. The nip rolls also draw the film away from the die. The tube is slit and wound as a single-film layer onto a roll. The properties of the comparative film 1 are listed in Table 2.

Table 1: Resin production and characterization data for inventive and comparative example 1.

Description	Inventive Example 1	Comparative Example 1
Resin MI (g/10 minutes)	0.80	0.80
Resin density (g/cc)	0.917	0.917
Catalyst	HEC-3	HEC-3
Ti/40Mg	3	3
Al/Ti	1.5	3.5
Rx. Temp (°C)	175	190
M <sub>hc</sub>	103000	143000
M <sub>c</sub>	64234	54815
M <sub>p</sub>	76542	71007
M <sub>hc</sub> /M <sub>p</sub>	1.35	2.01
M <sub>c</sub> /M <sub>p</sub>	0.84	0.77
% HD fraction - ATREF	10.6	15.4

T<sub>hc</sub>, lowest temperature in the valley between copolymer and high crystalline fraction

M<sub>v</sub>, viscosity average molecular weight from ATREF

M<sub>hc</sub>, Average M<sub>v</sub> for fraction above T<sub>hc</sub> from ATREF

M<sub>c</sub>, Avg M<sub>v</sub> of copolymer between 60-90 °C - ATREF

M<sub>p</sub>, Average M<sub>v</sub> of whole polymer from ATREF

% HD fraction, area under the curve above T<sub>hc</sub>

5

Table 2: Properties of films made from Inventive example 1 and Comparative example 1.

Description		Inventive Example 1	Comparative Example 1
Target thickness	mil	2	2
Dart A	g	724	533
Gloss 45°		91	70
Haze	%	5.6	10.6
Normalized MD Tear	g/mil	477	469

10 The following prophetic examples further illustrate the invention. Unless otherwise indicated, all parts and percentages are by weight.

### SPECIFIC EMBODIMENTS

Example 2:

15 A monolayer 15 mil thick protective film is made from a blend comprising 80 wt% of Inventive Example 1, 20 wt% of a maleic anhydride (MAH) modified ethylene/1-octene copolymer (ENGAGE™ 8400 polyethylene grafted at a level of about 1 wt% MAH, and having a post-modified MI of about 1.25 g/10min and a density of about 0.87 g/cc), 1.5 wt%

of Lupersol® 101, 0.8 wt% of tri-allyl cyanurate, 0.1 wt% of Chimassorb® 944, 0.2 wt% of Naugard® P, and 0.3 wt% of Cyasorb® UV 531. The melt temperature during film formation is kept below about 120°C to avoid premature crosslinking of the film during extrusion. This film is then used to prepare a solar cell module. The film is laminated at a  
5 temperature of about 150°C to a superstrate, e.g., a glass cover sheet, and the front surface of a solar cell, and then to the back surface of the solar cell and a backskin material, e.g., another glass cover sheet or any other substrate. The protective film is then subjected to conditions that will ensure that the film is substantially crosslinked.

Example 3:

10 The procedure of Example 2 is repeated except that the blend comprised 90 wt% Inventive Example 1 and 10 wt% of a maleic anhydride (MAH) modified ethylene/1-octene (ENGAGE™ 8400 polyethylene grafted at a level of about 1 wt% MAH, and having a post-modified MI of about 1.25 g/10min and a density of about 0.87 g/cc), and the melt temperature during film formation was kept below about 120°C to avoid premature  
15 crosslinking of the film during extrusion.

Example 4:

The procedure of Example 2 is repeated except that the blend comprised 97 wt% Inventive Example 1 and 3 wt% of vinyl silane (no maleic anhydride modified ENGAGE™ 8400 polyethylene), and the melt temperature during film formation was kept below about  
20 120°C to avoid premature crosslinking of the film during extrusion.

Formulations and Processing Procedures:

Step 1: Use ZSK-30 extruder with Adhere Screw to compound resin and additive package with or without Amplify.

