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(54) Title: COMPOSITION CONTAINING A LOW VISCOSITY ETHYLENE/ALPHA-OLEFIN COPOLYMER OR A LOW VISCOSITY FUNCTIONALIZED ETHYLENE/ALPHA-OLEFIN COPOLYMER

(57) Abstract: The present disclosure provides a composition that includes a low viscosity ethylene/a- olefin copolymer or a low viscosity functionalized ethylene/a-olefin copolymer and a solvent. Each copolymer has a melt viscosity less than or equal to 20.0 Pa»s (177°C). The solvent is a non- aromatic and halogen-free solvent. The solvent has a boiling point from 100 °C to 170 °C. The composition has a Relative Energy Difference (RED) less than or equal to 1.05 (J/cc)112, based on the Hansen solubility parameter.

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COMPOSITION CONTAINING A LOW VISCOSITY ETHYLENE/ALPHA-OLEFIN COPOLYMER OR A LOW VISCOSITY FUNCTIONALIZED ETHYLENE/ALPHA-OLEFIN COPOLYMER

FIELD

[0001] The present disclosure is directed to compositions containing a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymer,and a solvent; and articles including the same.

BACKGROUND

[0002] Olefin-based polymers have been widely used in many applications because of their low cost and ease in polymer property design. Such polymers are finding many relatively new applications, for example, as shoe soles in the footwear industry. Currently the materials used in footwear midsole are dominated by ethylene vinyl acetate copolymers (EVA). Compared with EVA, olefin-based polymers have several advantages, such as imparting less weight to the final article, which is a general trend in sole designs for footwear products.

[0003] However, olefin-based polymers are typicallynon-polar in nature, making them difficult to be bonded, painted, and printed, due to a low surface energy. For example, in the footwear assembling process, the midsole is typically bonded with both the outsole (usually made of vulcanized rubber or thermoplastic polyurethane) and the shoe upper (usually made from natural/artificial leather). Similar bonding is used in other applications, such as toys and sporting goods.

[0004] To enhance the surface energy and thus improve the bondability and paintability of olefin-based polymers, techniques such as flame treatment, plasma treatment, and acid treatment have been used. These techniques, however, are complicated, costly, andhazardous to workers. A need exists for a composition that is safe, effective and easy to apply for improving the bondability and paintability of olefin-based polymers.

SUMMARY

[0005] The present disclosure is directed to compositions suitable as primers for application to substrates formed from olefin-based polymers. The present disclosure also provides articles containing the present composition.

[0006] In an embodiment, the present composition includes a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymer. Each polymer has a melt viscosity less than or equal to 20.0 Pa•s (177°C). The composition also includes a non-aromatic and halogen-free solvent. The solvent has a boiling point from 100 °C to 170 °C.The composition has a Relative Energy Difference (RED) less than or equal to 1.05 $(J/cc)^{1/2}$, based on the Hansen solubility parameter.

[0007] In an embodiment, the low viscosity ethylene/α-olefin copolymer or the low viscosity functionalized ethylene/α-olefin copolymer, each has the following properties:a) an Mw/Mn from 1.5 to 5.0, andb) a density from 0.855 to 0.900 g/cc.

[0008] In an embodiment, the solvent is selected from a hydrocarbon, an ether, a ketone, an ester, and combinations thereof.

[0009] The present disclosure provides an article. In an embodiment, the article includes a substrate formed from at least one olefin-based polymer, and a layer adhered to the substrate surface. The layer includes a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymer, each copolymer having a melt viscosity less than or equal to 20.0 Pa-s (177°C).

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 is a graph depicting the tensile shear stress of a primer composition in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0011] The present disclosure provides a composition. The composition includes a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymer and a solvent. Eachcopolymer has amelt viscosity less than or equal to 20.0 Pa-s (177°C). The solvent is a non-aromatic and halogen-free solvent. The solvent has a boiling point from 100°C to 170°C. The composition has a Relative Energy Difference (RED) less than or equal to 1.05 $(J/cc)^{1/2}$, based on the Hansen solubility parameter.Thepresent composition may comprise a combination of two or more embodiments as described herein.

1. Low viscosity ethylene/α-olefin copolymer

[0012] In an embodiment, the composition includes a low viscosity ethylene/α-olefin copolymer. A "low viscosity ethylene/α-olefin copolymer," as used herein, is an ethylene-based polymer,with aC_3-C_{10}α-olefin comonomer, theethylene/α-olefin copolymer having a melt viscosity from1.0 Pascal-second (Pa-s) to less than 20.0 Pa-s, or 15.0 Pa-s, or 10.0 Pa-s, or 8.0 Pa-s. Melt viscosity is measured using a Brookfield rotational viscometer in accordance with ASTM D 1084 (at 177°C, 350°F). Nonlimiting examples of suitable C_3-C_{10} α-olefin comonomer include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene and 1-octene.

[0013] The low viscosity ethylene/α-olefin copolymer can have a melt viscosity from 1.0 Pa-s, or 2.0 Pa-s, or 3.0 Pa-s, or 4.0 Pa-s, or 5.0 Pa-s, or 6.0 Pa-s, to less than 20.0 Pa-s, or 15.0 Pa-s, or 10.0 Pa-s, or8.0 Pa-s.

[0014] In an embodiment, the low viscosity ethylene/α-olefin copolymer has an Mw/Mn from 1.5 to 5.0 and a density from 0.85 g/cc to 0.90 g/cc.

[0015] In an embodiment, the low viscosity ethylene/α-olefin copolymer has a melt viscosity from 1.0 Pa-s to less than 10.0 Pa-s.

[0016] In an embodiment the low viscosity ethylene/α-olefin copolymer has one, some, or all of the following properties: a melt viscosity from 1.0 Pa-s to less than 10.0 Pa-s, a density from 0.86 g/cc to 0.88 g/cc, and a weight average molecular weight (Mw) less than 25,000, an Mw/Mn from 1.5 to 2.5, a melting temperature (Tm) from 68-70°C (DSC), a melt index (I2) greater than 500 g/10 minute, and a crystallinity less than 25%, or from 5% to less than 25% (as determined by DSC).

[0017] In an embodiment, the low viscosity ethylene/α-olefin copolymer is a homogeneously branched substantially linear ethylene/α-olefin copolymer. A "homogeneously-branchedethylene/α-olefin copolymer," as used herein, is an ethylene/α-olefin interpolymer, in which the α-olefin comonomer is randomly distributed within a given polymer molecule, and all of the polymer molecules have the same or substantially the same comonomer-to-ethylene ratio.

[0018] Homogeneously branched substantially linear ethylene/α-olefin interpolymer is described in U.S. Patent Nos. 5,272,236; 5,278,272; 6,054,544; 6,335,410 and 6,723,810; each incorporated herein by reference. Substantially linear ethylene/α-olefin interpolymer has long chain branching. The long chain branches have the same comonomer distribution as the polymer backbone, and can have about the same length as the length of the polymer backbone. The term "substantially linear," typically, is in reference to a polymer that is substituted, on average, with "0.01 long chain branches per 1000 carbons" to "3 long chain branches per 1000 carbons." The length of a long chain branch is longer than the carbon length of a short chain branch, formed from the incorporation of one comonomer into the polymer backbone.

[0019] Some polymers may be substituted with 0.01 long chain branches per 1000 total carbons to 3 long chain branches per 1000 total carbons, further from 0.01 long chain branches per 1000 total carbons to 2 long chain branches per 1000 total carbons, and further from 0.01 long chain branches per 1000 total carbons to 1 long chain branch per 1000 total carbons.

[0020] The substantially linear homogeneously branched linear ethylene/α-olefin interpolymers form a unique class of ethylene polymers. They differ substantially from the conventional, homogeneously branched linear ethylene/α-olefin interpolymers, as discussed above, and, moreover, they are not in the same class as conventional heterogeneous "Ziegler-Natta catalyst polymerized" linear ethylene polymers (for example, ultra-low density polyethylene (ULDPE), linear low density polyethylene (LLDPE) or high density polyethylene (HDPE), made, for example, using the technique disclosed by Anderson et al., in U.S. Patent 4,076,698); nor are they in the same class as high pressure, free-radical initiated, highly branched polyethylenes, such as, for example, low density polyethylene (LDPE), ethylene-acrylic acid (EAA) copolymers and ethylene vinyl acetate (EVA) copolymer.