25 Step 2: Dry the material from Step 2 for 4 hours at 100°F maximum (use W&C canister dryers).

Step 3: With material hot from dryer, add melted DiCup + Silane + TAC, tumble blend for 15 min and let soak for 4 hours.

Table 3 Formulation

Sample No.	1
Example 1	94.7
4-Hydroxy-TEMPO	0.05
Cyasorb UV 531	0.3
Chimassorb 944 LD	0.1
Tinuvin 622 LD	0.1
Naugard P	0.2
<b>Additives below added via soaking step</b>	
Dicap-R Peroxide	2
Gamma-methacrylo-propyl-trimethoxysilane (Dow Corning Z-6030)	1.75
Sartomer SR-507 Tri-Allyl Cyanurate (TAC)	0.8
Total	100

## Test Methods and Results:

The adhesion with glass is measured using silane-treated glass. The procedure of glass treatment is adapted it from a procedure in Gelest, Inc. "Silanes and Silicones, Catalog 3000 A".

Approximately 10 mL of acetic acid is added to 200 mL of 95% ethanol in order to make the solution slightly acidic. Then, 4 mL of 3-aminopropyltrimethoxy silane is added with stirring, making a -2% solution of silane. The solution sits for 5 minutes to allow for hydrolysis to begin, and then it is transferred to a glass dish. Each plate is immersed in the solution for 2 minutes with gentle agitation, removed, rinsed briefly with 95% ethanol to remove excess silane, and allowed to drain. The plates are cured in an oven at 110°C for 15 minutes. Then, they are soaked in a 5% solution of sodium bicarbonate for 2 minutes in order to convert the acetate salt of the amine to the free amine. They are rinsed with water, wiped dry with a paper towel, and air dried at room temperature overnight.

The method for testing the adhesion strength between the polymer and glass is the 180° peel test. This is not an ASTM standard test, but it is used to examine the adhesion with glass for PV modules. The test sample is prepared by placing uncured film on the top of the glass, and then curing the film under pressure in a compression molding machine. The molded sample is held under laboratory conditions for two days before the test. The adhesion strength is measured with an Instron machine. The loading rate is 2 in/min, and the test is run under ambient conditions. The test is stopped after a stable peel region is

observed (about 2 inches). The ratio of peel load over film width is reported as the adhesion strength.

Several important mechanical properties of the cured films are evaluated using tensile and dynamic mechanical analysis (DMA) methods. The tensile test is run under  
5 ambient conditions with a load rate of 2 in/min. The DMA method is conducted from -100 to 120°C.

The optical properties are determined as follows: Percent of light transmittance is measured by UV-vis spectroscopy. It measures the absorbance in the wavelength of 250 nm to 1200 nm. The internal haze is measured using ASTM D1003-61.

10 The results are reported in Table 4. The EVA is a fully formulated film available from Etimex.



Table 4

Test Results	
Key Properties	EVA
Elongation to break (%)	411.7
STDV*	17.5
Tensile strength at 85°C (psi)	51.2
STDV*	8.9
Elongation to break at 85°C (%)	77.1
STDV*	16.3
Adhesion with glass (N/mm)	7
% of transmittance	>97
STDV*	0.1
Internal Haze	2.8
STDV*	0.4

\*STDV = Standard Deviation.

- 5        The adhesion with glass is measured using silane-treated glass. The procedure of glass treatment is adapted it from a procedure in Gelest, Inc. "Silanes and Silicones, Catalog 3000 A":

Approximately 10 mL of acetic acid is added to 200 mL of 95% ethanol in order to make the solution slightly acidic. Then, 4 mL of 3-aminopropyltrimethoxy silane is added  
 10    with stirring, making a -2% solution of silane. The solution sits for 5 minutes to allow for hydrolysis to begin, and then it is transferred to a glass dish. Each plate is immersed in the solution for 2 minutes with gentle agitation, removed, rinsed briefly with 95% ethanol to remove excess silane, and allowed to drain. The plates are cured in an oven at 110°C for 15  
 15    minutes. Then, they are soaked in a 5% solution of sodium bicarbonate for 2 minutes in order to convert the acetate salt of the amine to the free amine. They are rinsed with water, wiped dry with a paper towel, and air dried at room temperature overnight.

The optical properties are determined as follows: Percent of light transmittance is measured by UV-vis spectroscopy. It measures the absorbance in the wavelength of 250 nm to 1200 nm. The internal haze is measured using ASTM D1003-61.

#### 20    Example 5: Copolymer Polyethylene-Based Encapsulant Film

Inventive Example 1 (made by The Dow Chemical Company) is used in this example. Several additives are selected to add functionality or improve the long term stability of the resin. They are UV absorbent Cyasorb UV 531, UV-stabilizer Chimassorb

944 LD, antioxidant Tinuvin 622 LD, vinyltrimethoxysilane (VTMS), and peroxide Luperox-101. The formulation in weight percent is described in Table 5.

5 Table 5  
Film Formulation

Formulation	Weight Percent
Example 1	97.34
Cyasorb UV 531	0.3
Chimassorb 944 LD	0.1
Tinuvin 622 LD	0.1
Irganox-168	0.08
Silane (Dow Corning Z-6300)	2
Luperox-101	0.08
Total	100

### Sample Preparation

10 Inventive Example 1 pellets are dried at 40°C for overnight in a dryer. The pellets and the additives are dry mixed and placed in a drum and tumbled for 30 minutes. Then the silane and peroxide are poured into the drum and tumbled for another 15 minutes. The well-mixed materials are fed to a film extruder for film casting.

Film is cast on a film line (single screw extruder, 24-inch width sheet die) and the processing conditions are summarized in Table 6.

15 Table 6  
Process Conditions

Sample #	RPM	Amp	Extruder Die						
			Head P (psi)	Zone 1 (F)	Zone 2 (F)	Zone 3 (F)	Adapter (F)	Adapter (C)	Die (C)
1	25	22	2,940	300	325	350	350	182	140

An 18-19 mil thick film is saved at 5.3 feet per minute (ft/min). The film sample is sealed in an aluminum bag to avoid UV-irradiation and moisture.

Test Methods and Results

## 1. Optical Property:

The light transmittance of the film is examined by UV-visible spectrometer (Perkin Elmer UV-Vis 950 with scanning double monochromator and integrating sphere accessory).

- 5 Samples used for this analysis have a thickness of 15 mils. Both films show above 90% of transmittance over the wavelength range from 400 to 1100 nm.

## 2. Adhesion to Glass:

The method used for the adhesion test is a 180° peel test. This is not an ASTM standard test, but has been used to examine the adhesion with glass for photovoltaic module and auto laminate glass applications. The test sample is prepared by placing the film on the top of glass under pressure in a compression molding machine. The desired adhesion width is 1.0 inch. The frame used to hold the sample is 5 inches by 5 inches. A Teflon<sup>™</sup> sheet is placed between the glass and the material to separate the glass and polymer for the purpose of test setup. The conditions for the glass/film sample preparation are:

- 15 (1) 160°C for 3 minutes at 80 pounds per square inch (psi) (2000 lbs)
- (2) 160°C for 30 minutes at 320 psi (8000 lbs)
- (3) Cool to room temperature at 320 psi (8000 lbs)
- (4) Remove the sample from the chase and allow 48 hours for the material to condition at room temperature before the adhesion test.

20 The adhesion strength is measured with a materials testing system (Instron 5581). The loading rate is 2 inches/minutes and the tests are run at ambient conditions (24°C and 50% RH). A stable peel region is needed (about 2 inches) to evaluate the adhesion to glass. The ratio of peel load in the stable peel region over the film width is reported as the adhesion strength.