[0021] Nonlimiting examples of suitable low viscosity ethylene/α-olefin copolymerinclude AFFINITY^{TM} GAPolyolefin Elastomers, available from The Dow Chemical Company, Midland, Michigan, USA.

[0022] The low viscosity ethylene/α-olefin copolymer may comprise a combination of two or more embodiments as described herein.

2. *Low viscosity functionalized ethylene/α-olefin copolymer*

[0023] In an embodiment, the composition includes a low viscosity functionalized ethylene/α-olefin copolymer. A "low viscosity functionalized ethylene/α-olefin copolymer," as used herein, is the previously described low viscosity ethylene/α-olefin copolymerthat has been modified to introduce an element other than carbon and hydrogen. The functional group can be selected from primary or secondary amines, alcohols, thiols, aldehydes, carboxylic acids and derivatives thereof (anhydrides),silanes, and sulfonic acids.

[0024] In an embodiment, the low viscosity functionalized ethylene/α-olefin copolymer can have a melt viscosity from 1.0 Pa-s, or 2.0 Pa-s, or 3.0 Pa-s, or 4.0 Pa-s, or 5.0 Pa-s, or 6.0 Pa-s to less than 20.0 Pa-s, or 15.0 Pa-s, or 13 Pa-s.

[0025] In an embodiment, the low viscosity functionalized ethylene/α-olefin copolymer has an Mw/Mn from 1.5 to 5.0 and a density from 0.85 g/cc to 0.90 g/cc.

[0026] In an embodiment, the low viscosity functionalized ethylene/α-olefin copolymer has a melt viscosity less than 15.0 Pa-s, or from 1.0 Pa-s to less than 15.0 Pa-s.

[0027] In an embodiment, the low viscosity functionalized ethylene/α-olefin copolymer is a maleic anhydride (MAH) grafted ethylene/α-olefin copolymer (MAH-g-ethylene/α-olefin copolymer). The low viscosityMAH-g-ethylene/α-olefin copolymer contains from 0.5 wt% to 2.0 wt% maleic anhydride. Weight percent is based on total weight of the MAH-g-ethylene/α-olefin copolymer.

[0028] In an embodiment, the low viscosity functionalizedethylene/α-olefin copolymer has one, some, or all of the following properties: a melt viscosity from 1.0 Pa-s to less than 15.0 Pa-s, a density from 0.86 g/cc to 0.88 g/cc, and a weight average molecular weight (Mw) less than 25,000, an Mw/Mn from 1.5 to 2.5, a melting temperature (Tm) from 68-70°C (DSC), a melt index (I2) greater than 500 g/10 minute and a crystallinity less than 25%, or from 5% to less than 25% (as determined by DSC).

[0029] The copolymer component of the present composition may be the low viscosity ethylene/α-olefin copolymer, the low viscosity functionalized ethylene/α-olefin copolymer, or a combination thereof.

[0030] Non-limiting examples of suitable low viscosity functionalized ethylene/α-olefin copolymer include AFFINITY™GA Polyolefin Elastomer available from The Dow Chemical Company, Midland, Michigan, USA.

[0031] The low viscosity functionalized ethylene/α-olefin copolymer may comprise a combination of two or more embodiments as described herein.

3. Solvent

[0032] The composition includes a solvent. The solvent is non-aromatic and halogen-free.The solvent has a boiling point from 100 °C to 170 °C. The solvent is select from hydrocarbon, ether, ketone, ester, and combinations thereof.

[0033] An "aromatic" compound, as used herein, is a closed-ring hydrocarbon with conjugated double bonds. The simplest aromatic compound is benzene.The term "halogen-free," as used herein, is the void or the absence of a halogen atom, such as F, Cl, Br, andI.Accordingly, the present "non-aromatic and halogen-free hydrocarbon solvent" is void of both an aromatic compound and halogen.

[0034] In an embodiment, the solvent is a non-aromatic and halogen-free hydrocarbon with a boiling point from 100 °C, or 120 °C to 140 °C, or 170 °C.The hydrocarbon may be saturated or unsaturated, and may be linear, branched, or ringed. In a further embodiment, the hydrocarbon contains from 5 to 7, or 10, or 12 carbon atoms.

[0035] Nonlimiting examples of suitable non-aromatic and halogen-free hydrocarbon solvent include ethylcyclohexane, methylcyclohexane, propylcyclopentane, isopropylcyclopentane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, 1,4-dimethylcyclohexane, 1,1-dimethylcyclohexane, 1-methylcyclohexene, 4-methylcyclohexene, dipentene, and combinations thereof.

[0036] In an embodiment, the solvent is a non-aromatic and halogen-free ether with a boiling point from 100 °C, or 120 °C to 140 °C, or 170 °C. The ether may be saturated or unsaturated, and may be linear, branched, or ringed. In a further embodiment, the ether contains from 2, or 3, or 4 to 6, or, 8, or 10 carbon atoms.

[0037] Nonlimiting examples of suitable non-aromatic and halogen-free ether include 1,1-diethoxyethane, dibutyl ether, ethylene glycol diethyl ether, and combinations thereof.

[0038] In an embodiment, the solvent is a non-aromatic and halogen-free ketone with a boiling point from 100 °C, or 120 °C to 140 °C, or 170 °C. The ketone may be saturated or unsaturated, and may be linear, branched, or ringed. In a further embodiment, the ketone contains from 2, or 4 to 5, or 6, or 7, or 8, or 9, or 10 carbon atoms.

[0039] Nonlimiting examples of suitable non-aromatic and halogen-free ketone include cyclopropyl methyl ketone, diethyl ketone, diisobutyl ketone, dipropyl ketone, ethyl butyl ketone, 4-methyl-3-penten-2-one, methyl isobutyl ketone, methyl n-butyl ketone, methyl n-propyl ketone, and combinations thereof.

[0040] In an embodiment, the solvent is a non-aromatic and halogen-free ester with a boiling point from 100 °C, or 120 °C to 140 °C, or 170 °C. The ester may be saturated or unsaturated, and may be linear, branched, or ringed. In a further embodiment, the ester contains from 3, or 4 to 5, or, 6, or, 7, or 8, or 9, or 10carbon atoms.

[0041] Nonlimiting examples of suitable non-aromatic and halogen-free ester include 2-methoxy methyl lactate, N-propyl propionate, and combinations thereof.

[0042] The non-aromatic and halogen-free solvent may be any combination of the foregoing hydrocarbons, ethers, ketones, and esters.

[0043] In an embodiment, the solvent is ethylcyclohexane.

[0044] In an embodiment, the composition includes the low viscosity functionalized ethylene/α-olefin copolymer dissolved in ethylcyclohexane. In a further embodiment, the low viscosity functionalized ethylene/α-olefin copolymer is low viscosity MAH-g-ethylene/α-olefin copolymer that is completely dissolved in the ethylcyclohexane at ambient temperate. The term "completely dissolved," as used herein, is the condition where no, or substantially no, solid phase of the low viscosity functionalized ethylene/α-olefin copolymer is visible in the composition at ambient temperature.

4. *Relative Energy Difference*

[0045] The composition has a relative energy difference (RED) less than or equal to 1.05 $(J/cc)^{1/2}$.The RED value is based on the Hansen solubility parameter.