25 The effect of temperature and moisture on adhesion strength is examined using samples aged in hot water (80°C) for one week. These samples are molded on glass, then immersed in hot water for one week. These samples are then dried under laboratory conditions for two days before the adhesion test. In comparison, the adhesion strength of the same commercial EVA film as described above is also evaluated under the same

conditions. The adhesion strength of the experimental film and the commercial sample are shown in Table 7.

Table 7

Tests Results of Adhesion to Glass

<b>Sample Information</b>	<b>Conditions for Molding on Glass</b>	<b>Aging Condition</b>	<b>Adhesion Strength (N/mm)</b>
<b>Commercial Film (cured)</b>	160°C, one hr	none	10
<b>Commercial Film (cured)</b>	160°C, one hr	80°C in water for one week	1

5

### 3. Water Vapor Transmission Rate (WVTR):

The water vapor transmission rate is measured using a permeation analysis instrument (Mocon Permatran W Model 101 K). All WVTR units are in grams per square meter per day ( $\text{g}/(\text{m}^2\text{-day})$ ) measured at 38°C and 50°C and 100% RH, an average of two specimens. The commercial EVA film as described above is also tested to compare the moisture barrier properties. The inventive film and the commercial film thickness are 15 mils, and both films are cured at 160°C for 30 minutes. The results of WVTR testing are reported in Table 8.

10

Table 8 Summary of WVTR Test Results

<b>Film</b>	<b>Specimen</b>	<b>WVTR at 38C <math>\text{g}/(\text{m}^2\text{-day})</math></b>	<b>WVTR at 50C <math>\text{g}/(\text{m}^2\text{-day})</math></b>	<b>Thick (mil) mil</b>	<b>Permeation at 38C (g- mil)/ (<math>\text{m}^2\text{-day}</math>)</b>	<b>Permeation at 50C (g- mil)/ (<math>\text{m}^2\text{-day}</math>)</b>
<b>Com- mercial Film</b>	A	44.52	98.74	16.80	737	1660
	B	44.54	99.14	16.60	749	1641
	avg.	44.53	98.94	16.70	743	1650

15

### Example 6:

Two set of samples are prepared to demonstrate that UV absorption can be shifted by using different UV-stabilizers. Inventive Example 1 polyolefin (density 0.915 g/cc, melt index 0.8), are used and Table 9 reports the formulations with different UV-stabilizers (all

- amounts are in weight percent). The samples are made using a mixer at a temperature of 190°C for 5 minutes. Thin films with a thickness of 16 mils are made using a compressing molding machine. The molding conditions are 10 minutes at 160°C, and then cooling to 24°C in 30 minutes. The UV spectrum is measured using a UV/Vis spectrometer such as a
- 5 Lambda 950. The results show that different types (and/or combinations) of UV-stabilizers can allow the absorption of UV radiation at a wavelength below 360 nm.

Table 9 Example 1 with Different UV-Stabilizers

Sample	Example 1	Absorber UV-531	Cyasorb UV2908	Cyasorb UV3529	Chimassorb UV-119	Chimassorb 944-LD	Tinuvin 622-LD
1	100						
2	99.7	0.3					
3	99.7		0.3				
4	99.7			0.3			
5	99.7				0.3		
6	99.5					0.25	0.25
7	99.85	0.15					

- Another set of samples are prepared to examine UV-stability. Inventive Example 1
- 10 is selected for this study. Table 10 reports the formulations designed for encapsulant polymers for photovoltaic modules with different UV-stabilizers, silane and peroxide, and antioxidant. These formulations are designed to lower the UV absorbance and at the same time maintain and improved the long term UV-stability.

Table 10

Example 1 with Different UV-Stabilizers, Silanes, Peroxides and Antioxidants

Samples	Example 1	Absorber UV 531	Cyasorb UV 2908	Cyasorb UV 3529	Univil 4050	Doverphos S-9228	Hostavin N30	Chimassorb UV 119	Chimassorb 944 LD	Tinuvin 622 LD	Western 399	Irgafos 166
C 1	99.8										0.2	
C 2	99.3	0.3							0.1	0.1	0.2	
C 3	99.5	0.3							0.1	0.1		
1	99.5		0.5									
2	99.5			0.5								
3	99.5							0.5				
4	99.5								0.5			
5	99.7			0.3						0.5		
6	99.3			0.7								
7	99.5				0.5							
8	99.5						0.5					
9	99.4	0.3				0.1			0.1	0.1		
10	99.3	0.3							0.1	0.1		0.2
11	99.3			0.5								0.2

Although the invention has been described in considerable detail through the preceding description and examples, this detail is for the purpose of illustration and is not to be construed as a limitation on the scope of the invention as it is described in the appended claims. All United States patents, published patent applications and allowed patent  
5 applications identified above are incorporated herein by reference.

What is claimed is:

1. An electronic device module comprising:
  - A. at least one electronic device, and
  - B. a polymeric material in intimate contact with at least one surface of the electronic device, the polymeric material comprising
    - (1) a polyolefin copolymer characterized as having has an average  $M_v$  and a valley temperature between the interpolymer and high crystalline fraction,  $T_{hc}$ , such that the average  $M_v$  for a fraction above  $T_{hc}$  from ATREF divided by average  $M_v$  of the whole polymer from ATREF ( $M_{hc}/M_p$ ) is less than about 1.95 and wherein the copolymer has a CDBI of less than 60%,
    - (2) optionally, a vinyl silane,
    - (3) optionally, free radical initiator or a photoinitiator in an amount of at least about 0.05 wt% based on the weight of the copolymer, and
    - (4) optionally, a co-agent in an amount of at least about 0.05 wt% based upon the weight of the copolymer.
2. The module of Claim 1 in which the electronic device is a solar cell.
3. The module of Claim 1 in which the free radical initiator is present.
4. The module of Claim 3 in which the coagent is present.
5. The module of Claim 4 in which the free radical initiator is a peroxide.
6. The module of Claim 1 in which the polymeric material is in the form of a monolayer film in intimate contact with at least one face surface of the electronic device.
7. The module of Claim 1 in which the polymeric material further comprises a scorch inhibitor in an amount from about 0.01 to about 1.7 wt%.
8. The module of Claim 1 further comprising at least one glass cover sheet.
9. The module of Claim 3 in which the free radical initiator is a photoinitiator.



10. The module of Claim 1 which the polymeric material further comprises a polyolefin polymer grafted with an unsaturated organic compound containing at least one ethylenic unsaturation and at least one carbonyl group.
11. The module of Claim 10 in which the unsaturated organic compound is maleic anhydride.
12. The module of Claim 1 in which the vinyl silane is at least one of vinyl tri-ethoxy silane and vinyl tri-methoxy silane.
13. The module of Claim 17 in which the free radical initiator is a peroxide.
14. The module of Claim 18 in which the co-agent is present.
15. The module of Claim 1 in which the polyolefin copolymer is crosslinked such that the copolymer contains less than about 85 percent xylene soluble extractables as measured by ASTM 2765-95.
16. The module of Claim 1 in which the polymeric material is in the form of a monolayer film in intimate contact with at least one face surface of the electronic device.
17. The module of Claim 1 in which the polymeric material further comprises a scorch inhibitor in an amount from about 0.01 to about 1.7 wt%.
18. The module of Claim 1 further comprising at least one glass cover sheet.
19. The module of Claim 1 in which the polymeric material further comprises a polyolefin polymer grafted with an unsaturated organic compound containing at least one ethylenic unsaturation and at least one carbonyl group.
20. The module of Claim 19 in which the unsaturated organic compound is maleic anhydride.