[0046] The concept of a numerical solubility parameter, capable of describing the solubility properties of a solvent or polymer, was first described by Hildebrand. Charles Hansen divided the Hildebrand solubility parameter into three partial solubility parameters, namely dispersion (δ_d), polar (δ_p), and hydrogen-bonding (δ_h), each having values in $(J/cc)^{1/2}$. These three Hansen solubility parameters, or HSP, define a point, in three-dimensional solubility space, that describes the solubility properties of a solvent. HSP theory states that solvents with similar HSP should be compatible or soluble in each other. Polymers are larger molecules, which exhibit a more complex solubility behavior than pure solvents, and their solubility properties are best described as a sphere in solubility space, with the three HSP parameters, as its center coordinates, and a radius R (also in $(J/cc)^{1/2}$ that defines the size of the solubility sphere. The interaction between a solvent and a polymer is calculated as an Energy Difference (ED) using the equation 1:

$$\text{Equation 1} \qquad ED = (4\,(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2)^{1/2},$$

where the subscripts 1 and 2 denote the HSP of the solvent and the polymer, respectively. If the ED is divided by the radius R of the sphere, one obtains the Relative Energy Difference or RED value (Equation 2).

$$\text{Equation 2} \qquad RED = \frac{(4\,(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2)^{1/2}}{R}$$

[0047] Solvents with RED ≤ 1 (J/cc)$^{1/2}$ should interact strongly with the polymer by swelling it or dissolving it. In theory, the closer the RED is to zero, the stronger the interaction. In practice, this is not always observed, as the determination of solvent solubility parameters always has an error associated with it.

[0048] To characterize a polymer by its HSP and R values, it is necessary to actually measure, or at least visually rate, its solubility in a set of solvents with known solubility parameters. The solubility behavior is then fitted with a computer program that minimizes the radius of interaction, while maintaining the best agreement with the empirical solubility observations. A tailored SOLFIT program for modeling solvent properties is used.

[0049] Once a polymer is characterized by its HSP and R values, a search for suitable solvents in a solvent HSP database can be conducted, using RED as the key criteria. This search can be simplified using a spreadsheet-type program, like Microsoft Excel, containing the solvent database and programmed to solve Equation 2. A second solvent modeling program allows for evaluation of other criteria, such as solvent class and boiling point. A tailored single computer program is used to perform these functions. If lacking in the database, the HSP of a given solvent can be calculated by various methods described by Hansen in his book "Hansen Solubility Parameters – A User's Handbook", 2nd Edition, CRC Press, 2007. Solvent HSP values not available in our database are calculated using the Yamamoto Molecular Break method (Y-MB) contained within the commercial HSPiP program. This program returns the HSP values for a solvent structure entered in the SMILES format (molecular structures that omit hydrogens).

[0050] In an embodiment, the composition includes a low viscosity functionalized ethylene/α-olefin copolymer and solvent as disclosed above, and the RED value is less than or equal to 1.04 (J/cc)$^{1/2}$, or less than or equal to 1.00 (J/cc)$^{1/2}$, or less than or equal to 0.90 (J/cc)$^{1/2}$or less than or equal to 0.80 (J/cc)$^{1/2}$.

[0051] In an embodiment, the composition has a solution viscosity, at 23°C, 5 wt% polymer(based on weight of composition), from 0.010 Pa-s to 0.040 Pa-s (Brookfield test; RPM = 30).In a further embodiment, the composition includes 5 wt% low viscosity functionalized ethylene/α-olefin copolymer and ethylcyclohexane and the composition has a solution viscosity at 23°C of 0.023 Pa-s.

[0052] In an embodiment, the composition has a solution viscosity, at 23°C, 10 wt% polymer (based on weight of composition), from 0.040 Pa-s to 0.080 Pa-s (Brookfield test, RPM=30). In a further embodiment, the composition includes 10 wt% low viscosity functionalized ethylene/α-olefin copolymer and ethylcyclohexane and the composition has a solution viscosity at 23°C of 0.063 Pa-s.

5. *Additional components*

[0053] The composition may include one, some, or all of the following additional components: a non-functionalized ethylene/α-olefin interpolymer, a chlorinated polyethylene, an ethyl vinyl acetate copolymer (28% VA), an isocyanate, and a pigment.

[0054] In an embodiment, the composition includes from 1 wt%, or 5 wt% to 10 wt%, or 15 wt% of the low viscosity ethylene/α-olefin copolymer, or the low viscosity functionalized ethylene/α-olefin copolymer, or a combination thereof and from 99 wt% to 90 wt%, or 85 wt% of the solvent. Weight percent is based on total weight of the composition.

[0055] The present composition may be applied as a primer composition to olefin-based polymers to promote adhesion and paintability. A pigment may be added to the primer composition to create a paint formulation for polyolefins.

[0056] The present composition may comprise two or more embodiments disclosed herein.

6. *Article*

[0057] The present disclosure provides an article. The article includes a substrate formed from at least one olefin-based polymer. The article also includes a layer on a surface of the substrate of a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymerhaving a melt viscosity less than or equal to 20.0 Pa-s. The low viscosity ethylene/α-olefin copolymer is any low viscosity ethylene/α-olefin copolymer or any low viscosity functionalized ethylene/α-olefin copolymeras described herein. The low viscosity ethylene/α-olefin copolymer contacts and adheres to the substrate surface and forms a layer on the surface of the olefin-based polymer. The layer of the low viscosity ethylene/α-olefin copolymermay be continuous or discontinuous. The layer of the low viscosity ethylene/α-olefin copolymer may be coextensive or non-coextensive with the substrate surface.

[0058] The substrate may be formed from anolefin-based polymer, a propylene-based polymer, an ethylene-based polymer, an olefin block copolymer, and blends thereof. The substrate may be a thermoplastic olefin (TPO). The substrate can be extruded, thermoformed, thermoset, injection molded, blow molded, and any combination thereof.

[0059] The untreated article (*i.e.*, the article without the layer of low viscosity ethylene/α-olefin copolymer) can be composed solely of the substrate. Alternatively, the untreated article is a multi-component (or a multi-layer) object, of which the olefin-based polymer substrate is one of a plurality of components (or one of a plurality of layers). Nonlimiting examples of suitable articles include automobile parts (bumper, fascia, trim interior/exterior parts), foam, shoes (outer sole, inner sole, upper sole) consumer electronics (computers, cell phones, hand-held data devices), consumer appliances (refrigerator, range, blender), toys, footwear, adhesives, films, laminates, and fibers.

[0060] In an embodiment, the substrate surface isformed from an olefin-based polymer. The present composition is applied to the substrate surface. Nonlimiting techniques by which to apply the present composition to the substrate surface include spray coating, dip coating, bar coating, brush coating, roll coating, curtain coating, and combinations thereof.

[0061] In an embodiment, the present composition is applied at a thickness (typically 20 microns to 120 microns) that will produce a dry layer of the low viscosity ethylene/α-olefin copolymerhaving a thickness from 1 micron, or 5 microns, or 8 microns to 10 microns, or 15 microns, or 20 microns on the substrate surface.

[0062] In an embodiment, the present composition is sprayed onto the olefin-based polymer surface of the substrate.

[0063] In an embodiment, the substrate surface includes an ethylene/alpha-olefin copolymer.

[0064] In an embodiment, the substrate surface includesan olefin block copolymer. An “olefin block copolymer” (or “OBC”), as used herein, is a multi-block or segmented copolymer and includes two or more chemically distinct regions or segments (referred to as “blocks”) joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion. In certain embodiments, the blocks differ in the amount or type of comonomer incorporated therein, the density, the amount of crystallinity, the crystallite size attributable to a polymer of such composition, the type or degree of tacticity (isotactic or syndiotactic), regio-regularity or regio-irregularity, the amount of branching, including long chain branching or hyper-branching, the homogeneity, or any other chemical or physical property. The olefin block copolymer is characterized by unique distributions of polydispersity index (PDI or M_w/M_n), block length distribution, and/or block number distribution due to the unique process making of the copolymers. More specifically, when produced in a continuous process, embodiments of the OBC may possess a PDI ranging from 1.7 to 8; or from 1.7 to 3.5; or from 1.7 to 2.5; and from 1.8 to 2.5; or from 1.8 to 2.1. When produced in a batch or semi-batch process, embodiments of the OBC may possess a PDI ranging from 1.0 to 2.9; or from 1.3 to 2.5; or from 1.4 to 2.0; or from 1.4 to 1.8.

[0065] In an embodiment, the OBC is an ethylene/α-olefin multi-block copolymer. The ethylene/α-olefin multi-block copolymer comprises a majority mole fraction of units derived from ethylene, the ethylene comprising at least 50 mol %, or at least 60 mol %, or at least 70 mol %, or at least 80 mol % with the remainder of the multi-block copolymer comprising the comonomer. The ethylene/α-olefin multi-block copolymer further includes ethylene and the co-polymerizable α-olefin comonomer in polymerized form, characterized by multiple (*i.e.*, two or more) blocks or segments of two or more polymerized monomer units differing in chemical or physical properties (block interpolymer), and is a multi-block copolymer. In some embodiments, the multi-block copolymer may be represented by the following formula:

$$(AB)_n$$

where n is at least 1, preferably an integer greater than 1, such as 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100, or higher; “A” represents a hard block or segment; and “B” represents a soft block or segment. The A’s and B’s are linked in a linear fashion, not in a branched or a star fashion. “Hard” segments refer to blocks of polymerized units in which ethylene is present in an amount greater than 95 weight percent in some embodiments, and in other embodiments greater than 98 weight percent. In other words, the comonomer content in the hard segments is less than 5 weight percent in some embodiments, and in other embodiments, less than 2 weight percent of the total weight of the hard segments. In some embodiments, the hard segments comprise all, or substantially all, ethylene.

[0066] The “soft” segments, on the other hand, refer to blocks of polymerized units in which the comonomer content is greater than 5 weight percent of the total weight of the soft segments in some embodiments, greater than 8 weight percent, greater than 10 weight percent, or greater than 15 weight percent in various other embodiments. In some embodiments, the comonomer content in the soft segments may be greater than 20 weight percent, greater than 25 eight percent, greater than 30 weight percent, greater than 35 weight percent, greater than 40 weight percent, greater than 45 weight percent, greater than 50 weight percent, or greater than 60 weight percent in various other embodiments.

[0067] Because the respective distinguishable segments or blocks formed from two or more monomers are joined into single polymer chains, the polymer cannot be completely fractionated using standard selective extraction techniques. For example, polymers containing regions that are relatively crystalline (high density segments) and regions that are relatively amorphous (lower density segments) cannot be selectively extracted or fractionated using differing solvents. In an embodiment, the quantity of extractable polymer using either a dialkyl ether or an alkane solvent is less than 10, or less than 7, or less than 5, or less than 2, percent of the total polymer weight.

[0068] In addition, the OBC disclosed herein possesses a PDI fitting a Schulz-Flory distribution rather than a Poisson distribution. The present OBC is produced by the polymerization process described in U.S. Patent No. 7,858,706 and U.S. Patent No. 7,608,668 which results in a product having both a polydisperse block distribution as well as a polydisperse distribution of block sizes. This results in the formation of OBC product having distinguishable physical properties. The theoretical benefits of a polydisperse block distribution have been previously modeled and discussed in Potemkin, Physical Review E (1998) 57 (6), pp. 6902-6912, and Dobrynin, J. Chem.Phys. (1997) 107 (21), pp 9234-9238.

[0069] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (A) Mw/Mn from 1.7 to 3.5, at least one melting point, Tm, in degrees Celsius, and a density, d, in grams/cubic centimeter, where in the numerical values of Tm and d correspond to the relationship:

$$Tm > -2002.9 + 4538.5(d) - 2422.2(d)^2.$$

[0070] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (B) Mw/Mn from 1.7 to 3.5, and is characterized by a heat of fusion, ΔH in J/g, and a delta quantity, ΔT, in degrees Celsius defined as the temperature difference between the tallest DSC peak and the tallest Crystallization Analysis Fractionation ("CRYSTAF") peak, wherein the numerical values of ΔT and ΔH have the following relationships:

$$\Delta T > -0.1299 (\Delta H) + 62.81 \text{ for } \Delta H \text{ greater than zero and up to 130 J/g}$$

$$\Delta T \geq 48°C \text{ for } \Delta H \text{ greater than 130 J/g}$$

wherein the CRYSTAF peak is determined using at least 5 percent of the cumulative polymer, and if less than 5 percent of the polymer has an identifiable CRYSTAF peak, then the CRYSTAF temperature is 30°C.

[0071] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (C) elastic recovery, Re, in percent at 300 percent strain and 1 cycle measured with a compression-molded film of the ethylene/α-olefin interpolymer, and has a density, d, in grams/cubic centimeter, wherein the numerical values of Re and d satisfy the following relationship when ethylene/α-olefin interpolymer is substantially free of crosslinked phase:

$$Re > 1481 - 1629(d).$$

[0072] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (D) a molecular weight fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a molar comonomer content of at least 5 percent higher than that of a comparable random ethylene interpolymer fraction eluting between the same temperatures, wherein said comparable random ethylene interpolymer has the same comonomer(s) and has a melt index, density and molar comonomer content (based on the whole polymer) within 10 percent of that of the ethylene/α-olefin interpolymer.

[0073] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (E) a storage modulus at 25°C, G'(25°C), and a storage modulus at 100°C, G'(100°C), wherein the ratio of G'(25°C) to G'(100°C) is in the range of about 1:1 to about 9:1.

[0074] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (F) a molecular fraction which elutes between 40°C and 130°C when fractionated using TREF, characterized in that the fraction has a block index of at least 0.5 and up to about 1 and a molecular weight distribution, Mw/Mn, greater than about 1.3.

[0075] In an embodiment, the ethylene/α-olefin multi-block copolymer is defined as having (G) average block index greater than zero and up to about 1.0 and a molecular weight distribution, Mw/Mn greater than about 1.3.

[0076] The ethylene/α-olefin multi-block copolymer may have any combination of properties (A)-(G) set forth above.

[0077] Nonlimiting examples of suitable comonomer include straight-chain/branched α-olefin of 3 to 30 carbon atoms, such as propylene, 1-butene, 1-pentene, 3-methyl-l-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1- octadecene and 1-eicosene; cyclo-olefins of 3 to 30, or 3 to 20, carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; di-and polyolefins, such as butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-

hexadiene, 1,3-hexadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylidenenorbornene, vinyl norbornene, dicyclopentadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene; and 3-phenylpropene, 4-phenylpropene, 1,2-difluoroethylene, tetrafluoroethylene, and 3,3,3-trifluoro-1-propene.

[0078] In an embodiment, the comonomer in the ethylene/α-olefin multi-block copolymer is selected from propylene, butene, hexene, and octene.

[0079] In an embodiment, the ethylene/α-olefin multi-block interpolymer excludes styrene.

[0080] In an embodiment, the ethylene/α-olefin multi-block interpolymer is an ethylene/octene multi-block copolymer.

[0081] In an embodiment, the soft segment of the ethylene/octene multi-block copolymer includes from 5 mol%, 7 mol%, or 9 mol%, or 11 mol%, or 13 mol%, or 15 mol% to 18 mol% to 20 mol% units derived from octene. The ethylene/octene multi-block copolymer has a density from 0.866 g/cc to 0.887 g/cc. The ethylene/octene multi-block copolymer has a melt index (MI) from 0.5 g/10 min, or 5.0 g/10 min, or 10.0 g/10 min, or 15 g/10 min, to 20 g/10 min, or 25 g/10 min, or 30 g/10 min.

[0082] In an embodiment, the article also includes a layer of a coating material. The coating material is applied to the layer of the low viscosity ethylene/α-olefin copolymer. The coating material contacts and adheres to the layer of low viscosity ethylene/α-olefin copolymer, thereby adhering to the substrate surface and forming a three component structure: substrate surface/low viscosity ethylene/α-olefin copolymer/coating material (outermost layer). Nonlimiting techniques by which to apply the coating material include spray coating, dip coating, bar coating, brush coating, roll coating, curtain coating, and combinations thereof.

[0083] In an embodiment, a layer of a coating material is on a layer of low viscosity maleic anhydride grafted ethylene/α-olefin copolymer which is adhered to the surface of the substrate formed from olefin-based polymer, such as OBC.

[0084] In an embodiment, the present composition is mixed with the coating material to form a mixture. The mixture is subsequently applied to the substrate surface to coat the substrate by way of any of the application techniques disclosed above. When the coating material is dry, the coating material, the low viscosity ethylene/α-olefin copolymer, and the substrate surface form a three component structure (or layer structure) with the low viscosity ethylene/α-olefin copolymer adhering the coating material to the substrate surface.