FIG. 1

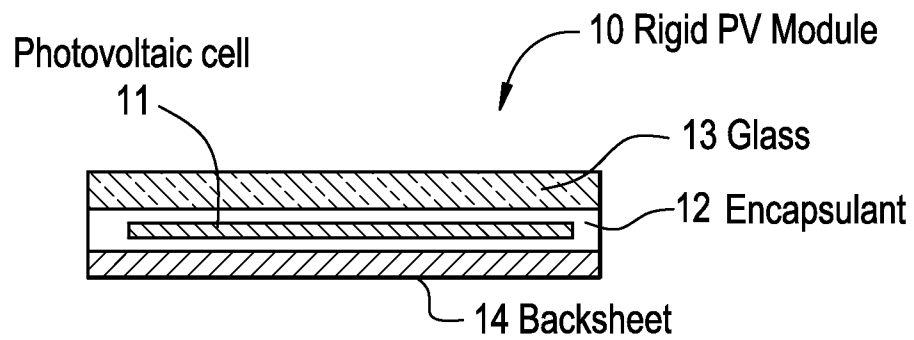


FIG. 2

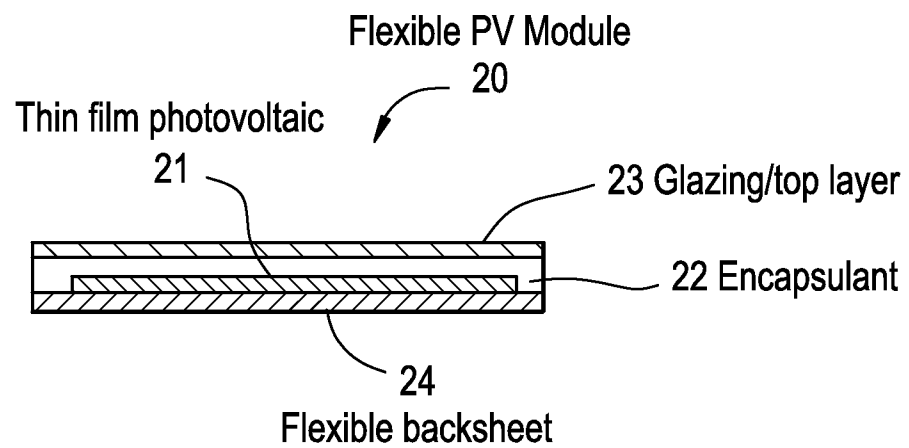
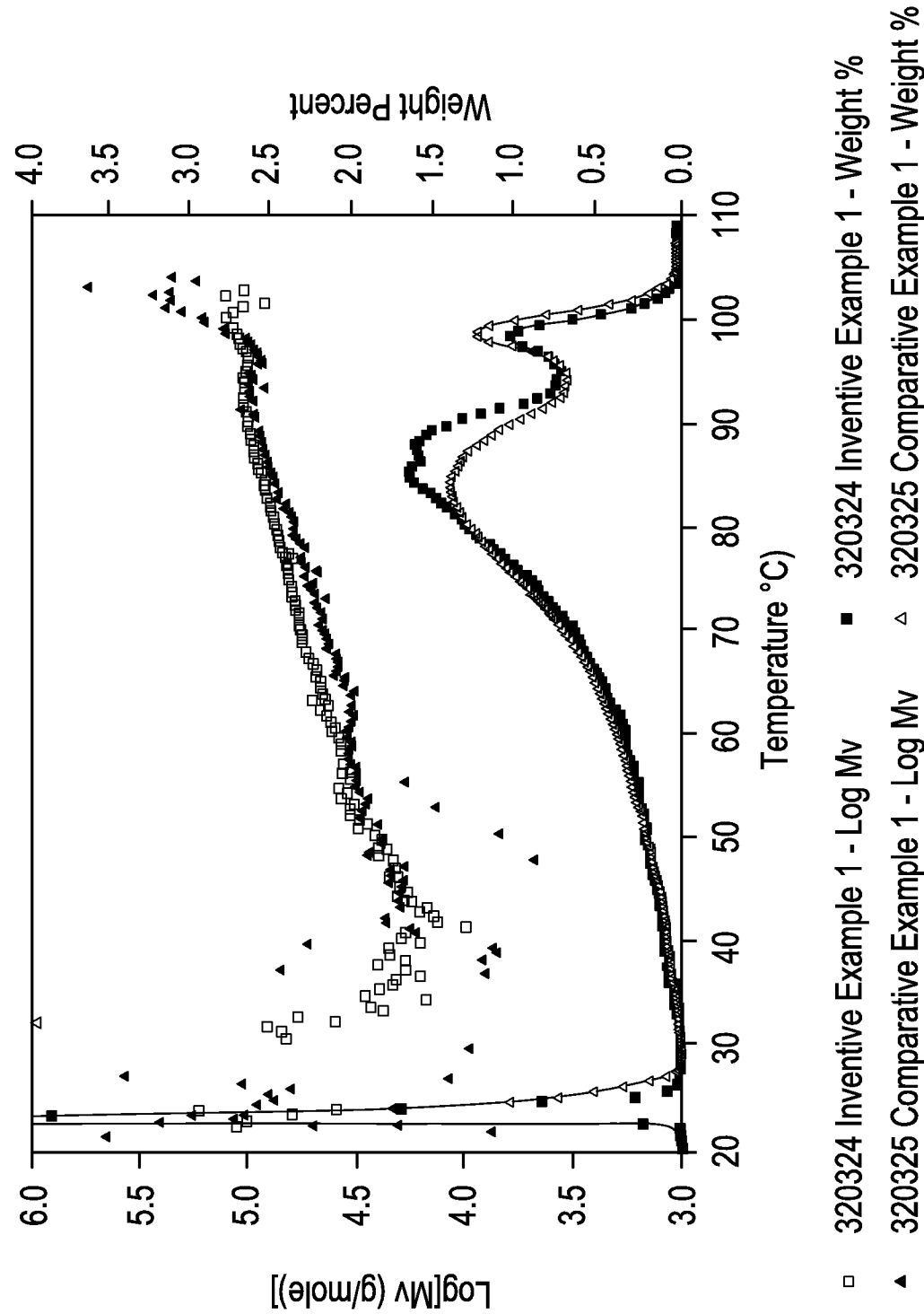