[0085] In an embodiment, the coating material is a paint. The paint includes a solvent, a binder, a pigment, and optional additives. Nonlimiting examples of solvent for the coating material include toluene, xylene, methyl ethyl ketone, methyl isobutyl ketone and water. The pigment may include inorganic materials such as titanium dioxide (rutile), mica flakes, iron oxide, silica, aluminum, and the like.

[0086] Nonlimiting examples of binder include acrylic polymers, alkyd resins, cellulose based materials, such as cellulose acetate butyrate, melamine resins, carbamate resins, polyester resins, vinyl acetate resins, urethane resins, and any combination thereof. Nonlimiting examples of additives for the coating material include catalysts, thickeners, stabilizers, emulsifiers, texturizers, adhesion promoters, UV stabilizers, flatteners (de-glossing agents), biocides, polyols, alcohols, and any combination thereof.

[0087] In an embodiment, the coating material is an adhesive composition, such as a glue.

[0088] The present article may comprise two or more embodiments disclosed herein.

DEFINITIONS

Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight, and all test methods are current as of the filing date of this disclosure.

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

[0089] The terms “comprising”, “including”, “having” and their derivatives do not exclude the presence of any additional component or procedure. The term, “consisting essentially of” excludes any other component or procedure, except those essential to operability. The term “consisting of” excludes any component or procedure not specifically stated.

[0090] The term, “ethylene-based polymer,” as used herein, refers to a polymer that comprises, in polymerized form, a majority amount of ethylene monomer (based on the weight of the polymer), and optionally may comprise one or more comonomers.

[0091] The term, “ethylene/α-olefin interpolymer,” as used herein, refers to an interpolymer that comprises, in polymerized form,a majority amount of ethylene monomer (based on the weight of the interpolymer), and at least one α-olefin.

[0092] The term, “ethylene/α-olefin copolymer,” as used herein, refers to a copolymer that comprises, in polymerized form,a majority amount of ethylene monomer (based on the weight of the copolymer), and an α-olefin, as the only two monomer types.

[0093] The term "interpolymer," as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers (employed to refer to polymers prepared from two different types of monomers), and polymers prepared from more than two different types of monomers.

[0094] The term, “olefin-based polymer,” as used herein, refers to a polymer that comprises, in polymerized form, a majority amount of olefin monomer, for example ethylene or propylene (based on the weight of the polymer), and optionally may comprise one or more comonomer.

[0095] The term "polymer," as used herein, 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 (employed to refer to polymers prepared from only one type of monomer, with the understanding that trace amounts of impurities can be incorporated into the polymer structure), and the term interpolymer as defined hereinafter.

TEST METHODS

[0096] Density is measured in accordance with ASTM D-792.

[0097] *Differential Scanning Calorimetry* (DSC) is used to measure crystallinity in polyethylene (PE) based samples and polypropylene (PP) based samples. About five to eight milligrams of sample is weighed and placed in a DSC pan. The lid is crimped on the pan to ensure a closed atmosphere. The sample pan is placed in a DSC cell, and then heated, at a rate of approximately 10°C/min, to a temperature of 180°C for PE (230°C for PP). The sample is kept at this temperature for three minutes. Then the sample is cooled at a rate of 10°C/min to -60°C for PE (-40°C for PP), and kept isothermally at that temperature for three minutes. The sample is next heated at a rate of 10°C/min, until complete melting (second heat). The percent crystallinity is calculated by dividing the heat of fusion (H_f), determined from the second heat curve, by a theoretical heat of fusion of 292 J/g for PE (165 J/g, for PP), and multiplying this quantity by 100 (e.g., for PE, % cryst. = (H_f / 292 J/g) x 100; and for PP, % cryst. = (H_f / 165 J/g) x 100).

[0098] Unless otherwise stated, melting point(s) (T_m) of each polymer is determined from the second heat curve obtained from DSC, as described above (peak Tm). The crystallization temperature (T_c) is measured from the first cooling curve (peak Tc).

[0099] *Fourier Transform Infrared Spectroscopy (FTIR) Analysis-Maleic Anhydride Content*

[00100] The concentration of maleic anhydride is determined by the ratio of peak heights of the maleic anhydride at wave number 1791 cm^{-1} to the polymer reference peak, which, in case of polyethylene, is at wave number 2019 cm^{-1}. Maleic anhydride content is calculated by multiplying this ratio with the appropriate calibration constant. The equation used for maleic grafted polyolefins (with reference peak for polyethylene) has the following form, as shown in Equation 3.

MAH (wt%) = A * {[FTIR PeakArea@ 1791 cm-1]/[FTIR PeakArea 2019 cm-1] + B* [FTIR PeakArea@ 1712 cm-1]/[FTIR_PeakArea@ 2019 cm-1]} (Equation 3)

[00101] The calibration constant Acan be determined using ^{13}C NMR standards. The actual calibration constant may differ slightly depending on the instrument and polymer. The second component at wave number 1712 cm^{-1} accounts for the presence of maleic acid, which is negligible for freshly grafted material. Over time however, maleic anhydride is readily converted to maleic acid in the presence of moisture. Depending on surface area, significant hydrolysis can occur in just a few days under ambient conditions. The acid has a distinct peak at wave number 1712 cm^{-1}. The constant B in Equation 3 is a correction for the difference in extinction coefficients between the anhydride and acid groups.

[00102] The sample preparation procedure begins by making a pressing, typically 0.05 to 0.15 millimeters in thickness, in a heated press, between two protective films, at 150-180°C for one hour. Mylar and Teflon are suitable protective films to protect the sample from the platens. Aluminum foil must never be used (maleic anhydride reacts with aluminum). Platens should be under pressure (~10 ton) for about five minutes. The sample is allowed to cool to room temperature, placed in an appropriate sample holder, and then scanned in the FTIR. A background scan should be run before each sample scan, or as needed. The precision of the test is good, with an inherent variability of less than ± 5%. Samples should be stored with desiccant to prevent excessive hydrolysis. Moisture content in the product has been measured as high as 0.1 weight percent. The conversion of anhydride to acid however is reversible with temperature, but may take up to one week for complete conversion. The reversion is best performed in a vacuum oven at 150°C; a good vacuum (near 30 inches Hg) is required. If the vacuum is less than adequate the sample tends to oxidize resulting in an infrared peak at approximately 1740 cm^{-1}, which will cause the values for the graft level to be too low.Maleic anhydride and acid are represented by peaks at about 1791 and 1712 cm^{-1}, respectively.

[00103] *Gel Permeation Chromatography*

[00104] The average molecular weights and molecular weight distributions for ethylene-based polymers are determined with a chromatographic system, consisting of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220. The column and carousel compartments are operated at 140°C for ethylene-based polymers. The columns are three Polymer Laboratories 10-micron, Mixed-B columns. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of "0.1 gram of polymer' in "50 milliliters" of solvent. The solvent used to prepare the samples contains 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for two hours at 160°C. The injection volume is "100 microliters," and the flow rate is 1.0 milliliters/minute. Calibration of the GPC column set is performed with narrow molecular weight distribution polystyrene standards, purchased from Polymer Laboratories (UK). The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)):

$$M_{polyethylene} = A \text{ x } (M_{polystyrene})^{B} ,$$

where M is the molecular weight, A has a value of 0.4315 and B is equal to 1.0. Polyethylene equivalent molecular weight calculations were performed using VISCOTEK TriSEC software Version 3.0. The molecular weights for polypropylene-based polymers can be determined using Mark-Houwink ratios according to ASTM D6474.9714-1, where, for polystyrene a = 0.702 and log K = -3.9, and for polypropylene, a = 0.725 and log K = -3.721. For polypropylene-based samples, the column and carousel compartments are operated at 160°C.

[00105] *Melt Viscosity*

[00106] Melt viscosity is measured in accordance with ASTM D 3236 (350°F), using a Brookfield Digital Viscometer (Model DV-III, version 3), and disposable aluminum sample chambers. The spindle used, in general, is a SC-31 hot-melt spindle, suitable for measuring viscosities in the range from 10 to 100,000 centipoise. The sample is poured into the chamber, which is, in turn, inserted into a Brookfield Thermosel, and locked into place. The sample chamber has a notch on the bottom that fits the bottom of the Brookfield Thermosel, to ensure that the chamber is not allowed to turn when the spindle is inserted and spinning. The sample (approximately 8-10 grams of resin) is heated to the required temperature, until the melted sample is about one inch below the top of the sample chamber. The viscometer apparatus is lowered, and the spindle submerged into the sample chamber. Lowering is continued, until the brackets on the viscometer align on the Thermosel. The viscometer is turned on, and set to operate at a shear rate which leads to a torque reading in the range of 40 to 60 percent of the total torque capacity, based on the rpm output of the viscometer. Readings are taken every minute for about 15 minutes, or until the values stabilize, at which point, a final reading is recorded.

[00107] *Melt Index*

[00108] Melt index (I2, or MI) of an ethylene-based polymer is measured in accordance with ASTM D-1238, condition 190°C/2.16 kg. For high I2 polymers (I2 greater than, or equal to, 200 g/mole, melt index is preferably calculated from Brookfield viscosity as described in U.S. Patents Nos. 6,335,410; 6,054,544; 6,723,810. $I2(190°C/2.16kg) = 3.6126[10^{(\log(\ )-6.6928)/-1.1363}]-9.31851$, where = melt viscosity, in cP, at 350°F.

[00109] *Solution Viscosity*

[00110] The Brookfield viscosity of the solution composites is measured by using a Brookfield Digital Viscometer (Model DV-C) equipped with No.3 spindle. A150 ml sample is poured into a disposable plastic beaker. The viscometer apparatus is lowered, and the spindle submerged into the sample. Lowering is continued, until the top marked line is immersed into the sample. The viscometer is turned on with a rotor speed of 30 rpm, and the viscosity is recorded after the values become stable.

[00111] Tensile shear stress (σ, unit: megapascal (MPa)) is calculated by the following equation: $\sigma = F_m/S$, where S is the area (unit: mm^2) of the glued part.

[00112] Some embodiments of the present disclosure will now be described in detail in the following Examples.

EXAMPLES

1. Materials

[00113] Materials for inventive examples and comparative samples are provided in Table 1 below.

Table 1: Polymers used in the Experimental Adhesive (HMA) Formulations

Polymer	Structure	I2*	Melt Viscosity (177°C)	Tm °C	Tg °C	Density (g/cc)	MAH (wt%)
1[b]	Low viscosity MAH-g-ethylene/octene random copolymer	660	13.0	68.0	-58.0	0.878	1.1

a) GPC results.
b) MAH-g-homogeneously branched ethylene/octene copolymer.
* I2--Melt index is calculated from the following equation (See US patent 6,335,410):
I2(190°C/2.16kg) =
$3.6126[10^{(\log()-6.6928)/-1.1363}]-9.31851$, where = Melt viscosity, in cP, at 350°F.

2. *Polymer 1*

[00114] Polymer 1 is prepared according to the procedure described below.

Low viscosity ethylene/octene copolymer with a melt viscosity range of 6.0 to 17.0 Pa-s. Nominal 1000 MI, 0.87 g/cc.
Maleic Anhydride (MAH - DeGussa DHBP or equivalent)
Hydrobrite 380 – hydrotreated paraffinic oil to dilute peroxide as needed. (1:1 ratio of peroxide: oil).
Luperox 101 – 2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane (290.44 g/mol).
Barrel, Gear Pump, and Die Temperature settings:
Feed barrel – cooling (49 °C)
Barrel # 3: 120 °C, injection of maleic at injection port 3a and peroxide at port 4a
Barrel # 4 – 11: 235 °C
Transfer lines and Gear pump: 150°C
Die: 204°C
Screw Speed 386 rpm
MAH 16.25 lb/hr
MAH % Feed 1.55%
"1:1 Oil:POX" 3.6 lb/hr
"1:1 Oil:POX" % Feed 0.34%
Pure POX Feed 0.17%
Vac. Pressure 20 cm Hg

[00115] Polymer 1 is made on a "92mm" co-rotating twin screw extruders (TSE). The process is summarized in the following steps: (a) the TSE is set to run at the selected barrel temperature profiles, and the screw speeds set to the desired RPMs; (b) polymer pellets are fed into the extruder hopper of the extruder by a gravimetrically, controlled auger feeder, at the desired polymer feed rate; (c) molten MAH is injected into the barrel; (d) peroxide is added via a 1:1 mineral oil solution, at a target feed rate, and injected into the barrel, downstream from the MAH; (e) kneading blocks distributed the reactive ingredients and heated the polymer melt through mechanical energy dissipation, and the reaction occurred following thermal decomposition of peroxide initiator; (f) volatile unreacted components and byproducts are removed at a vacuum port; (g) the melt is cooled in the final barrel section and fed to a gear pump; (h) the gear pump feeds a die, from which the melt travels to an underwater pelletizer. A pellet slurry cooling line of sufficient length is used to achieve residence time greater than 60 seconds, to cool pellets to less than 25°C). The pelletized product isdried and collected.

3. *RED Calculation*

[00116] Experimental Procedures

[00117] *Determination of Initial Hansen Solubility Sphere for the Polymer 1.*

[00118] This determination requires that the solubility of the polymer (Polymer 1) be evaluated in 18 solvents having a range of polarity and hydrogen bonding properties. A list of the solvents used is given below in Table A.

Table A

Chemical Name	**Trade Designation or Alternate Name**
Acetonitrile	Acetonitrile
Ethylene Glycol n-Butyl Ether	Butyl CELLOSOLVE^{TM} Glycol Ether
Dibutyl Ether	Dibutyl ether
Dimethyl Formamide	Dimethyl Formamide
Dimethyl Sulfoxide	Dimethyl Sulfoxide
Methanol	Methyl Alcohol
2-Butanone	Methyl Ethyl Ketone
4-Methyl-2-pentanone	Methyl Isobutyl Ketone
n-Butyl Acetate	n-Butyl Acetate
n-Heptane	n-Heptane
1-Propanol	n-Propyl Alcohol
o-Dichlorobenzene	1,2-Dichlorobenzene
Tetrachloroethylene	Perchloroethylene
1,2-Propanediol	Propylene Glycol
Tetrahydrofuran	Tetrahydrofuran
Toluene	Methylbenzene
Propylene Carbonate	Propylene Carbonate
Water	Water

[00119] Samples are prepared by weighing 0.5g of the polymer beads into a 5-dram vial. The first test solvent (5.0 ml) is added into the vial with a pipette, and the vial is then capped with a polyethylene-lined lid, and labeled with the solvent loaded. This procedure is repeated with the remaining 17 test solvents. The final polymer concentration in the vial is 10% (weight/volume relationship). The vials are placed in an Eberbach shaker on the low setting. After 24 hours, the samples are removed from the shaker, and allowed to sit for 30 minutes, before they are visually rated on a scale of 1 to 6, as per the criteria shown in Table B.

Table B: Solubility Ratings for SOLFIT program

Rating	Rating Description	Explanation of Rating
1	Completely soluble	No visible polymer particles
2	Almost soluble	Only a small amount of polymer particles left
3	Strongly swollen	Polymer beads swelled in size and or broken into smaller swollen particles
4	Swollen	Polymer beads have significantly swollen in size
5	Slightly swollen	Polymer beads show some swelling
6	Insoluble	Polymer beads unchanged

[00120] The numerical ratings are then entered into the SOLFIT program to obtain the HSP and R values for the polymer, and a report is generated. The report lists the final parameters and R values calculated for the polymer. The report also lists the solvents used in the evaluation, their HSP values (as stored in the database), the ratings of the visual observations, and their RED values with the polymer.

[00121] Table C below provides RED values and HSP parameters for compositions containing Polymer 1 and the 18 solvents of Table A.