FIG. 3



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2011/04Q492

A. CLASSIFICATION OF SUBJECT MATTER  
INV. B32B17/10 H01L31/048  
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)  
B32B H01L

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 practical, 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	US 2008/115825 AI (PATEL RAJEN M [US] ET AL) 22 May 2008 (2008-05-22) paragraphs [0001] - [0114] ; claims 1-25; figures 1,2 -----	1-20
A.P	Wo 2010/111869 AI (DOW GLOBAL TECHNOLOGIES INC [US] ; YUN XIAOBING [CN] ; WASTIANI RISDIANT) 7 October 2010 (2010-10-07) claims 1-16 -----	1-20
A	EP 1 164 167 AI (BRIDGESTONE CORP [JP] ) 19 December 2001 (2001-12-19) cited in the application claims 1-15 -----	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

### \* Special categories of cited documents :

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"&" document member of the same patent family

Date of the actual completion of the international search

4 August 2011

Date of mailing of the international search report

12/08/2011

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

Ansorge, Markus

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2011/04Q492

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008115825 A1	22-05-2008	NONE	
-----			
WO 2010111869 A1	07-10-2010	WO 2010111931 A1	07-10-2010
		US 2010324202 A1	23-12-2010
		WO 2010117792 A2	14-10-2010
-----			
EP 1164167 A1	19-12-2001	AU 7960200 A	14-05-2001
		WO 0132772 A1	10-05-2001
		US 2001045229 A1	29-11-2001
-----			