Table C

SOLFIT RESULTS

Run Name : Determination of HSP and R values

Resin : Polymer 1

Fitting Function : 24.75 (Spherical)

	Initial Parameters	Final Parameters	
Hansen Dispersion Parameter :	17.55	17.27	√ (J/cc)
Hansen Polar Parameter :	9.00	6.82	√ (J/cc)
Hansen Hydrogen Bonding Parameter :	11.65	0.71	√ (J/cc)
Solubility Sphere Radius :	8.52	6.12	√ (J/cc)

Solvent Details :

Solvent Name	Hansen Dispersion Parameter (√(J/cc))	Hansen Polar Parameter (√(J/cc))	Hansen Hydrogen Bonding Parameter (√(J/cc))	Solubility Category	R.E.D
ACETONITRILE	15.30	18.00	6.10	5	2.13
BUTYL CELLOSOLVE GLYCOL ETHER SOLVENT	16.00	7.60	12.30	6	1.94
DIBUTYL ETHER	15.30	3.40	3.30	3	0.95
DIMETHYL FORMAMIDE	17.40	13.70	11.30	6	2.06
DIMETHYL SULFOXIDE	18.40	16.40	10.20	6	2.23
METHYL ALCOHOL	15.10	12.30	22.30	6	3.71
METHYL ETHYL KETONE	16.00	9.00	5.10	5	0.90
METHYL ISOBUTYL KETONE	15.30	6.10	4.10	5	0.86
N-BUTYL ACETATE	15.80	3.70	6.30	6	1.15
N-HEPTANE	15.30	0.00	0.00	3	1.29
N-PROPYL ALCOHOL	16.00	6.80	17.40	6	2.76
O-DICHLOROBENZENE	19.20	6.30	3.30	2	0.76
PERCHLOROETHYLE	18.30	5.70	0.00	1	0.40

NE					
PROPYLENE CARBONATE	20.00	18.00	4.10	6	2.11
PROPYLENE GLYCOL	16.80	9.40	23.30	6	3.72
TETRAHYDROFURAN	16.80	5.70	8.00	3	1.22
TOLUENE	18.00	1.40	2.00	3	0.94
WATER (for dilute organics in water)	19.50	17.80	17.60	6	3.37

[00122] *Screening Database for Potential Solvents*

[00123] Once the Polymer1is characterized, its HSP and R values are entered into a polymer database and an RED search is conducted against solvents in the database. The RED is fixed at a maximum value of 1.05, the solvent boiling point is allowed to range from 100 °C to 170 °C, and aromatic and halogenated solvents are excluded from the search. The following report is obtained.

[00124] Table D below provides RED values and HSP parameters for compositions with Polymer 1 and several different solvents.

Table D

Relative Energy Distance(R.E.D) Details
(Based on work area substance List)

Resin Details :
Resin Name : Polymer 1
Hansen Dispersion Parameter : 17.27 √ (J/cc)
Hansen Polar Parameter : 6.82 √ (J/cc)
Hansen Hydrogen Bonding Parameter : 0.71 √ (J/cc)
Solubility Sphere Radius : 6.1 √ (J/cc)

Search Criteria returning 24 Solvents :
24 Solvents with a RED Value < 1.05

Solvent Name	Relative Energy Distance	Hansen Dispersion Parameter (√(J/cc))	Hansen Polar Parameter (√(J/cc))	Hansen Hydrogen Bonding Parameter (√(J/cc))	Boiling Point °C
1,1-DIMETHYLCYCLOHEXANE	0.92	16.30	1.80	2.30	118.0
1,2-DIMETHYLCYCLOHEXANE	1.00	16.50	1.30	2.80	124.0
1,3-DIMETHYLCYCLOHEXANE	0.85	16.80	3.20	4.30	121.0

1,4-DIMETHYLCYCLOHEXANE	0.85	16.80	2.70	3.70	120.0
2-METHOXY METHYL LACTATE	1.00	15.80	6.20	6.00	130.2
4-METHYLCYCLOHEXENE	0.96	16.90	2.10	4.10	102.0
ACETAL (1,1-DIETHOXYETHANE)	1.04	15.20	5.40	5.30	103.6
CYCLOPROPYL METHYL KETONE	0.95	17.00	11.10	4.60	112.7
DIBUTYL ETHER	0.95	15.30	3.40	3.30	139.9
DIETHYL KETONE	0.82	15.80	7.60	4.70	102.0
DIISOBUTYL KETONE	0.86	16.00	3.70	4.10	142.1
DIPENTENE (LIMONENE)	0.94	16.70	2.30	4.10	170.0
DIPROPYL KETONE	0.86	15.80	5.70	4.90	145.0
ETHYL BUTYL KETONE	0.72	16.20	5.00	4.10	145.0
ETHYLCYCLOHEXANE	1.03	16.50	1.00	2.50	130.0
ETHYLENE GLYCOL DIETHYL ETHER	0.99	15.40	5.40	5.20	121.5
ISOPROPYLCYCLOPENTANE	0.95	16.40	1.50	2.10	126.7
MESITYL OXIDE (4-METHYL-3-PENTEN-2-ONE)	0.94	16.40	6.10	6.10	129.7
METHYL ISOBUTYL KETONE	0.86	15.30	6.10	4.10	116.0
METHYL N-BUTYL KETONE	0.86	15.30	6.10	4.10	127.6
METHYL N-PROPYL KETONE	0.79	16.00	7.60	4.70	102.3
METHYLCYCLOHEXANE	1.03	16.70	1.00	2.70	100.9
N-PROPYL PROPIONATE	0.98	15.70	5.80	5.70	122.5
PROPYLCYCLOPENTANE	0.95	16.40	1.50	2.10	131.0

4. *Evaluation of Potential Solvents*

[00125] Two solvents from the list, namely ethylcyclohexane and d-limonene, are evaluated for compatibility with Polymer 1 at the 10% w/v concentration. The polymer/solvent mixtures are prepared in a 5-dram vial as described before, and gently heated with a heat gun, to get the polymer beads to melt. During this process, the vial is placed on, and off, a vortex mixer for about 15 seconds, at a time to get the contents to mix, until a clear solution was observed. The vials are left standing on a lab bench overnight. A clear homogeneous solution is still present in each vial after 24 hours, demonstrating good compatibility.

[00126] Since ethyl cyclohexane and polymer have RED of 1.03 and form a solution, it follows that other solvents in the table which have the same or lower RED should also dissolve the polymer (ex. d-limonene dissolves the polymer and the RED is 0.94).

A. Solvents examined in this study are shown in Table E

Table E: Solvents

Solvent	Boiling Point (°C)	RED Value
Ethyl cyclohexane	130.0	1.03
Dimethyl formamide	150-154	2.06

[00127] Inventive Example1 (IE1):

[00128] Ethylcyclohexane (90g), and low viscosity MAH-g-ethylene/octene copolymer(10g of Polymer 1) having a meltviscosity of 13 Pa•S, a melt index of 660 g/10min, and a density of 0.87 g/ml,are mixed together in a beaker, and heated to 90 °C, with magnetic stirring for about 10 min, to totally dissolve the pellets, and form a homogeneous solution. The obtained solution remains in liquid form after being cooled to room temperature. The solution remains stable for 30 days (or longer) according to the lab test data and visible inspection.

[00129] Comparative Sample 1 (CS1)

[00130] Dimethyl formamide (90g), and low viscosity MAH-g-ethylene/octene copolymer (10g of Polymer 1) having a melt viscosity of 13 Pa•S, a melt index of 660 g/10min, and a density of 0.87 g/ml, are mixed together in a beaker, and heated to 90 °C, with magnetic stirring for 30 min. The pellets melted and stick together. The pellets cannot be dissolved to obtain a homogeneous solution, which is undesired.

[00131] ComparativeSample 2 (CS2)

[00132] Ethyl cyclohexane (90g), and ethylene/octene copolymer grafted maleic anhydride (10g) having a melt index of 0.3 g/10 min, and a density of 0.87 g/ml, are mixed together in a beaker, and heated to 90 °C, with magnetic stirring for 30 min. The ethylene/octene copolymer grafted maleic anhydride of CS2 is not a low viscosity functionalized ethylene/α-olefin copolymer as defined in the present disclosure. Rather, the ethylene/octene copolymer grafted maleic anhydride of CS2 has a melt viscosity of 1620 Pa-s. The pellets melted and stick to the bottom of the beaker. The pellets cannot be dissolved to obtain a homogeneous solution, which is undesired.

[00133] The above mentioned IE1 is used to improve the bonding strength of two rectangular substrates, each substrate formed from a polypropylene/OBC blend. Each substrate has a width of 1 cm. Each substrate is first cleaned manually with acetone. Then the substrates are left in a fume hood for several minutes to remove the acetone.The primer composition prepared in IE-1 is heated to 70 °C, before applying to the substrate surfaces as a thin film. The primer composition is manually brushed onto the substrate surfaces. After the primer dries, a two-part adhesive (Loctite 3038) is applied onto the primed surface (denoted as "Primer" in Figure 1). Next, the two rectangular substrates arepressed and glued together with an overlapped area about 1~2 cm^2.

[00134] In Figure 1, Control – is Loctite 3038 (glue only)

[00135] Peel Strength Testing: The glued specimen is conditioned at room temperature, for at least 24 hours, before testing the peel strength. The peel strength is tested on an INSTRON 5566 machine. The maximum tensile force (F_m, unit: N) is recorded, and the tensile shear stress (σ, unit: MPa) is calculated by the following equation: $\sigma = F_m/S$, where S was the area (unit: mm^2) of the glued part.As seen in Figure 1, the tensile shear stress for the Primer treated surfaces is greater than the tensile shear stress for surfaces treated with glue only. Figure 1 demonstrates that the bonding strength,is significantly improved after the application of IE-1 primer composition to the polypropylene/OBC substrates.

[00136] It is specifically intended that the present disclosure not be limited to the embodiments and illustrations contained herein, but include modified forms of those embodiments including portions of the embodiments and combinations of elements of different embodiments as come within the scope of the following claims.

CLAIMS

1. A composition comprising:

a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymer, eachcopolymer having a melt viscosity less than or equal to 20.0 Pa•s (177°C); and

a non-aromatic and halogen-free solvent with a boiling point from 100 °C to 170 °C, and wherein the composition has a Relative Energy Difference (RED)less than or equal to 1.05 $(J/cc)^{1/2}$, based on the Hansen solubility parameter.

2. The composition of claim 1 wherein the low viscosity ethylene/α-olefin copolymer or the low viscosity functionalized ethylene/α-olefin copolymer, each has the following properties:

a)an Mw/Mn from 1.5 to 5.0, and
b) a density from 0.855 to 0.900 g/cc.

3. The composition of any of claims 1-2, wherein the low viscosity ethylene/α-olefin copolymer or the low viscosity functionalized ethylene/α-olefin copolymer, each has a melt viscosity from 1.0 Pa-s to less than 15.0 Pa-s.

4. The composition of any of claims 1-3, comprising a low viscosity ethylene/α-olefin copolymerhaving a melt viscosity less than or equal to 10.0 Pa•s (177°C);

a) an Mw/Mn from 1.5 to 2.5; and
b) a density from 0.86 to 0.88.

5. The composition of any of claims 1-3 wherein the composition comprises a low viscosity functionalized ethylene/α-olefin copolymer having a melt viscosity less than 15.0 Pa-s.

6. The composition of any of claims 1-5 wherein the solvent is selected from the group containing ethylcyclohexane, methylcyclohexane, propylcyclopentane, isopropylcyclopentane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, 1,4-dimethylcyclohexane, 1,1-dimethylcyclohexane, 1-methylcyclohexene, 4-methylcyclohexene, dipentene, and combinations thereof.

7. The composition of claim 6 wherein the solvent is ethylcyclohexane.

8. The composition of claim 1 comprising a low viscosity functionalized ethylene/α-olefin copolymer that is a low viscosity maleic anhydride grafted ethylene/α-olefin copolymer dissolved in ethylcyclohexane.

9. The composition of claim 8, wherein the low viscosity maleic anhydride grafted ethylene/α-olefin copolymer is completely dissolved in the ethylcyclohexane, at ambient temperature.

10. The composition of any of the previous claims, further comprising a pigment.

11. An article comprising at least one component formed from the composition of any of the previous claims.

12. An article comprising:

a substrate formed from at least one olefin-based polymer; and

a layer of a low viscosity ethylene/α-olefin copolymer or a low viscosity functionalized ethylene/α-olefin copolymer, each copolymer having a melt viscosity less than or equal to 20.0 Pa-s (177°C) adhered to a surface of the substrate.

13. The article of claim 12 wherein the olefin-based polymer is an ethylene/α-olefin copolymer.

14. The article of claim 12 wherein the olefin-based polymer is an olefin block copolymer.

15. The article of any of claims 12-14, comprising a layer of a coating material on the layer of low viscosity ethylene/α-olefin copolymer or low viscosity functionalized ethylene/α-olefin copolymer.

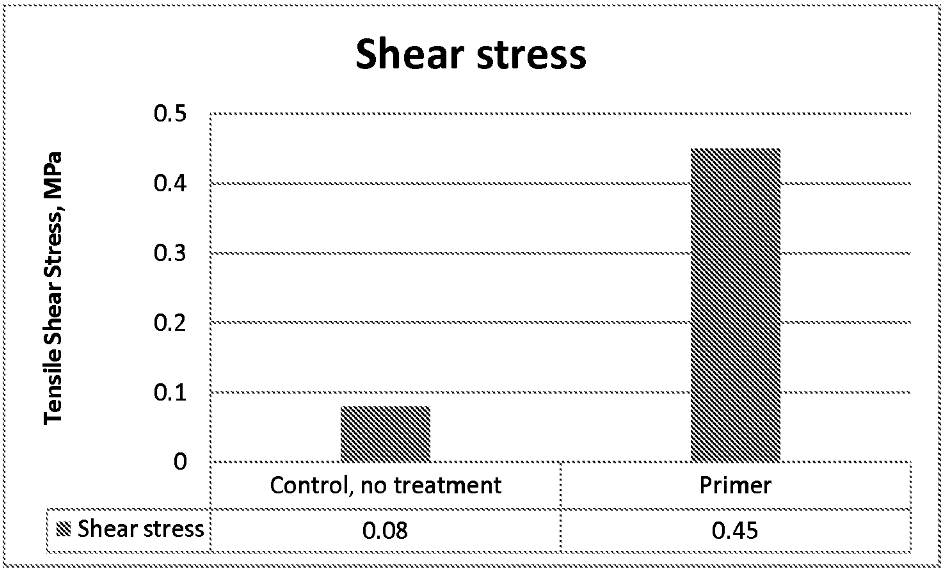
Shear stress
Tensile Shear Stress, MPa
0.5
0.4
0.3
0.2
0.1
0
Control, no treatment
Primer
▨ Shear stress
0.08
0.45

Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2012/081401

A. CLASSIFICATION OF SUBJECT MATTER

See the extra sheet

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)

IPC: C08L23/-, C08F51/-, C08K, C09J

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

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

CNKI, CNABS, DWPI, SIPOABS, Googlescholar: DOW, primer, ethylene, octane, olefin, low viscosity, melt viscosity, relative energy difference,

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN101466809A(DOW GLOBAL TECHNOLOGIES INC) 24. Jun 2009 (24.06.2009) See claims 1-3, table 3	1-15
A	CN101336254A(DOW GLOBAL TECHNOLOGIES INC) 31. Dec 2008 (31.08.2008) See the whole document	1-15
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A	CN1965004A(EXXONMOBIL CHEM PATENTS INC)16. May 2007 (16.05.2007) See the whole document	1-15

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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

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

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

"& "document member of the same patent family

Date of the actual completion of the international search
08. Jun 2013 (08.06.2013)

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2012/081401

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International application No.
PCT/CN2012/081401

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2012/081401

Continuation of second sheet:

A. CLASSIFICATION OF SUBJECT MATTER

C08L 23/08 (2006.01) i

C08L 23/20 (2006.01) i

C08L 51/06 (2006.01) i

C08K 5/04 (2006.01) i

C09J 151/06(2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC