

ADHESIVE COMPOSITIONS OF PROPYLENE-BASED
AND ETHYLENE-BASED POLYMERS

PRIORITY CLAIM

5 [0001] The present application claims priority to and the benefit of U.S.S.N. 61/702,788, filed September 19, 2012, the disclosure of which is hereby incorporated by reference herein in its entirety.

FIELD OF THE INVENTION

10 [0002] The present invention pertains to adhesive compositions based on blends of propylene-based polymers and ethylene-based polymers and their applications. In particular, the invention pertains to adhesive compositions comprising, *inter alia*, propylene-based polymers having a heat of fusion of at least 60 J/g, and ethylene-based polymers having a heat of fusion of 1 to 100 J/g, wherein heat of fusion is measured by differential scanning calorimetry.

15 BACKGROUND OF THE INVENTION

[0003] Hot melt adhesives are thermoplastic materials that can be heated to a melt, and then applied to various substrates. A bond is formed upon cooling and resolidification of the melt. These hot melt adhesives have the drawback of often becoming brittle below the glass transition temperature. Historically, ethylene-based semi-crystalline polymers like
20 polyethylene and ethylene vinyl acetate copolymer (EVA) have been used in various adhesive applications; however, such polymers have many problems in their end use applications. For example, semi-crystalline linear low density polyethylene (LLDPE) can be used in hot melt adhesive applications where the crystalline network formed on cooling makes a good adhesive free of tack, but the high level of crystallinity causes the material to
25 be brittle. For this reason other monomers, such as vinyl acetate (VA) or alpha-olefins, are often co-polymerized with ethylene to break up some of the crystallinity and soften the adhesive. Thus the use of ethylene-based hot melt adhesives is limited when low temperature conditions of use are desired.

[0004] PCT Publication Nos. WO 1997/33921 and WO 98/03603 teach the use of
30 ethylene-based copolymers in hot melt adhesives and that these copolymers are useful in some applications, but suffer in that they have higher melt viscosity, hence poorer processing, due to higher chain entanglement density, poorer adhesion to low energy surfaces due to mismatched surface energy, and poorer cohesion due to lower glass transition temperature (T_g) than propylene-based copolymers. T_g values of polyethylene and polypropylene are
35 about -100°C and -10°C, respectively. Generally, the observed strength or cohesion is

governed by polymer chain segmental viscosity. Therefore, one wants to compare the cohesion of two polymers by normalizing the test temperature and polymer T_g in order to minimize the contribution from differences in viscoelasticity.

[0005] U.S. Patent No. 5,397,843 discloses blended polymer compositions comprising an admixture of (a) a copolymer of ethylene and an alpha-olefin and (b) an amorphous polypropylene, and/or amorphous polyolefin, or mixtures thereof, which have a crystallinity of less than 20 wt%.

[0006] U.S. Patent No. 5,548,014 discloses hot melt adhesives comprising a tackifier and a high weight average molecular weight (M_w), narrow molecular weight distribution (MWD), narrow CD (composition distribution) ethylene/alpha-olefin copolymer(s) and a low M_w , narrow MWD, narrow MWD ethylene/alpha-olefin copolymer prepared with either supported or unsupported cyclopentadienyl derivatives of Group IV and catalysts for applications in hot melt adhesives, particularly in automotive product assembly, packaging and food packaging.

[0007] U.S. Patent Nos. 5,530,054 and 6,207,748 disclose hot melt adhesives comprising ethylene/alpha-olefin copolymers prepared with either supported or unsupported metallocene-alumoxane catalysts for hot melt adhesives applications in automotive product assembly, packaging and food packaging, wherein these ethylene copolymers have M_w ranging from about 20,000 to about 100,000, and comonomer weight percent ranging from about 6 to about 30.

[0008] PCT Publication No. WO 97/33921 discloses adhesives and processes for preparing the same, comprising at least one first homogeneous ethylene/alpha-olefin interpolymer, and optionally at least one tackifier, and optionally at least one plasticizer.

[0009] PCT Publication No. WO 98/03603 discloses hot melt adhesives comprising at least one first homogeneous linear or substantially linear ethylene polymer having a particular density and melt viscosity at 350°F (177°C), and an optional wax and tackifier. In particular, disclosed is a hot melt adhesive characterized by: a) at least one homogeneous linear or substantially linear interpolymer of ethylene with at least one C_3 to C_{20} alpha-olefin interpolymer having a density from 0.850 g/cm³ to 0.895 g/cm³; b) optionally, at least one tackifying resin; and c) optionally, at least one wax wherein the hot melt adhesive has a viscosity of less than about 5000 cPs (50 grams/(cm.sec) or 5000 mPa·sec) at 150°C.

[0010] The present invention is directed in general to providing improved adhesive compositions of propylene-based and ethylene-based polymer, and processes or methods for

making such compositions. These inventive adhesive compositions cover important attributes from both types of polymer.

SUMMARY OF THE INVENTION

[0011] The present invention is directed to adhesive compositions and hot melt adhesives and their commercial applications. In one or more embodiments, the adhesive compositions comprise a propylene-based polymer component comprising more than 50 wt% of propylene and at least one first comonomer, said propylene-based polymer having a Brookfield viscosity of at least 250 mPa·sec measured by ASTM D-3236 at 190°C and a heat of fusion of at least 60 J/g measured by differential scanning calorimetry and a characteristic time (t_c), hereinafter defined, in the range from 1 to 1000 nanoseconds. The compositions further comprise an ethylene-based polymer component comprising more than 50 wt% ethylene and at least one second comonomer, said ethylene-based polymer having a Brookfield viscosity of at least 250 mPa·sec measured by ASTM D-3236 at 190°C and a heat of fusion in the range from 1 to 100 J/g measured by differential scanning calorimetry and a characteristic time (t_c), in the range from 1 to 1500 nanoseconds. Said at least one first comonomer and said at least one second comonomer are the same or different. The resulting adhesive compositions and hot melt adhesives exhibit good Brookfield viscosity, good set time value, and good fiber tear performance over a range of temperatures.

DETAILED DESCRIPTION OF THE INVENTION

[0012] One or more specific embodiments of the present invention relates to an adhesive composition comprising (a) at least one propylene-based copolymer comprising more than 50 wt% propylene and at least one first comonomer, said propylene-based polymer having a Brookfield viscosity of at least 250 mPa·sec measured by ASTM D-3236 at 190°C and a heat of fusion of at least 60 J/g measured by differential scanning calorimetry and (b) at least one ethylene-based polymer comprising more than 50 wt% ethylene and at least one second comonomer, said ethylene-based polymer having a Brookfield viscosity of at least 250 mPa·sec measured by ASTM D-3236 at 190°C and a heat of fusion of 1 to 100 J/g measured by differential scanning calorimetry, wherein said at least one first comonomer and said at least one second comonomer are the same or different.

[0013] Further embodiments of the adhesive compositions described herein and their individual components are described in greater detail below.

Definitions

[0014] As used herein, the term "characteristic time" abbreviated as " t_c " in units of nanoseconds is defined by the following Equation 1:

$$t_c = \frac{BV}{\text{Density} \times \text{Heat of Fusion}} \quad (\text{Equation 1})$$

wherein said BV is the Brookfield viscosity of said propylene-based polymer or said ethylene-based polymer measured by ASTM D-3236 at 190°C in units of mPa·sec, said
 5 Density is the density of said propylene-based polymer or said ethylene-based polymer in units of g/cm³ at 23°C, and said Heat of Fusion is the heat of fusion of said propylene-based polymer or said ethylene-based polymer in units of J/g.

[0015] As used herein, the term “copolymer” is meant to include polymers having two or more monomers, optionally with other monomers, and may refer to interpolymers, terpolymers, etc. The term “polymer” as used herein includes homopolymers and
 10 copolymers.

Propylene-Based Polymer Component

[0016] In one or more embodiments of the present invention, the adhesive compositions described herein comprise a propylene-based polymer component, which in turn may
 15 comprise one or more propylene-based polymer(s). In one embodiment, the propylene-based polymer component comprises more than 50 wt% propylene-derived units and at least one first comonomer-derived unit. The first comonomer is an alpha-olefin, and is preferably ethylene. The first comonomer is selected from the group consisting of ethylene and a C₄ to C₂₀ alpha-olefin. In some embodiments, the propylene-based polymer component is a
 20 random copolymer and in other embodiments the propylene-based polymer component is an elastomeric random copolymer. In some embodiments, the propylene-based polymers comprise units derived from propylene and from about 3 to about 50 mol% units derived from ethylene and/or a C₄ to C₁₀ alpha-olefin or from about 2 to about 40 mol% units derived from ethylene and/or a C₄ to C₁₀ alpha-olefin. In another embodiment, the first comonomer
 25 may comprise at least one C₄ to C₈ alpha-olefin. In one or more embodiments, the first comonomer units may derive from ethylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, and/or 1-decene, preferably 1-hexene and 1-octene. The embodiments described below are discussed with reference to ethylene as the first comonomer, but the embodiments are equally applicable to other propylene copolymers with other alpha-olefin comonomers, or
 30 to propylene terpolymers with ethylene and another alpha-olefin comonomer. In this regard, the copolymer may simply be referred to as propylene-based polymers with reference to ethylene as the alpha-olefin.

[0017] In one embodiment, the propylene-based polymers may include alpha-olefin derived first comonomer. In another embodiment, the propylene-based polymers comprise at least about 1 wt%, at least about 2 wt%, at least about 3 wt%, at least about 5 wt%, at least about 6 wt%, at least about 8 wt%, or at least about 10 wt% of at least one first comonomer selected from the group consisting of ethylene, C₄ to C₂₀ alpha-olefins, and combination thereof. Preferably, the propylene-based polymer comprises 90 wt% to 99 wt% of propylene-derived units and 10 wt% to 1 wt% of ethylene-derived units, based on the weight of the propylene-based polymer. In those or other embodiments, the propylene-based polymers may include up to about 50 wt%, or up to about 40 wt%, or up to about 30 wt%, or up to about 25 wt%, or up to about 20 wt%, or up to about 18 wt%, or up to about 16 wt%, or up to about 12 wt%, or up to about 10 wt% of at least one first comonomer selected from the group consisting of ethylene, C₄ to C₂₀ alpha-olefin, and combination thereof, where the percentage by weight is based upon the total weight of the propylene-derived and alpha-olefin derived units. Stated another way, the propylene-based polymers may include at least about 50 wt%, or at least about 60 wt%, or at least about 70 wt%, or at least about 75 wt%, or at least about 80 wt%, or at least about 82 wt%, or at least about 84 wt%, or at least about 86 wt%, or at least about 88 wt%, or at least about 90 wt% propylene-derived units; and in these or other embodiments, the copolymers may include up to about 99 wt%, or up to about 98 wt%, or up to about 97 wt%, or up to about 95 wt%, or up to about 94 wt%, or up to about 92 wt%, or up to about 90 wt% propylene-derived units, where the percentage by weight is based upon the total weight of the propylene-derived and alpha-olefin derived units.

[0018] In another embodiment, the propylene-based polymers comprise at least about 1 mol%, at least about 2 mol%, at least about 3 mol%, at least about 4 mol%, at least about 5 mol%, at least about 6 mol%, at least about 7 mol%, at least about 8 mol%, at least about 9 mol%, at least about 10 mol%, at least about 11 mol%, at least about 12 mol%, at least about 13 mol%, at least about 14 mol%, or at least about 15 mol% of at least one first comonomer selected from the group consisting of ethylene, C₄ to C₂₀ alpha-olefins, and combination thereof. In those or other embodiments, the propylene-based polymers may include up to about 50 mol%, or up to about 40 mol%, or up to about 33 mol%, or up to about 27 mol%, or up to about 25 mol%, or up to about 22 mol%, or up to about 17 mol% of at least one first comonomer selected from the group consisting of ethylene, C₄ to C₂₀ alpha-olefin, and combination thereof, where the percentage by mole is based upon the total number of moles of the propylene-derived and alpha-olefin derived units. Stated another way, the propylene-

based polymers may include at least about 50 mol%, or at least about 60 mol%, or at least about 67 mol%, or at least about 73 mol%, or at least about 75 mol%, or at least about 78 mol%, or at least about 83 mol% propylene-derived units; and in these or other embodiments, the copolymers may include up to about 97 mol%, or up to about 95 mol%, or up to about 95 mol%, or up to about 93 mol%, or up to about 88 mol%, or up to about 86 mol% propylene-derived units, where the mole percentage is based upon the total number of moles of the propylene-derived and alpha-olefin derived units.

[0019] The propylene-based polymers of one or more embodiments are characterized by having a single melting temperature as determined by differential scanning calorimetry (DSC). The melting point is defined as the temperature of the greatest heat absorption within the range of melting of the sample. The propylene-based polymer may show secondary melting peaks adjacent to the principal peak, but for purposes herein, these secondary melting peaks are considered together as a single melting point, with the highest of these peaks being considered the melting point (T_m) of the propylene-based polymer.

[0020] In one or more embodiments, the T_m of the propylene-based polymers (as determined by DSC) is less than about 130°C, or less than about 120°C, or less than about 110°C, or less than about 105°C, or less than about 100°C, or less than about 95°C, or less than about 90°C, or less than about 80°C, or less than about 70°C.

[0021] In one or more embodiments, the propylene-based polymers may be characterized by a heat of fusion (H_f), as determined by DSC. In one or more embodiments, the propylene-based copolymer may be characterized by a heat of fusion from greater than or equal to 50 J/g, or 55 J/g, or 60 J/g up to about 150 J/g, or up to about 140 J/g, or up to about 130 J/g, or up to about 120 J/g, or up to about 100 J/g, or up to about 90 J/g, or up to about 85 J/g, or up to about 80 J/g, or up to about 75 J/g, or to about 70 J/g, or up to about 65 J/g, or greater than about 60 J/g. Preferably, the heat of fusion measured by differential scanning calorimetry of the propylene-based polymer is from about 60 to about 150 J/g, or about 60 to about 120 J/g, or about 60 to about 100 J/g, or about 60 to about 80 J/g. The heat of fusion may be reduced by using additional comonomer, operating at higher polymerization temperatures, and/or using a different catalyst that provides reduced levels of steric constraints and favors more propagation errors for propylene insertion.

[0022] The propylene-based polymer can have a triad tacticity of three propylene units, as measured by ^{13}C NMR, of 75% or greater, 80% or greater, 82% or greater, 85% or greater, or 90% or greater. In one or more embodiments, ranges include from about 50% to about

99%; in other embodiments, from about 60% to about 99%; in other embodiments, from about 75% to about 99%; in other embodiments, from about 80% to about 99%; and in other embodiments, from about 60% to about 97%. Triad tacticity is determined by the methods described in U.S. Patent Application Publication No. 2004/0236042. If the triad tacticity of the copolymer is too high, the level of stereo-irregular disruption of the chain is too low and the material may not be sufficiently flexible for its purpose in a coating or tie layer. If the triad tacticity is too low, the bonding strength may be too low.

[0023] In one or more embodiments, the propylene-based polymer may have a percent crystallinity of from about 25% to about 60%, from about 25% to about 50%, or from about 30% to about 40%, determined according to DSC procedures. Percent crystallinity may be determined by dividing the heat of fusion of a sample by the heat of fusion of a 100% crystalline polymer, which is 207 joules/gram for isotactic polypropylene according to Bu, H.-S.; Cheng, S. Z. D.; Wunderlich, B., *Makromol. Chem. Rapid Commun.*, 1988, 9, 75.

[0024] In one or more embodiments, the propylene-based polymer may have a density of from about 0.85 g/cm³ to about 0.92 g/cm³, or from about 0.87 g/cm³ to about 0.90 g/cm³, or from about 0.88 g/cm³ to about 0.89 g/cm³ at room temperature as measured per the ASTM D-792 test method.

[0025] In one or more embodiments, the propylene-based polymer may have a melt flow rate (MFR), as measured according to the ASTM D-1238, 2.16 kg weight @ 230°C, greater than or equal to about 0.3 dg/min, or at least about 0.5 dg/min, or at least about 0.8 dg/min, or at least about 1.0 dg/min. In these or other embodiments, the melt flow rate may be equal to or less than about 7000 dg/min, or less than about 6000 dg/min, or less than about 5000 dg/min, or less than about 4000 dg/min, or less than about 3000 dg/min, or less than about 2000 dg/min, or less than about 1000 dg/min, or less than about 900 dg/min, or less than about 700 dg/min, or less than about 500 dg/min, 350 dg/min, or less than about 250 dg/min, or less than about 100 dg/min.

[0026] In one or more embodiments, the propylene-based polymer may have a melt flow rate (MFR), as measured according to the ASTM D-1238, 2.16 kg weight @ 230°C, greater than or equal to about 250 dg/min, greater than or equal to about 500 dg/min, or greater than or equal to about 1,000 dg/min, or greater than or equal to about 1,500 dg/min, or greater than or equal to about 2,000 dg/min, or greater than or equal to about 2,500 dg/min, or greater than or equal to about 3,000 dg/min, or greater than or equal to about 4,000 dg/min, or greater than or equal to about 5,000 dg/min, or greater than or equal to about 6,000 dg/min, or greater than or equal to about 7,000 dg/min.

[0027] In one or more embodiments, the propylene-based polymer can have a weight average molecular weight (M_w) of about 100,000 g/mole or less, for example, from about 5,000 to about 100,000 g/mole, or from about 5,000 to about 75,000 g/mole, or from about 5,000 to about 50,000 g/mole, or from about 10,000 to about 50,000 g/mole, or from about 20,000 to about 50,000 g/mole, or from about 30,000 to about 50,000 g/mole, or from about 35,000 to about 50,000 g/mole.

[0028] In one or more embodiments, the propylene-based polymer can have a number average molecular weight (M_n) of from about 2,500 to about 50,000 g/mole, or from about 2,500 to about 37,500 g/mole, or from about 2,500 to about 25,000 g/mole, or from about 15,000 to about 25,000 g/mole.

[0029] In one or more embodiments, the propylene-based polymer can have a Z-average molecular weight (M_z) of from about 10,000 to about 7,000,000 g/mole, or from about 50,000 to about 1,000,000 g/mole, or from about 80,000 to about 700,000 g/mole, or from about 100,000 to about 500,000 g/mole.

[0030] In one or more embodiments, the molecular weight distribution (MWD), the ratio of the weight-average molecular weight (M_w) to a number-average molecular weight (M_n), of the propylene-based polymer may be from about 1 to about 40, or from about 1 to about 15, or from about 1.8 to about 5, or from about 1.8 to about 3. Preferably, the ratio of a weight-average molecular weight (M_w) to a number-average molecular weight (M_n) in the range from 2 to 10, or 2 to 8, or 2 to 6 or 2 to 4.

[0031] Weight-average molecular weight, M_w , molecular weight distribution (MWD), M_w/M_n where M_n is the number-average molecular weight, and the branching index, $g'(vis)$, are characterized using a High Temperature Size Exclusion Chromatograph (SEC), equipped with a differential refractive index detector (DRI), an online light scattering detector (LS), and a viscometer. Experimental details not shown below, including how the detectors are calibrated, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, 6812-6820, (2001).

[0032] Solvent for the SEC experiment is prepared by dissolving 6 g of butylated hydroxy toluene as an antioxidant in 4 L of Aldrich reagent grade 1,2,4 trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.7 μ m glass pre-filter and subsequently through a 0.1 μ m Teflon filter. The TCB is then degassed with an online degasser before entering the SEC. Polymer solutions are prepared by placing the dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160°C with

continuous agitation for about 2 hr. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/mL at room temperature and 1.324 g/mL at 135°C. The injection concentration ranged from 1.0 to 2.0 mg/mL, with lower concentrations being used for higher molecular weight samples. Prior to running each sample the DRI detector and the injector are purged. Flow rate in the apparatus is then increased to 0.5 mL/min, and the DRI was allowed to stabilize for 8-9 hr before injecting the first sample. The LS laser is turned on 1 to 1.5 hr before running samples.

[0033] The concentration, c , at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, I_{DRI} , using the following equation:

$$c = K_{DRI} I_{DRI} / (dn/dc)$$

where K_{DRI} is a constant determined by calibrating the DRI, and dn/dc is the same as described below for the LS analysis. Units on parameters throughout this description of the SEC method are such that concentration is expressed in g/cm³, molecular weight is expressed in kg/mol, and intrinsic viscosity is expressed in dL/g.

[0034] The light scattering detector used is a Wyatt Technology High Temperature mini-DAWN. The polymer molecular weight, M , at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, LIGHT SCATTERING FROM POLYMER SOLUTIONS, Academic Press, 1971):

$$[K_0 c / \Delta R(\theta, c)] = [1/MP(\theta)] + 2A_2 c$$

where $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration determined from the DRI analysis, A_2 is the second virial coefficient, $P(\theta)$ is the form factor for a monodisperse random coil (described in the above reference), and K_0 is the optical constant for the system:

$$K_0 = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

in which N_A is the Avogadro's number, and dn/dc is the refractive index increment for the system. The refractive index, $n = 1.500$ for TCB at 135°C and $\lambda = 690$ nm. In addition, $A_2 = 0.0015$ and $dn/dc = 0.104$ for ethylene polymers, whereas $A_2 = 0.0006$ and $dn/dc = 0.104$ for propylene polymers.

[0035] The molecular weight averages are usually defined by considering the discontinuous nature of the distribution in which the macromolecules exist in discrete

fractions i containing N_i molecules of molecular weight M_i . The weight-average molecular weight, M_w , is defined as the sum of the products of the molecular weight M_i of each fraction multiplied by its weight fraction w_i :

$$M_w = \sum w_i M_i = (\sum N_i M_i^2 / \sum N_i M_i)$$

- 5 since the weight fraction w_i is defined as the weight of molecules of molecular weight M_i divided by the total weight of all the molecules present:

$$w_i = N_i M_i / \sum N_i M_i.$$

[0036] The number-average molecular weight, M_n , is defined as the sum of the products of the molecular weight M_i of each fraction multiplied by its mole fraction x_i :

10
$$M_n = \sum x_i M_i = \sum N_i M_i / \sum N_i$$

since the mole fraction x_i is defined as N_i divided by the total number of molecules

$$x_i = N_i / \sum N_i.$$

- [0037] In the SEC, a high temperature Viscotek Corporation viscometer is used, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure
15 transducers. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

20
$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

where c was determined from the DRI output.

[0038] The branching index (g' , also referred to as $g'(\text{vis})$) is calculated using the output of the SEC-DRI-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{\text{avg}}$, of the sample is calculated by:

25
$$[\eta]_{\text{avg}} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

where the summations are over the chromatographic slices, i , between the integration limits.

[0039] The branching index g' is defined as:

$$g' = \frac{[\eta]_{\text{avg}}}{k M_v^\alpha}$$

where $k = 0.000579$ and $\alpha = 0.695$ for ethylene polymers; $k = 0.0002288$ and $\alpha = 0.705$ for propylene polymers; and $k = 0.00018$ and $\alpha = 0.7$ for butene polymers.

[0040] M_v is the viscosity-average molecular weight based on molecular weights determined by the LS analysis:

$$M_v = (\sum c_i M_i^w / \sum c_i)^{1/\alpha},$$

[0041] In another embodiment, the propylene-based polymers described above also have a viscosity (also referred to a Brookfield viscosity or melt viscosity) of greater than 250 mPa·sec at 190°C or 177°C (as measured by ASTM D-3236). The viscosity may be 50,000 mPa·sec or less, or 40,000 mPa·sec or less, or 30,000 mPa·sec or less, or 20,000 mPa·sec or less, or 10,000 mPa·sec or less, or 8,000 mPa·sec or less, or 5,000 mPa·sec or less, or 4,000 mPa·sec or less, or 3,000 mPa·sec or less, or 1,500 mPa·sec or less, or between 250 and 50,000 mPa·sec, or between 250 and 25,000 mPa·sec, or between 250 and 20,000 mPa·sec, or between 250 and 15,000 mPa·sec, or between 250 and 10,000 mPa·sec, or between 250 and 5,000 mPa·sec, or between 500 and 15,000 mPa·sec, or between 1,000 and 15,000 mPa·sec, or between 1,500 and 15,000 mPa·sec, or between 2,000 and 15,000 mPa·sec, or between 3,000 and 15,000 mPa·sec, or between 4,000 and 15,000 mPa·sec, or between 5,000 and 15,000 mPa·sec, or between 2,500 and 12,500 mPa·sec, or between 3,000 and 12,000 mPa·sec, or between 3,500 and 11,000 mPa·sec, or between 4,000 and 10,000 mPa·sec, or between 5,000 and 10,000 mPa·sec, or between 500 and 10,000 mPa·sec, or between 500 and 9,000 mPa·sec, or between 500 and 8,000 mPa·sec, or between 500 and 7,000 mPa·sec, or between 500 and 6,000 mPa·sec, or between 500 and 5,000 mPa·sec, or between 500 and 4,000 mPa·sec, or between 500 and 3,000 mPa·sec, as measured by ASTM D-3236 at 190°C or 177°C.

[0042] In another embodiment, the propylene-based polymers described above also have a viscosity (also referred to a Brookfield viscosity or melt viscosity) of greater than 250 mPa·sec at 190°C, or greater than 500 mPa·sec, or greater than 1,000 mPa·sec, or greater than 2,000 mPa·sec, or greater than 3,000 mPa·sec, or greater than 4,000 mPa·sec, or greater than 5,000 mPa·sec, as measured by ASTM D-3236 at 190°C or 177°C.

[0043] In another embodiment, the propylene-based polymer has a characteristic time (τ_c), as defined by Equation 1 above, is from or 1 to 1000 nanoseconds, or 1 to 900 nanoseconds, or 1 to 800 nanoseconds, or 1 to 700 nanoseconds, or 1 to 600 nanoseconds, or 1 to 500 nanoseconds, or 1 to 400 nanoseconds, or 1 to 300 nanoseconds, or 1 to 200 nanoseconds, or 1 to 100 nanoseconds.

[0044] In one or more embodiments, the adhesive compositions described herein may comprise from about 1 wt% to about 99 wt%, or from about 5 wt% to about 90 wt%, or from about 5 wt% to about 80 wt%, or from about 10 wt% to about 60 wt% of the propylene-based polymer component.

5 Ethylene-Based Polymer Component

[0045] In one or more embodiments of the present invention, the adhesive compositions described herein comprise an ethylene-based polymer component, which in turn may comprise one or more ethylene-based polymer(s). In one embodiment, the ethylene-based polymer component comprises more than 50 wt% ethylene-derived units and at least one
10 second comonomer-derived units. The second comonomer is an alpha-olefin, and is preferably octene. The second comonomer is selected from the group consisting of C₃ to C₂₀ alpha-olefin. In some embodiments, the ethylene-based polymer component is a random copolymer and in other embodiments the ethylene-based polymer component is an elastomeric random copolymer. In some embodiments, the ethylene-based polymers
15 comprise units derived from ethylene and from about 3 to about 50 mol% units derived from C₃ to C₁₀ alpha-olefin or from about 2 to about 40 mol% units derived from ethylene and/or a C₃ to C₁₀ alpha-olefin. In another embodiment, the second comonomer may comprise at least one C₃ to C₈ alpha-olefin. In one or more embodiments, the second comonomer units may derive from propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, and/or 1-decene, preferably 1-hexene and 1-octene. The embodiments described below are discussed
20 with reference to octene as the second comonomer, but the embodiments are equally applicable to other octene copolymers with other alpha-olefin comonomers, or to octene terpolymers with ethylene and another alpha-olefin comonomer. In this regard, the copolymer may simply be referred to as ethylene-based polymers with reference to octene as
25 the alpha-olefin.

[0046] In one embodiment, the ethylene-based polymers may include alpha-olefin derived second comonomer. In another embodiment, the ethylene-based polymers comprise at least about 1 wt%, at least about 2 wt%, at least about 3 wt%, at least about 5 wt%, at least about 6 wt%, at least about 8 wt%, or at least about 10 wt% of at least one second
30 comonomer selected from the group consisting of C₃ to C₂₀ alpha-olefins, and combination thereof. Preferably, the ethylene-based polymer comprises 51 wt% to 99 wt% of ethylene-derived units and 49 wt% to 1 wt% of octene-derived units, based on the weight of the ethylene-based polymer. In those or other embodiments, the ethylene-based polymers may

include up to about 49 wt%, or up to about 39 wt%, or up to about 29 wt%, or up to about 19 wt%, or up to about 15 wt%, or up to about 15 wt%, or up to about 8 wt%, or up to about 5 wt%, or up to about 1 wt% of at least one second comonomer selected from the group consisting of C₃ to C₂₀ alpha-olefin, preferably 1-octene, and combinations thereof, where
5 the percentage by weight is based upon the total weight of the ethylene-derived and alpha-olefin derived units. Stated another way, the ethylene-based polymers may include at least about 51 wt%, or at least about 60 wt%, or at least about 70 wt%, or at least about 75 wt%, or at least about 80 wt%, or at least about 82 wt%, or at least about 84 wt%, or at least about 86 wt%, or at least about 88 wt%, or at least about 90 wt% ethylene-derived units; and in these
10 or other embodiments, the copolymers may include up to about 99 wt%, or up to about 98 wt%, or up to about 97 wt%, or up to about 95 wt%, or up to about 94 wt%, or up to about 92 wt%, or up to about 90 wt% ethylene-derived units, where the percentage by weight is based upon the total weight of the ethylene-derived and alpha-olefin derived units.

[0047] In another embodiment, the ethylene-based polymers comprise at least about 1
15 mol%, at least about 2 mol%, at least about 3 mol%, at least about 4 mol%, at least about 5 mol%, at least about 6 mol%, at least about 7 mol%, at least about 8 mol%, at least about 9 mol%, at least about 10 mol%, at least about 11 mol%, at least about 12 mol%, at least about 13 mol%, at least about 14 mol%, or at least about 15 mol% of at least one second comonomer selected from the group consisting of C₃ to C₂₀ alpha-olefins, and combinations
20 thereof. In those or other embodiments, the ethylene-based polymers may include up to about 50 mol%, or up to about 40 mol%, or up to about 33 mol%, or up to about 27 mol%, or up to about 25 mol%, or up to about 22 mol%, or up to about 17 mol% of at least one second comonomer selected from the group consisting of C₃ to C₂₀ alpha-olefin, and combinations thereof, where the percentage by mole is based upon the total number of moles of the
25 ethylene-derived and alpha-olefin derived units. Stated another way, the ethylene-based polymers may include at least about 50 mol%, or at least about 60 mol%, or at least about 67 mol%, or at least about 73 mol%, or at least about 75 mol%, or at least about 78 mol%, or at least about 83 mol% ethylene-derived units; and in these or other embodiments, the copolymers may include up to about 97 mol%, or up to about 95 mol%, or up to about 95
30 mol%, or up to about 93 mol%, or up to about 88 mol%, or up to about 86 mol% ethylene-derived units, where the mole percentage is based upon the total number of moles of the ethylene-derived and alpha-olefin derived units.

[0048] The ethylene-based polymers of one or more embodiments are characterized by having a single melting temperature as determined by differential scanning calorimetry (DSC). The melting point is defined as the temperature of the greatest heat absorption within the range of melting of the sample. The ethylene-based polymer may show secondary melting peaks adjacent to the principal peak, but for purposes herein, these secondary melting peaks are considered together as a single melting point, with the highest of these peaks being considered the melting point (T_m) of the ethylene-based polymer.

[0049] In one or more embodiments, the T_m of the ethylene-based polymers (as determined by DSC) is less than about 110°C, or less than about 100°C, or less than about 90°C, or less than about 80°C, or less than about 70°C, or less than about 60°C, or less than about 50°C, or less than about 40°C, or less than about 30°C.

[0050] In one or more embodiments, the ethylene-based polymers may be characterized by a heat of fusion (H_f), as determined by DSC. In one or more embodiments, the ethylene-based copolymer may be characterized by a heat of fusion from about 1 J/g, or about 25 J/g, or about 35 J/g, or about 45 J/g, or about 50 J/g up to about 100 J/g, or up to about 90 J/g, or up to about 80 J/g, or up to about 75 J/g, or to about 70 J/g, or up to about 65 J/g, or up to about 60 J/g, or up to about 55 J/g, or up to about 50 J/g, or up to about 45 J/g, or up to about 40 J/g, or up to about 35 J/g, or up to about 30 J/g, or up to about 20 J/g, or up to about 10 J/g. Preferably, the heat of fusion measured by differential scanning calorimetry of the ethylene-based polymer is from about 1 J/g to about 80 J/g, or about 1 J/g to about 60 J/g, or about 1 J/g to about 40 J/g, or about 1 J/g to about 20 J/g. The heat of fusion may be reduced by using additional comonomer, operating at higher polymerization temperatures, and/or using a different catalyst that provides reduced levels of steric constraints and favors more propagation errors for ethylene insertion.

[0051] In one or more embodiments, the ethylene-based polymer may have a percent crystallinity of from about 0.3% to about 40%, from about 0.5% to about 30%, or from about 1% to about 25%, or from about 5% to about 20%, determined according to DSC procedures. Percent crystallinity may be determined by dividing the heat of fusion of a sample by the heat of fusion of a 100% crystalline polymer, which is 293 joules/gram for polyethylene according to Wunderlich, B. Macromolecular Physics, Volume 1, P. 388, Academic Press, 1973.

[0052] In one or more embodiments, the ethylene-based polymer may have a density of from about 0.85 g/cm³ to about 0.92 g/cm³, or from about 0.87 g/cm³ to about 0.90 g/cm³, or

from about 0.88 g/cm³ to about 0.89 g/cm³ at room temperature as measured per the ASTM D-792 test method.

[0053] In one or more embodiments, the ethylene-based polymer may have a melt flow rate (MFR), as measured according to the ASTM D-1238, 2.16 kg weight @ 230°C, greater than or equal to about 0.3 dg/min, or at least about 0.5 dg/min, or at least about 0.8 dg/min, or at least about 1.0 dg/min. In these or other embodiments, the melt flow rate may be equal to or less than about 7000 dg/min, or less than about 6000 dg/min, or less than about 5000 dg/min, or less than about 4000 dg/min, or less than about 3000 dg/min, or less than about 2000 dg/min, or less than about 1000 dg/min, or less than about 900 dg/min, or less than about 700 dg/min, or less than about 500 dg/min, 350 dg/min, or less than about 250 dg/min, or less than about 100 dg/min.

[0054] In one or more embodiments, the ethylene-based polymer may have a melt flow rate (MFR), as measured according to the ASTM D-1238, 2.16 kg weight @ 230°C, greater than or equal to about 250 dg/min, greater than or equal to about 500 dg/min, or greater than or equal to about 1,000 dg/min, or greater than or equal to about 1,500 dg/min, greater than or equal to about 2,000 dg/min, or greater than or equal to about 2,500 dg/min, or greater than or equal to about 3,000 dg/min, or greater than or equal to about 4,000 dg/min, or greater than or equal to about 5,000 dg/min, or greater than or equal to about 6,000 dg/min, or greater than or equal to about 7,000 dg/min.

[0055] In one or more embodiments, the ethylene-based polymer can have a weight average molecular weight (M_w) of about 100,000 g/mole or less, for example, from about 5,000 to about 100,000 g/mole, or from about 5,000 to about 75,000 g/mole, or from about 5,000 to about 50,000 g/mole, or from about 10,000 to about 50,000 g/mole, or from about 20,000 to about 50,000 g/mole, or from about 30,000 to about 50,000 g/mole, or from about 35,000 to about 50,000 g/mole.

[0056] In one or more embodiments, the ethylene-based polymer can have a number average molecular weight (M_n) of from about 2,500 to about 50,000 g/mole, or from about 2,500 to about 37,500 g/mole, or from about 2,500 to about 25,000 g/mole, or from about 15,000 to about 25,000 g/mole.

[0057] In one or more embodiments, the ethylene-based polymer can have a Z-average molecular weight (M_z) of from about 10,000 to about 7,000,000 g/mole, or from about 50,000 to about 1,000,000 g/mole, or from about 80,000 to about 700,000 g/mole, or from about 100,000 to about 500,000 g/mole.

[0058] In one or more embodiments, the molecular weight distribution (MWD), the ratio of the weight-average molecular weight (M_w) to a number-average molecular weight (M_n), of the ethylene-based polymer may be from about 1 to about 40, or from about 1 to about 15, or from about 1.8 to about 5, or from about 1.8 to about 3. Preferably, the ratio of a weight-average molecular weight (M_w) to a number-average molecular weight (M_n) in the range
5 from 1 to 10, or 1 to 8, or 1 to 6, or 1 to 4.

[0059] In another embodiment, the ethylene-based polymers described above also have a viscosity (also referred to a Brookfield viscosity or melt viscosity) of at least 250 mPa·sec at 190°C or 177°C (as measured by ASTM D-3236). The viscosity may be 50,000 mPa·sec or
10 less, or 40,000 mPa·sec or less, or 30,000 mPa·sec or less, or 20,000 mPa·sec or less, or 10,000 mPa·sec or less, or 8,000 mPa·sec or less, or 5,000 mPa·sec or less, or 4,000 mPa·sec or less, or 3,000 mPa·sec or less, or 1,500 mPa·sec or less, or between 250 and 50,000 mPa·sec, or between 250 and 25,000 mPa·sec, or between 250 and 20,000 mPa·sec, or between 250 and 15,000 mPa·sec, or between 250 and 10,000 mPa·sec, or between 250 and
15 5,000 mPa·sec, or between 500 and 15,000 mPa·sec, or between 1,000 and 15,000 mPa·sec, or between 1,500 and 15,000 mPa·sec, or between 2,000 and 15,000 mPa·sec, or between 3,000 and 15,000 mPa·sec, or between 4,000 and 15,000 mPa·sec, or between 5,000 and 15,000 mPa·sec, or between 2,500 and 12,500 mPa·sec, or between 3,000 and 12,000 mPa·sec, or between 3,500 and 11,000 mPa·sec, or between 4,000 and 10,000 mPa·sec, or
20 between 5,000 and 10,000 mPa·sec, or between 500 and 10,000 mPa·sec, or between 500 and 9,000 mPa·sec, or between 500 and 8,000 mPa·sec, or between 500 and 7,000 mPa·sec, or between 500 and 6,000 mPa·sec, or between 500 and 5,000 mPa·sec, or between 500 and 4,000 mPa·sec, or between 500 and 3,000 mPa·sec, as measured by ASTM D-3236 at 190°C or 177°C.

[0060] In another embodiment, the ethylene-based polymers described above also have a viscosity (also referred to a Brookfield viscosity or melt viscosity) of greater than 250 mPa·sec at 190°C, or greater than 500 mPa·sec, or greater than 1,000 mPa·sec, or greater than 2,000 mPa·sec, or greater than 3,000 mPa·sec, or greater than 4,000 mPa·sec, or greater than 5,000 mPa·sec, as measured by ASTM D-3236 at 190°C or 177°C.

[0061] In another embodiment, the ethylene-based polymer has a characteristic time (t_c), as defined by Equation 1 above, from 1 to 1500 nanoseconds, or 1 to 1200 nanoseconds, or 1 to 1000 nanoseconds, or 1 to 800 nanoseconds, or 1 to 600 nanoseconds, or 1 to 200 nanoseconds, or 1 to 100 nanoseconds, or 1 to 500 nanoseconds.

[0062] In one or more embodiments, the adhesive compositions described herein may comprise from about 1 wt% to about 99 wt%, or from about 5 wt% to about 90 wt%, or from about 5 wt% to about 80 wt%, or from about 10 wt% to about 60 wt% of the ethylene-based polymer component.

5 Adhesive Composition of the Propylene-Based and Ethylene-Based Polymers

[0063] In one or more embodiments of the adhesive composition of this invention, the ratio of the characteristic time (t_c) of said propylene-based polymer to said characteristic time (t_c) of said ethylene-based polymer is from 1 to 1000, or 1 to 800, or 1 to 600, or 1 to 400, or 1 to 200.

10 [0064] In one or more embodiments of this invention, the first comonomer of the propylene-based polymer and the second comonomer of the ethylene-based polymer are different. Preferably, the first comonomer is ethylene and the second comonomer is octene.

[0065] In one or more embodiments of this invention, the adhesive composition has a Brookfield viscosity measured by ASTM D-3236 at 177°C is from 250 to 30,000 mPa·sec, or
15 1,000 to 4500 mPa·sec, or 700 to 8000 mPa·sec, or 900 to 6000 mPa·sec, or 1100 to 4000 mPa·sec, or 1300 to 3000 mPa·sec, or 1500 to 2000 mPa·sec.

[0066] In one or more embodiments of this invention, the adhesive composition has a melting temperature measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min is no more than 130°C, or no more than 125°C, or no more than
20 120°C, or no more than 115°C.

[0067] In one or more embodiments of this invention, the adhesive composition has one or more of the following properties: a Brookfield viscosity of 250 to 5000 mPa·sec measured by ASTM D-3236 at 177°C; a percent fiber tear at 25°C greater than or equal to 85%; a percent fiber tear at 2°C greater than or equal to 80%; a percent fiber tear at -18°C greater
25 than or equal to 75%; an adhesion set time of 6 seconds or less; and a melting temperature (T_m) of 130°C or less measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min.

[0068] In one or more embodiments, the adhesive composition of this invention comprises: (a) a propylene-based polymer comprising from 50 wt% to 100 wt% propylene-derived units and from 0 wt% to 50 wt% ethylene-derived units, said propylene-based
30 polymer having a Brookfield viscosity in the range of 250 to 25,000 mPa·sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range of 60 to 150 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a

characteristic time (t_c) in the range from 1 to 1000 nanoseconds; and (b) an ethylene-based polymer comprising from 50 wt% to 100 wt% ethylene-derived units and from 0 wt% to 50 wt% octene-derived units, said ethylene-based polymer having a Brookfield viscosity in the range of 250 to 50,000 mPa·sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range of 1 to 100 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1500 nanoseconds, wherein said characteristic time (t_c) is defined by Equation 1:

$$t_c = \frac{BV}{\text{Density} \times \text{Heat of Fusion}} \quad (\text{Equation 1}).$$

[0069] In one or more embodiments, the invention includes a hot melt adhesive composition comprising: (a) 40 wt% to 60 wt% of a propylene-based polymer based on the weight of said hot melt adhesive, said propylene-based polymer comprising from 50 wt% to 100 wt% propylene-derived units and 0 wt% to 50 wt% ethylene-derived units, said propylene-based polymer having a Brookfield viscosity in the range of 250 to 25,000 mPa·sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range of 60 to 150 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1000 nanoseconds; (b) 40 wt% to 60 wt% of an ethylene-based polymer based on the weight of said hot melt adhesive, said ethylene-based polymer comprising from 50 wt% to 100 wt% ethylene-derived units and from 0 wt% to 50 wt% octene-derived units, said ethylene-based polymer having a Brookfield viscosity in the range of 250 to 50,000 mPa·sec measured by ASTM D-3236 at 190°C, and a heat of fusion in the range of 1 to 100 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1500 nanoseconds, wherein said characteristic time (t_c) is defined by Equation 1; and (c) at least one of a functionalized component, a tackier component, a process oil component, a wax component, an antioxidant component, or a mixture thereof.

[0070] In one or more embodiments of the invention, the adhesive composition has a viscosity greater than about 250 mPa·sec, or greater than about 500 mPa·sec, or greater than about 1,000 mPa·sec, or greater than about 2,000 mPa·sec, or greater than about 5,000 mPa·sec (measured at 177°C). Viscosity may be determined via ASTM D-3236.

[0071] In one or more embodiments, the adhesive composition of this invention further comprises one or more additives. The additives are selected from the group consisting of a

functionalized component, a tackifier component, a process oil component, a wax component, an antioxidant component, or a mixture thereof.

Functionalized Component

[0072] By "functionalized component" is meant that the component (e.g., polymer) is contacted with a functional group, and, optionally, a catalyst, heat, initiator, or free radical source to cause all or part of the functional group to incorporate, graft, bond to, physically attach to, and/or chemically attach to the polymer.

[0073] The adhesive composition may comprise one or more additives including functional components. In this section we discuss these functional components in further detail. Typically, the component to be functionalized is combined with a free radical initiator and a grafting monomer or other functional group (such as maleic acid or maleic anhydride) and is heated to react the monomer with the polymer, copolymer, oligomer, etc., to form the functionalized component. Multiple methods exist in the art for functionalizing polymers that may be used with the polymers described here. These include selective oxidation, free radical grafting, ozonolysis, epoxidation, and the like.

[0074] Examples of suitable functionalized components for use in this invention include, but are not limited to, functionalized olefin polymers, (such as functionalized C_2 to C_{40} homopolymers, functionalized C_2 to C_{40} copolymers, functionalized higher M_w waxes), functionalized oligomers, (such as functionalized low M_w waxes, functionalized tackifiers), beta nucleating agents, and combinations thereof.

[0075] Functionalized olefin polymers and copolymers useful in this invention include maleated polyethylene, maleated metallocene polyethylene, maleated metallocene polypropylene, maleated ethylene propylene rubber, maleated polypropylene, maleated ethylene copolymers, functionalized polyisobutylene (typically functionalized with maleic anhydride typically to form a succinic anhydride), and the like.

[0076] Preferred functionalized waxes useful as functionalized components herein include those modified with an alcohol, an acid, a ketone, an anhydride, and the like. Preferred examples include waxes modified by methyl ketone, maleic anhydride or maleic acid. Preferred functionalized waxes useful herein include maleated polypropylene was available from Chusei under the tradename MAPP 40, maleated metallocene waxes (such as TP LICOCENE PPI602 available from Clariant in Augsburg, Germany); maleated polyethylene waxes and maleated polypropylene waxes available from Eastman Chemical in Kingsport, Tennessee under the tradenames EPOLENE C-16, EPOLENE C-18, EPOLENE

E43, and EPOLENE G-3003; maleated polypropylene wax LICOMONT AR 504 available from Clariant; grafted functional polymers available from Dow Chemical Co. under the tradenames AMPLIFY EA 100, AMPLIFY EA 102, AMPLIFY 103, AMPLIFY GR 202, AMPLIFY GR 205, AMPLIFYGR 207, AMPLIFY GR 208, AMPLIFY GR 209, and
5 AMPLIFY VA 200; CERAMER maleated ethylene polymers available from Baker Hughes under the tradenames CERAMER 1608, CERAMER 1251, CERAMER 67, and CERAMER 24; and ethylene methyl acrylate co and terpolymers.

[0077] Useful waxes include polypropylene waxes having an M_w of 15,000 or less, preferably from 3,000 to 10,000 and a crystallinity of 5 wt% or more, preferably 10 wt% or
10 more, having a functional group content (preferably maleic anhydride) of up to 10 wt%.

[0078] Additional preferred functionalized polymers for use as functional components herein include A-C X596A, A-C X596P, A-C X597A, A-C X597P, A-C X950P, A-C X1221, A-C 395A, A-C 395A, A-C 1302P, A-C 540, A-C 54A, A-C 629, A-C 629A, A-C 307, and A-C 307A available from Honeywell.

15 [0079] UNILIN long chain alcohols, available from Baker Hughes, are also useful as functionalized components herein, particularly UNILIN 350, UNILIN 425, UNILIN 550, and UNILIN 700.

[0080] UNICID linear, primary carboxylic acids, available from Baker Hughes, are also useful as functionalized components herein, particularly UNICID 350, UNICID 425,
20 UNICID 550, and UNICID 700.

[0081] Preferred functionalized hydrocarbon resins that may be used as functionalized components in this invention include those described in WO 03/025084; WO 03/025037; WO 03/025036; and EP 1 295 926 A1; which are incorporated by reference herein.

[0082] In a preferred embodiment, a hydrocarbon resin is functionalized with an
25 unsaturated acids or anhydrides containing at least one double bond and at least one carbonyl group and used as the functionalized component of this invention. Preferred hydrocarbon resins that can be functionalized are listed below as tackifiers. Representative acids include carboxylic acids, anhydrides, esters and their salts, both metallic and non-metallic. Preferably, the organic compound contains an ethylenic unsaturation conjugated with a
30 carbonyl group ($-C=O$). Examples include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, alpha-methyl crotonic, and cinnamic acids as well as their anhydrides, esters and salt derivatives. Particularly preferred functional groups include maleic acid and maleic anhydride. Maleic anhydride is particularly preferred. The unsaturated acid or anhydride is preferably present at about 0.1 wt% to about 10 wt%, preferably at about 0.5 wt% to about 7

wt%, even more preferably at about 1 wt% to about 4 wt%, based upon the weight of the hydrocarbon resin and the unsaturated acid or anhydride. In a preferred embodiment, the unsaturated acid or anhydride comprises a carboxylic acid or a derivative thereof selected from the group consisting of unsaturated carboxylic acids, unsaturated carboxylic acid derivatives selected from esters, imides, amides, anhydrides and cyclic acid anhydrides, or mixtures thereof.

[0083] In a preferred embodiment, the functionalized component is present at 0.005 wt% to 99 wt%, preferably 0.01 wt% to 99 wt%, preferably 0.05 wt% to 90 wt%, preferably between 0.1 wt% and 75 wt%, more preferably between 0.5 wt% and 60 wt%, more preferably between 1 wt% and 50 wt%, more preferably between 1.5 wt% and 40 wt%, more preferably between 2 wt% and 30 wt%, more preferably between 2 wt% and 20 wt%, more preferably between 2 wt% and 15 wt%, more preferably between 2 wt% and 10 wt%, more preferably between 2 wt% and 5 wt%, based upon the weight of the blend. Preferably, the functionalized component is present at 0.005 wt% to 10 wt%, more preferably 0.01 wt% to 10 wt%, based upon the weight of the blend.

[0084] In other embodiments, the functionalized component is present at from 0.01 wt% to 5 wt%, preferably from 0.01 wt% to 4 wt%, preferably from 0.01 wt% to 3 wt%, preferably from 0.01 wt% to 2 wt%, preferably from 0.01 wt% to 1 wt%, preferably from 0.01 wt% to 0.5 wt% or less, preferably from 0.01 wt% to 0.1 wt%, based upon the weight of the adhesive composition. In some preferred embodiments, the functionalized component is present in an amount from 1 wt% to 5 wt%, from 1 wt% to 4 wt%, or from 2.0 wt% to 4.0 wt%. In some preferred embodiments, a functionalized component is not present in the adhesive.

Tackifier Resin Component

[0085] In one or more embodiments of the present invention, the adhesive compositions described herein comprise a tackifier resin component, which may in turn comprise one or more hydrocarbon tackifier resins described herein.

[0086] In general, the tackifier resin component includes amorphous materials that can be added to an adhesive composition to achieve modification of adhesive characteristics. The tackifier resin component can be a low molecular weight natural or synthetic resin which is compatible with the polyolefin(s) and which provide the desired enhancement of film properties. Natural resins are defined as resins of plant or animal origin which include but are not limited to rosins such as gum, wood, or tall oil rosins. Synthetic resins are defined as

resins resulting from controlled chemical reactions, such as hydrocarbon resins. Examples of hydrocarbon resins include coal tar resins, petroleum resins, and turpentine resins.

[0087] Examples of suitable tackifier resin components, include, but are not limited to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood
5 rosins, wood rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, phenolic resins, hydrogenated terpenes, modified terpenes, hydrogenated rosin acids, and hydrogenated rosin
10 esters. In some embodiments, the tackifier is hydrogenated.

[0088] In other embodiments, the tackifier is non-polar, by which is meant that the tackifier is substantially free of monomers having polar groups. Preferably, the polar groups are not present; however, if present, they comprise not more than 5 wt%, preferably not more than 2 wt%, even more preferably no more than 0.5 wt%, of the tackifier. In some
15 embodiments, the tackifier has a softening point (Ring and Ball, as measured by ASTM E-28) of 80°C to 150°C, preferably 100°C to 130°C. In another embodiment, the resin is liquid and has an R and B softening point of between 10°C and 70°C.

[0089] The tackifier, if present, is typically present in an amount of at least about 1 wt%, at least about 10 wt%, at least about 20 wt%, at least 30 wt%, at least 40 wt%, at least 50
20 wt%, at least 60 wt%, at least 70 wt%.

[0090] Preferred hydrocarbon tackifier resins for use as tackifiers or modifiers include:

(a) Resins such as C_5/C_6 terpene resins, styrene terpenes, alpha-methyl styrene terpene resins, C_9 terpene resins, aromatic modified C_5/C_6 , aromatic modified cyclic resins, aromatic modified dicyclopentadiene based resins, or mixtures
25 thereof. Additional preferred resins include those described in WO 91/07472; and U.S. Patent Nos. 5,571,867; 5,171,793; and 4,078,132. Typically these resins are obtained from the cationic polymerization of compositions containing one or more of the following monomers: C_5 diolefins (such as 1-3 pentadiene, isoprene, etc.); C_5 olefins (such as 2-methylbutenes, cyclopentene, etc.); C_6 olefins (such as hexene); C_9 vinylaromatics (such as styrene, alpha methyl styrene, vinyltoluene, indene, methyl indene, etc.); cyclics (such as dicyclopentadiene, methyl dicyclopentadiene, etc.); and/or terpenes (such as limonene, carene, etc.);
30 and

(b) Resins obtained by the thermal polymerization of dicyclopentadiene, and/or the thermal polymerization of dimers or oligomers of cyclopentadiene and/or methylcyclopentadiene, optionally with vinylaromatics (such as styrene, alpha-methyl styrene, vinyl toluene, indene, methyl indene).

5 [0091] In one embodiment, the tackifier resin component may comprise one or more hydrocarbon resins produced by the thermal polymerization of cyclopentadiene (CPD) or substituted CPD, which may further include aliphatic or aromatic monomers as described later. The hydrocarbon resin may be a non-aromatic resin or an aromatic resin. The hydrocarbon resin may have an aromatic content between 0% and 60%, preferably between
10 1% and 60%, or between 1% and 40%, or between 1% and 20%, or between 10% and 20%. In further embodiments, the hydrocarbon resin may have an aromatic content between 15% and 20%, or between 1% and 10%, or between 5% and 10%.

[0092] In another embodiment, the tackifier resin component may comprise hydrocarbon resins produced by the catalytic (cationic) polymerization of linear dienes. Such monomers
15 are primarily derived from Steam Cracked Naphtha (SCN) and include C₅ dienes such as piperylene (also known as 1,3-pentadiene). Polymerizable aromatic monomers can also be used to produce resins and may be relatively pure, e.g., styrene, methyl styrene, or from a C₅-aromatic SCN stream. Such aromatic monomers can be used alone or in combination with the linear dienes previously described. "Natural" monomers can also be used to produce
20 resins, e.g., terpenes such as α -pinene or β -carene, either used alone or in high or low concentrations with other polymerizable monomers. Typical catalysts used to make these resins are AlCl₃ and BF₃, either alone or complexed. Mono-olefin modifiers such as 2-methyl, 2-butene may also be used to control the molecular weight distribution (MWD) of the final resin. The final resin may be partially or totally hydrogenated as described in further
25 detail below.

[0093] As used herein, aromatic content and olefin content are measured by ¹H-NMR, as measured directly from the ¹H NMR spectrum from a spectrometer with a field strength greater than 300 MHz, preferably 400 MHz. Aromatic content is the integration of aromatic protons versus the total number of protons. Olefin proton or olefinic proton content is the
30 integration of olefinic protons versus the total number of protons.

[0094] In one or more embodiments, the tackifier resin component may be at least partially hydrogenated or substantially hydrogenated. As used herein, "at least partially hydrogenated" means that the material contains less than 90% olefinic protons, or less than

75% olefinic protons, or less than 50% olefinic protons, or less than 40% olefinic protons, or less than 25% olefinic protons. As used herein, "substantially hydrogenated" means that the material contains less than 5% olefinic protons, or less than 4% olefinic protons, or less than 3% olefinic protons, or less than 2% olefinic protons. The degree of hydrogenation is typically conducted so as to minimize and preferably avoid hydrogenation of the aromatic bonds.

[0095] In one or more embodiments, tackifier resin components described herein may be uniquely characterized as totally or substantially amorphous in nature. This means that a glass transition temperature (T_g) is detectable, e.g., by Differential Scanning Calorimetry (DSC) but they have no melting point (T_m). To characterize these resins, it is generally accepted to use a test that roughly correlates with T_g , such as softening point (SP), which provides approximate, but not exact, values. The softening point (SP) of the resins is measured by a ring-and-ball softening point test according to ASTM E-28.

[0096] In some embodiments, the tackifiers may have a softening point of from about 50°C to about 140°C, or from about 60°C to about 130°C, or from about 70°C to about 120°C, or from about 80°C to about 110°C.

[0097] Typically, in one or more embodiments of the invention, the tackifier resin component has a number average molecular weight (M_n) from about 400 to about 3000, a weight average molecular weight (M_w) from about 500 to about 6000, a z-average molecular weight (M_z) from about 700 to about 15,000, and a polydispersity (PD), defined as M_w/M_n , between about 1.5 and about 4. As used herein, molecular weights (number average molecular weight (M_n), weight average molecular weight (M_w), and z-average molecular weight (M_z) are measured by size exclusion chromatography using a Waters 150 Gel Permeation Chromatograph equipped with a differential refractive index detector and calibrated using polystyrene standards. Samples are run in tetrahydrofuran (THF) (45°C). Molecular weights are reported as polystyrene-equivalent molecular weights and are generally measured in g/mol.

[0098] In one or more embodiments of the invention, the tackifier resin component may comprise one or more oligomers such as dimers, trimers, tetramers, pentamers, and hexamers. The oligomers may be derived from a petroleum distillate boiling in the range of 30°C to 210°C. The oligomers may be derived from any suitable process and are often derived as a byproduct of resin polymerization. Suitable oligomer streams may have molecular weights

(M_n) between 130 and 500 g/mol, more preferably between 130 to 410 g/mol, more preferably between 130 and 350 g/mol, or between 130 and 270 g/mol, or between 200 and 350 g/mol, or between 200 and 320 g/mol. Examples of suitable oligomer streams include, but are not limited to, oligomers of cyclopentadiene and substituted cyclopentadiene, oligomers of C_4 to C_6 conjugated diolefins, oligomers of C_8 to C_{10} aromatic olefins, and combinations thereof. Other monomers may be present. These include C_4 to C_6 mono-olefins and terpenes. The oligomers may comprise one or more aromatic monomers and may be at least partially hydrogenated or substantially hydrogenated.

[0099] In one embodiment, the oligomers may be stripped from the resin before hydrogenation. The oligomers may also be hydrogenated with the resin and then stripped from the resin, yielding a hydrogenated resin and hydrogenated oligomers. In another embodiment, at least some of the oligomers are stripped before hydrogenation and at least some hydrogenated oligomers are stripped after hydrogenation. In yet another embodiment, the hydrogenated resin/oligomers product may be further processed together as a single mixture as described below. In yet another embodiment, the oligomers can be derived from any suitable source and hydrogenated (if necessary) before grafting so that the oligomers before grafting are typically at least partially hydrogenated and preferably substantially hydrogenated.

[0100] Examples of commercially available tackifiers include, but are not limited to, Escorez 2203, Escorez 1310LC, Escorez 1304, Escorez 5380, Escorez 5400, and Escorez 5600, manufactured by ExxonMobil Chemical Company; Piccotac 1905 and Eastotac H-100, manufactured by Eastman Chemicals; Quintone D and Quintone U 185, manufactured by Nippon Zeon; Marukares R100, manufactured by Maruzen; and Wingtack Extra and Wingtack Plus, manufactured by Cray Valley. Escorez 2101, Escorez 5690, and Escorez 2173, manufactured by ExxonMobil Chemical Company; Regalrez 5095, Regalrez 3102, Staybelite Ester 3, and Pentalyn H, manufactured by Eastman Chemicals; Quintone U 190, manufactured by Nippon Zeon; Wingtack 86, manufactured by Cray Valley; and Sylvalite RE 885 and Sylvatac RE 85, available from Arizona Chemical.

[0101] In one or more embodiments, the adhesive compositions described herein may comprise from about 5 wt% to about 50 wt%, or from about 10 wt% to about 40 wt%, or from about 15 wt% to about 35 wt% of the tackifier resin component.

Process Oil Component

[00102] In one or more embodiments of the present invention, one or more process oils may be added to the adhesive compositions described herein. As used herein, the term "process oil" means both petroleum derived process oils and synthetic plasticizers.

5 [00103] Examples of process oils suitable for use in the present invention include, but are not limited to, paraffinic or naphthenic oils such as Primol 352 or Sentinel PO 876, produced by ExxonMobil Chemical France; and Nyflex 222B, available from Nynas AB.

[00104] Further process oils suitable for use in the present invention include aliphatic naphthenic oils, white oils, and the like. Exemplary plasticizers and/or adjuvants include
10 mineral oils, polybutenes, phthalates, and the like. In one or more embodiments, the plasticizers may include phthalates, such as di-iso-undecyl phthalate (DIUP), di-iso-nonylphthalate (DINP), dioctylphthalates (DOP), and polybutenes, such as Parapol 950 and Parapol 1300 available from ExxonMobil Chemical Company in Houston, Texas. Further useful plasticizers include those described in WO 01/18109A1 and U.S. Application
15 Publication No. 2004/0106723, which are incorporated by reference herein.

[00105] In one or more embodiments, the adhesive compositions described herein may comprise from about 1 wt% to about 50 wt%, or from about 5 wt% to about 40 wt%, or from about 10 wt% to about 35 wt%, or from about 15 wt% to about 30 wt% of the optional process oil component.

20 Wax Component

[00106] In one or more embodiments of the present invention, one or more waxes may be added to the adhesive compositions described herein. Nonlimiting examples of waxes, which can be employed, include petroleum based and synthetic waxes. Waxes suitable for use in the present invention include paraffin waxes, microcrystalline waxes, polyethylene waxes,
25 polypropylene waxes, by-product polyethylene waxes, Fischer-Tropsch waxes, oxidized Fischer-Tropsch waxes, functionalized waxes such as hydroxy stearamide waxes and fatty amide waxes, and combinations thereof. In embodiments, the wax components may be of the same or different types of waxes, and may be miscible or immiscible. It is common in the art to use the terminology synthetic high melting point waxes to include high density low
30 molecular weight polyethylene waxes, by-product polyethylene waxes, and Fischer-Tropsch waxes, which are useful herein.

[00107] Modified waxes, such as vinyl acetate modified, maleic anhydride modified, oxidized waxes, and other polar waxes may also be used in an embodiment as previously mentioned. In one embodiment, the functionalized wax component is a single component but

serves a dual function as both the functionalized polyolefin component and one or more of the wax components. In another embodiment, the adhesive is essentially free of modified waxes, i.e., it is free of deliberately added modified waxes or contains less than 1 wt% of modified waxes. In an embodiment, the wax component comprises less than 2 wt% or less than 1 wt% modified waxes by weight of the total wax components.

[00108] Preferably, the wax components are paraffin waxes, microcrystalline waxes, Fischer-Tropsch synthetic waxes, and polyethylene waxes, all of which are a blend of linear and branched hydrocarbons. Paraffin waxes are complex mixtures of many substances. They mainly consist of saturated hydrocarbons.

[00109] Microcrystalline waxes are a type of wax produced by dewaxing petrolatum, as part of the petroleum refining process. Microcrystalline wax contains a higher percentage of isoparaffinic (branched) hydrocarbons and naphthenic hydrocarbons as compared with paraffin wax. It is characterized by the fineness of its crystals in contrast to the larger crystal of paraffin wax. It consists of high molecular weight saturated aliphatic hydrocarbons, and has a high melting point. Typical microcrystalline wax crystal structure is small and thin, making the wax crystals relatively more flexible than paraffin wax crystals.

[00110] Polyolefin waxes typically have a weight average molecular weight of from 500 to 20,000 g/mol and can be produced by thermal degradation of high molecular weight branched polyolefin polymers or by direct polymerization of olefins.

[00111] In one embodiment, the adhesive composition can comprise two wax components wherein the first wax component (i.e., the low molecular weight wax component) has a weight average molecular weight (g/mol) of from 500 to 10,000, from 1,000 to 10,000, from 2,000 to 10,000, from 3,000 to 10,000, from 4,000 to 10,000, from 5,000 to 10,000, from 6,000 to 10,000, from 7,000 to 10,000, from 8,000 to 10,000, and from 9,000 to 10,000; and the second wax component (i.e., the high molecular weight wax component) has a weight average molecular weight of from 1,000 to 20,000, from 2,000 to 20,000, from 3,000 to 20,000, from 4,000 to 20,000, from 5,000 to 20,000, from 6,000 to 20,000, from 7,000 to 20,000, from 8,000 to 20,000, from 9,000 to 20,000, from 10,000 to 20,000, and from 15,000 to 20,000. Suitable polymerization processes include, for example, high-pressure technologies, in which the olefins, generally ethylene, are reacted free-radically under high pressures and temperatures to form branched waxes, and also low-pressure or Ziegler processes, in which ethylene and/or higher 1-olefins are polymerized using organometallic catalysts. Polyethylene waxes produced using metallocene catalyst have a narrower molecular weight distribution, more uniform incorporation of comonomer, and lower melting

points, in comparison to the Ziegler-Natta technology. In one embodiment, the high molecular weight second wax component comprises a metallocene polyethylene wax.

[00112] In another embodiment, the molecular weight of a first wax component is sufficiently low to reduce set time, whereas a second wax component has a molecular weight sufficiently high to improve adhesion. In one embodiment, the difference between the weight average molecular weight of the first wax component (Mw_{wax1}) and the weight average molecular weight of the second wax component (Mw_{wax2}) is at least about 1000 g/mol ($(Mw_{wax2} - Mw_{wax1}) \geq 1000$ g/mol) or at least about 2000 g/mole ($(Mw_{wax2} - Mw_{wax1}) \geq 2000$ g/mole) or at least about 3000 g/mol ($(Mw_{wax2} - Mw_{wax1}) \geq 3000$ g/mole) or at least about 4000 g/mol ($(Mw_{wax2} - Mw_{wax1}) \geq 4000$ g/mol) or at least about 5000 g/mol ($(Mw_{wax2} - Mw_{wax1}) \geq 5000$ g/mol). In an embodiment, Mw_{wax1} is less than about 4000, for example, from about 450 to 4000 g/mole or from about 500 to 4000 g/mole, and Mw_{wax2} is above about 5000, for example, from about 5000 to 20,000 g/mole.

[00113] In one or more embodiments, the adhesive compositions described herein may comprise from about 1 wt% to about 50 wt%, or from about 1 wt% to about 40 wt%, or from about 1 wt% to about 30 wt%, or from about 1 wt% to about 20 wt% of the optional wax component.

Other Additives and Fillers

[00114] In some embodiments, one or more additional fillers or additives may be employed to achieve the properties and characteristics desired in the final adhesive formulation. Such additive and fillers are known in the art and may include, but are not limited to fillers, cavitating agents, antioxidants, surfactants, adjuvants, plasticizers, block, antiblock, colorants, color masterbatches, pigments, dyes, processing aids, UV stabilizers, neutralizers, lubricants, waxes, and/or nucleating agents. The additives may be present in any amount determined to be effective by those skilled in the art, such as, for example, from about 0.001 wt% to about 10 wt%.

[00115] Examples of suitable antioxidants include, but are not limited to, quinoline, e.g., trimethylhydroxyquinoline (TMQ); imidazole, e.g., zinc mercapto toluyol imidazole (ZMTI); and conventional antioxidants, such as hindered phenols, lactones, phosphates, and hindered amines. Further suitable anti-oxidants are commercially available from, for example, Ciba Geigy Corp. under the tradenames Irgafos 168, Irganox 1010, Irganox 1076, Irganox 3790, Irganox B225, Irganox 1035, Irgafos 126, Irgastab 410, and Chimassorb 944.

[00116] Fillers (regular- or nano-sized), cavitating agents, and/or nucleating agents suitable for use in the present invention may comprise granular, fibrous, and powder-like materials, and may include, but are not limited to, titanium dioxide, calcium carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads, mineral aggregates, talc, natural and synthetic clays, diatomaceous earth, and the like.

[00117] Processing aids, lubricants, waxes, and/or oils which may be employed in the adhesive compositions of the present invention include low molecular weight products such as wax, oil, or low Mn polymer (low meaning having a M_n less than 5000, preferably below 4000, or below 3000, or below 2500). Waxes may include polar or non-polar waxes, functionalized waxes, polypropylene waxes, polyethylene waxes, and wax modifiers.

[00118] In addition to waxes, additives also include conventional additives known in the art, including fillers, antioxidants, adjuvants, adhesion promoters, plasticizers, oils, low molecular weight polymers, block, antiblock, pigments, processing aids, UV stabilizers, neutralizers, lubricants, surfactant nucleating agents, oxidized polyolefins, acid modified polyolefins, and/or anhydride modified polyolefins. Additives are combined with polymer compositions as individual components, in masterbatches, or combinations thereof.

[00119] Fillers include conventional fillers known to those skilled in the art, including titanium dioxide, calcium carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads, mineral aggregates, talc, clay, and/or nanoclay.

[00120] Antioxidants include conventional antioxidants known to those skilled in the art, including phenolic antioxidants, such as Irganox 1010 and Irganox 1076, both available from Ciba-Geigy. In some embodiments, adhesive compositions include less than about 3 wt% anti-oxidant.

[00121] Oils include conventional oils known to those skilled in the art, including paraffinic or naphthenic oils such as Primol 352 or Primol 876 available from ExxonMobil Chemical France, S.A. in Paris, France. Preferred oils include aliphatic naphthenic oils.

[00122] Plasticizers include conventional plasticizers known to those skilled in the art, including mineral oils, phthalates, or polybutenes, such as Parapol 950 and Parapol 1300 formerly available from ExxonMobil Chemical Company in Houston, Texas. Preferred plasticizers include phthalates such as di-iso-undecyl phthalate (DIUP), di-iso-nonylphthalate (DINP), and dioctylphthalates (DOP).

[00123] Adhesion promoters include conventional adhesion promoters known to those skilled in the art. Adhesion promoters include polar acids; polyaminoamides, such as Versamid 115, 125, 140, available from Henkel; urethanes, such as isocyanate/hydroxy

terminated polyester systems, e.g., bonding agent TN/Mondur Cb-75 (Miles, Inc.); coupling agents, such as silane esters (Z-6020 from Dow Corning); titanate esters, such as Kr-44 available from Kenrich; reactive acrylate monomers, such as sarbox SB-600 from Sartomer; metal acid salts, such as Sarset 633 from Sartomer; and polyphenylene oxide.

5 [00124] Low number average molecular weight (M_n) polymers include conventional low M_n polymers known to those skilled in the art. Preferred low M_n polymers include polymers of lower alpha olefins such as propylene, butene, pentene, and hexene. A particularly preferred polymer includes polybutene having a M_n of less than 1000. An example of such a polymer is available under the tradename PARAPOL™ 950 from ExxonMobil Chemical
10 Company. PARAPOL™ 950 is a liquid polybutene polymer having a M_n of 950 and a kinematic viscosity of 220 cSt (220 mPa·sec) at 100°C, as measured by ASTM D-445. In some embodiments, polar and non-polar waxes are used together in the same composition.

[00125] Adhesive compositions are composed of less than about 30 wt% additives based on the total weight of the adhesive composition. Preferably, adhesive compositions include
15 less than about 25 wt% additives, or less than about 20 wt% additives, or less than about 15 wt% additives, or less than about 10 wt% additives. In some embodiments, additives are present at less than about 5 wt%, or less than about 3 wt%, or less than about 1 wt%, based upon the weight of the adhesive composition.

[00126] The additives described herein can be added to the blend in pure form or in master
20 batches.

Preparation of the Adhesive Composition

[00127] In one or more embodiments, the components of the adhesive compositions described herein may be blended by mixing, using any suitable mixing device at a temperature above the melting point of the components, e.g., at 130°C to 180°C, for a period
25 of time sufficient to form a homogeneous mixture, normally from about 1 to about 20 minutes depending on the type of mixing device.

[00128] In the case of continuous mixing as practiced by most commercial manufacturers, a twin screw extruder may be used to mix the adhesive components. First the propylene-based polymer components and additional components such as functionalized components
30 are introduced into the extruder and mixed until the polymers have melted and are well mixed. Then the tackifiers are added, followed by any process oils which may be desired. To the extent pigments, antioxidants, fillers, or other additives are used, they are normally

blended in with the block copolymer and propylene-based polymer components. The total mixing time is typically on the order of from about 1 to 5 minutes.

[00129] In the case of batch mixing, the propylene-based polymer components and additional components are added along with the tackifier resin component. Once all of the tackifier resin components have been added and homogeneous mix is achieved, the balance of the process oil, antioxidants, fillers, and any other additives are added. The total mixing time may run for up to 20 minutes.

[00130] Without being bound by theory, it is believed that neither the propylene-based polymer nor the ethylene-based polymers as components of the adhesive compositions will migrate to the surface of the adhesive composition because their molecular weights are not very low and the difference in crystallinity between these components is not very large as defined by the characteristic time (t_c) in Equation 1. The propylene-rich polymer and the ethylene-rich copolymer can be blended physically in any desired ratio to form the above adhesive compositions. Also, one polymer component can be prepared in one reactor and the other polymer component can be prepared in another reactor in a series reactor configuration or both copolymers can be made simultaneously in a parallel reactor configuration. The polymerizates of the two polymer components in any prescribed ratios can be subsequently mixed together and then subjected to finishing steps to form the base polymers (dual-reactor blends) of the adhesive compositions of this invention as described herein.

Applications

[00131] The adhesive compositions described herein may be applied to any substrate. Suitable substrates may include, but are not limited to, wood, paper, cardboard, plastic, plastic film, thermoplastic, thermoplastic elastomer (TPE), thermoplastic vulcanizate (TPV), rubber, metal, metal film, metal foil (such as aluminum foil and tin foil), metallized surfaces, cloth, nonwovens (particularly polypropylene spunbonded fibers or nonwovens), spunbonded fibers, cardboard, stone, plaster, glass (including silicon oxide (SiO_x) coatings applied by evaporating silicon oxide onto a film surface), foam, rock, ceramics, films, polymer foams (such as polyurethane foam), substrates coated with inks, dyes, pigments, PVDC, and the like, or combinations thereof. Additional substrates may include polyethylene, polypropylene, polyacrylates, acrylics, polyethylene terephthalate, or blends thereof. Corona treatment, electron beam irradiation, gamma irradiation, microwave or silanization may modify any of the above substrates.

[00132] The adhesive compositions of this invention may be applied to a substrate as a melt and then cooled. The adhesive composition may be applied to a substrate using

conventional coating techniques such as roller coaters, die coaters, and blade coaters, generally at a temperature of from about 150°C to about 200°C. In one or more embodiments, the adhesive composition is applied to a substrate using a slot die.

5 [00133] A slot die is a closed system where an adhesive composition is pumped through the system via a positive displacement pump. The slot die usually includes a rotating bar at the point of the outlet of the adhesive in order to maintain a smooth surface.

[00134] The substrate should be coated with sufficient adhesive composition to provide a dry coating weight of from about 10 to about 100, or from about 10 to about 50, or from about 15 to about 25 grams per square meter (gsm).

10 [00135] After coating, the coated substrate is cut to the required dimension. In the manufacture of tape, the substrate is slit into strips and rolled into a finished product. The substrate may also be cut into shaped items to provide labels or medicinal tapers. In one or more embodiments, a release liner may also be employed, if desired.

[00136] In one or more embodiments of the present invention, adhesive tapes may be 15 formed which comprise a substrate coated with one or more adhesive compositions as described herein. As used herein, the term "tape" is meant generically to encompass any manner of adhesive application including, but not limited to, tapes, labels, stickers, decals, packaging applications, and the like.

Properties of the Adhesive Composition

20 [00137] In order to measure set time, substrate fiber tear, adhesive test specimens are created by bonding the substrates together with a dot of about 0.3 grams of molten adhesive and compressing the bond with a 500-gram weight. The dot size is controlled by the adhesive volume such that the compressed disk which forms gives a uniform circle just inside the dimensions of the substrates.

25 [00138] Set time (also referred to as adhesive set time or dot set time) is defined as the time it takes for a compressed adhesive substrate construct to fasten together enough to give substrate fiber tear when pulled apart, and, thus, the bond is sufficiently strong to remove the compression. These set times are measured by trial and error by placing a molten dot of adhesive on to a file folder substrate (a typical manila letter size (1/3 cut) stock having a 30 minimum of 10% post-consumer recycle paper content provided by Simead Paper, stock number 153L, UPC number 10330) taped to a flat table. Three seconds later, a file folder tab (2.5 cm x 7.6 cm (1 inch by 3 inch)) is placed upon the dot and compressed with a 500-gram weight. The weight is allowed to sit for a predetermined time period from about 0.5 to about 10 seconds. The construct thus formed is pulled apart to check for a bonding level good

enough to produce substrate fiber tear. The procedure is repeated several instances while holding the compression for different periods, and the set time is recorded as the minimum time required for this good bonding to occur. Standards are used to calibrate the process.

[00139] Once a construct is produced it can be subjected to various insults to assess the effectiveness of the bond. Once a bond to a substrate fails a simple way to quantify the effectiveness of the adhesive is to estimate the area of the adhesive dot that retained substrate fibers as the construct failed along the bond line. This estimate is called percent substrate fiber tear. An example of good adhesion, after conditioning a sample for 15 hours at -12°C and attempting to destroy the bond, would be an estimate of 80% to 100% substrate fiber tear. It is likely that 0% substrate fiber tear under those conditions would signal a loss of adhesion.

[00140] The specimens for adhesion to a paper substrate for fiber tear testing are prepared using the same procedure as that described above. All substrate fiber tears were performed at conditions of 25°C, 2°C, and -18°C, wherein the specimens are aged at such conditions for about 12 hours. The bonds are separated by hand and a determination made as to the type of failure observed. The amount of substrate fiber tear is expressed herein as a percentage. All of the fiber tear tests are conducted using the paper substrate of a paperboard 84C (generic corrugated cardboard 200# stock provided by Huckster Packaging Supply, 6111 Griggs Road, Houston TX 77023).

[00141] Brookfield viscosity is measured using a Brookfield digital viscometer and a number 27 spindle according to ASTM D-3236 at either 177°C or 190°C (whichever temperature is specified).

[00142] Peak melting point (T_m), also referred to as melting point, peak crystallization temperature, (T_c), also referred to as crystallization temperature, glass transition temperature (T_g), heat of fusion (ΔH_f or H_f), and percent crystallinity were determined using the following differential scanning calorimetric (DSC) procedure (at second melt) according to ASTM D3418-03. DSC data were obtained using a TA Instruments model Q100 machine. Samples weighing approximately 5-10 mg were sealed in an aluminum hermetic sample pan. The DSC data were recorded by first gradually heating the sample to 200°C at a rate of 10°C/minute. The sample was kept at 200°C for 2 minutes then cooled to -90°C at a rate of 10°C/minute, followed by an isothermal for 2 minutes and heating to 200°C at 10°C/minute. Both the first and second cycle thermal events were recorded. Areas under the endothermic peaks of the second cycle were measured and used to determine the T_c , T_m , and H_f . The percent crystallinity is calculated using the formula, [area under the melting peak

(Joules/gram) / B (Joules/gram)] * 100, where B is the heat of fusion for the 100% crystalline homopolymer of the major monomer component. These values for B are obtained from Bu, H.-S.; Cheng, S. Z. D.; Wunderlich, B. *Makromol. Chem. Rapid Commun.* 1988, 9, 75, that a value of 207 J/g (B) is used as the heat of fusion for 100% crystalline polypropylene and from Wunderlich, B. *Macromolecular Physics*, Volume 1, P. 388, Academic Press, 1973, that a value of 293 J/g is used for the heat of fusion for 100% crystalline polyethylene. The melting and crystallization temperatures as well as the glass transition temperature reported here were obtained during the second heating/cooling cycle unless otherwise noted.

[00143] Polymer densities at 23°C were determined by the density column method according to ASTM D-1505-10.

EXAMPLES

[00144] The following examples are illustrative of the invention.

[00145] The weight percent ethylene-derived units (wt% C₂), of each propylene-ethylene random co-polymer (PEC), was determined by FTIR. The weight percent of octene-derived units (C₈) of each ethylene-octene random copolymer (EOC) was determined by ¹³C NMR. Weight-average molecular weights (M_w) were obtained by GPC-3D using the LS (light scattering) detector. The M_w/M_n ratio was determined using a differential refractive index (DRI) detector. The g' (g-prime) data were determined using a viscometer detector. BV denotes the Brookfield viscosity determined by ASTM D-3236. T_g, T_c, T_m, and H_f were determined as set forth above.

[00146] Materials used in the preparation of the adhesive compositions as identified in the examples are as follows.

[00147] "PEC-1", "PEC-2", and "PEC-3" are propylene-ethylene random copolymers (a propylene-based polymer) having the properties shown in Table 1.

[00148] "EOC-1" and "EOC-2" are ethylene-octene random copolymers (an ethylene-based polymer) having the properties shown in Table 2. EOC-1 and EOC-2 are Affinity GA 1900 and Affinity GA 1950, respectively, and are available from the Dow Chemical Company.

Table 1

	PEC-1	PEC-2	PEC-3
Wt% C ₃	95.8	98.2	95.3
Wt% C ₂	4.2	1.8	4.7
M _w , kg/mole	22	29	31
M _w /M _n	4.14	2.71	2.37
G'	0.776	0.785	0.84
BV@190°C, mPa·sec	260	525	583
T _g , °C	-4.5	-9.8	-7.5
T _c , °C	96	75	87
T _m , °C	129	112	123
H _f , J/g	78	62	85
% Crystallinity	38	30	41
Density, g/cm ³	0.8930	0.8982	0.8919
t _c , ns	3.73	9.43	7.69

Table 2

	EOC-1	EOC-2
Wt% C ₂	59	62
Wt% C ₈	41	38
M _w , kg/mole	22	26
M _w /M _n	2.17	1.98
G'	0.921	0.911
BV@190°C, mPa·sec	5412	11075
T _g , °C	-58	-53
T _c , °C	52	54
T _m , °C	69	73
H _f , J/g	47	50
% Crystallinity	16	17
Density, g/cm ³	0.8700	0.8740
t _c , ns	132	253

[00149] In terms of BV@190°C for PECs: PEC-1 < PEC-2 < PEC-3. In terms of
 5 BV@190°C for EOCs: EOC-1 < EOC-2. The PECs in Table 1 are very brittle and difficult to
 mold so that the densities shown in Table 1 are extrapolated values using the densities of
 PECs with various wt% C₂ based on our data and data from *Journal of Applied Polymer*
Science, Vol. 100, P. 1651-1658, 2006.

[00150] "Escorez 5400", available from ExxonMobil Chemical Company, is a cycloaliphatic hydrocarbon tackifier resin having a ring and ball softening point from about 100°C to about 106°C.

[00151] "Polywax 3000", available from Baker Petrolite, is a synthetic wax that is a fully saturated homopolymers of ethylene that have high degrees of linearity and crystallinity. Its density is about 0.98 g/cm³. This synthetic wax has narrow molecular weight distributions (M_w of 3300 g/mol, M_w/M_n of 1.10), a viscosity of 130 mPa·sec at a temperature of 149°C, a viscosity of 55 mPa·sec at a temperature of 190°C, a crystallization temperature of 115°C and a melting temperature of 127°C.

[00152] "A-C 596P" is a polypropylene-maleic anhydride copolymer from Honeywell, having a M_w of 12,000 g/mole, M_w/M_n of 2.18, viscosity at 190°C of 128 mPa·sec, a crystallization temperature of 102°C, a melting temperature of 133°C, and Mettler drop point of 143°C. A-C 596P is available from Honeywell.

[00153] Irganox 1010 is a phenolic antioxidant (stabilizer) having a melting point from about 110°C to about 125°C and a density (at 20°C) of about 1.15 g/cm³. Irganox 1010 is available from Ciba Specialty Chemicals, Switzerland.

[00154] The properties of Polywax 3000 and AC596P are shown in Table 3.

Table 3

	Wt% C ₂	M_w (kg/ mole)	M_w/M_n	g'	BV@190°C (mPa·sec)	T_c (°C)	T_m (°C)	H_f (J/g)
Polywax 3000	100	3.3	1.15	0.848	55	115	127	336
A-C 596P	0	12	5.92	0.99	128	102	133 143	64

Examples 1-7

[00155] Hot melt adhesive formulations (HMAs) of a propylene-based polymer, PEC-1, were prepared, in which 80 wt% PEC-1 was combined with an additive package comprised of Escorez 5400, Polywax 3000, A-C 596P, and Irganox 1010 at weight percentages of 8/8/3/1 was prepared (Sample 1). For comparison, additional HMAs in which PEC-1 is combined with the higher viscosity EOC-1, were prepared with the above additive package (Samples 2-6). A HMA based on 80 wt% EOC-1 and the additive package was also prepared (Sample 7). Table 4 shows the composition and performance of these HMAs which are based on PEC-1 and the higher viscosity EOC-1, along with the comparative HMAs of PEC-

1 and EOC-1 alone. As can be seen, the incorporation of PEC-1 into EOC-1 in the HMA lowered its viscosity. The adhesion of these HMAs is higher than that of the HMAs based on either single polymer alone, as shown by the fiber tear data in which all values are greater than 95% at different test temperatures. A higher adhesion is signified by a larger percentage of fiber tear. These HMAs may be suitable for use in applications with nonwovens, and in woodworking or other applications because short set time and low viscosity are not critical properties for these types of adhesive. Good packaging HMAs require shorter set times and lower HMA viscosities, or both.

Table 4

Example	1	2	3	4	5	6	7
PEC-1	80	56	48	50	48	24	--
EOC-1	--	24	32	50	32	56	80
Escorez 5400	8	8	8	8	8	8	8
Polywax 3000	8	8	8	8	8	8	8
A-C 596P	3	3	3	3	3	3	3
Irganox 1010	1	1	1	1	1	1	1
PEC-1/EOC-1, Wt. Ratio	100/0	70/30	60/40	50/50	40/60	30/70	0/100
HMA Performance							
Brookfield Viscosity@177°C (mPa·sec)	265	628	783	1160	1602	2017	3675
Set Time, seconds	1.5	3.0	3.0	4.0	5.0	6.0	5.0
% Fiber Tear, 25°C	0	97	99	100	100	100	93
% Fiber Tear, 2°C	0	98	100	100	99	100	95
% Fiber Tear, -18°C	0	97	97	99	99	99	96
T _m , °C	121	75	72	66	68	65	67
		120	120	118	119	118	118

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Examples 8-18

[00156] HMAs of two other propylene-based polymers, PEC-2 and PEC-3, were prepared, in which 80 wt% PEC-2 (Example 8) and 80 wt% PEC-3 (Example 13) were combined with the above additive package. For comparison, additional HMAs based on PEC-2 combined with the higher viscosity EOC-1 (Examples 9-12), and based on PEC-3 and the higher viscosity EOC-1 (Examples 14-18), were prepared with the above additive package. The HMA based on 80 wt% EOC-1 and the above additive package was also compared (Example 7). Table 5 shows the composition and performance of these HMAs which are based on PEC-2 and the higher viscosity EOC-1, along with the comparative HMAs of PEC-2 and

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EOC-1 alone. Table 6 shows the composition and performance of these HMAs which are based on PEC-3 and the higher viscosity EOC-1, along with the comparative HMAs of PEC-3 and EOC-1 alone. As can be seen, the incorporation of PEC-2 or PEC-3 into EOC-1 in the HMA lowered its viscosity. The adhesion of these HMAs (except Examples 9 and 10) is higher than that of the HMAs based on both single polymer alone, as shown by their fiber tear all greater than 85% at different test temperatures. Examples 11 and 15-17 represent good packaging HMAs with set times shorter than 3 seconds, degrees of fiber tear greater than 85% at all test temperatures, and low Brookfield viscosities at 177°C. The other HMAs based on PEC-2 or PEC-3 blended with EOC-1 may be suitable for use in applications with nonwovens, and in woodworking applications, due to the long set time and high viscosity. Good packaging HMAs require shorter set times and lower HMA viscosities, or both.

Table 5

Example	8	9	10	11	12	7
PEC-2	80	56	48	40	32	--
EOC-1	--	24	32	40	48	80
Escorez 5400	8	8	8	8	8	8
Polywax 3000	8	8	8	8	8	8
A-C 596P	3	3	3	3	3	3
Irganox 1010	1	1	1	1	1	1
PEC-2/EOC-1 Wt. Ratio	100/0	70/30	60/40	50/50	40/60	0/100
HMA Performance						
Brookfield Viscosity@177°C (mPa·sec)	385	773	958	1407	1807	3675
Set Time, sec	8.5	3.5	2.0	2.0	3.0	5.0
% Fiber Tear, 25°C	0	47	82	99	100	93
% Fiber Tear, 2°C	0	0	70	88	99	95
% Fiber Tear, -18°C	0	6.7	70	96	96	96
T _m , °C	122 132	64 117 128	73 119 127	66 119 128	65 119 128	67 118

Table 6

Example	13	14	15	16	17	18	7
PEC-3	80	56	48	50	48	24	--
EOC-1	--	24	32	50	32	56	80
Escorez 5400	8	8	8	8	8	8	8
Polywax 3000	8	8	8	8	8	8	8
A-C 596P	3	3	3	3	3	3	3
Irganox 1010	1	1	1	1	1	1	1
PEC-3/EOC-1, Wt. Ratio	100/0	70/30	60/40	50/50	40/60	30/70	0/100
HMA Performance							
Brookfield Viscosity@177°C (mPa·sec)	498	1075	1250	1607	2037	2690	3675
Set Time, sec	3.0	2.5	2.0	2.0	2.0	2.5	5.0
% Fiber Tear, 25°C	0	92	99	100	100	100	93
% Fiber Tear, 2°C	0	98	100	99	100	99	95
% Fiber Tear, -18°C	0	97	96	95	96	98	96
T _m , °C	121	75 120	73 120	71 120	73 120	63 119	67 118

Examples 19-21

[00157] HMAs based on the medium-viscosity PEC-2 and the high-viscosity EOC-2 were prepared. Table 7 shows the composition and performance of these HMAs. As can be seen, EOC-2 has a higher BV (Brookfield Viscosity) than EOC-1, such that HMAs based on a blend of EOC-2 and PEC-2 have higher BV@177°C. Good packaging HMAs require shorter set times and lower HMA viscosities, or both. Such HMAs containing PEC-2 and EOC-2 blends need higher amounts of additives, such as tackifiers, waxes or oils, to lower the melt viscosity so that the HMAs are more suitable for packaging HMA applications. Example 21 (32 wt% PEC-2 and 48 wt% EOC-2), however, shows much lower viscosity than Example 22 (80 wt% EOC-2) without any loss in adhesion to the paper substrate. The other HMAs based on PEC-2 and EOC-2 may be suitable for use in applications with nonwoven, and in woodworking applications, due to the long set time and/or high viscosity.

Table 7

Example	8	19	20	21	22
PEC-2	80	48	40	32	--
EOC-2	--	32	40	48	80
Escorez 5400	8	8	8	8	8
Polywax 3000	8	8	8	8	8
A-C 596P	3	3	3	3	3
Irganox 1010	1	1	1	1	1
PEC-2/EOC-2, Wt. Ratio	100/0	60/40	50/50	40/60	0/100
HMA Performance					
Brookfield Viscosity@177°C (mPa·sec)	385	1302	2122	3465	7675
Set Time, sec	8.5	5.0	3.5	3.5	4.0
% Fiber Tear, 25°C	0	72	63	100	99
% Fiber Tear, 2°C	0	6.7	72	100	95
% Fiber Tear, -18°C	0	13	100	98	98
T _m , °C	122 132	73 120 127	72 119 129	70 119 129	72 118

[00158] All the propylene-based and ethylene-based polymers used in the adhesive composition of the Examples above have a characteristic time (t_c) within the range of 0.1-10,000 nanoseconds (Tables 1 and 2).

[00159] Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges from any lower limit to any upper limit are contemplated unless otherwise indicated. Certain lower limits, upper limits, and ranges appear in one or more claims below. All numerical values are "about" or "approximately" the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[00160] To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[00161] While the foregoing is directed to embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

CLAIMS

What Is Claimed Is:

1. An adhesive composition comprising:

(a) at least one propylene-based polymer comprising more than 50 wt% of propylene-derived units and at least one first comonomer-derived units, said propylene-based polymer having a Brookfield viscosity of at least 250 mPa•sec measured by ASTM D-3236 at 190°C, a heat of fusion of at least 60 J/g measured by differential scanning calorimetry and a characteristic time (t_c) in the range from 1 to 1000 nanoseconds;

(b) an ethylene-based polymer comprising more than 50 wt% ethylene-derived units and at least one second comonomer-derived units, said ethylene-based polymer having a Brookfield viscosity of at least 250 mPa•sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range from 1 to 100 J/g measured by differential scanning calorimetry and a characteristic time (t_c) in the range from 1 to 1500 nanoseconds;

wherein said at least one first comonomer and said at least one second comonomer are the same or different;

wherein said characteristic time (t_c) in units of nanoseconds is defined by Equation 1:

$$t_c = \frac{BV}{\text{Density} \times \text{Heat of Fusion}} \quad (\text{Equation 1})$$

wherein said BV is the Brookfield viscosity of said propylene-based polymer or said ethylene-based polymer measured by ASTM D-3236 at 190°C in units of mPa•sec, said Density is the density of said propylene-based polymer or said ethylene-based polymer in units of g/cm³ at 23°C, and said Heat of Fusion is the heat of fusion of said propylene-based polymer or said ethylene-based polymer in units of J/g.

2. The adhesive composition of claim 1, wherein said at least one first comonomer is selected from the group consisting of ethylene and a C₄ to C₂₀ alpha-olefin.

3. The adhesive composition of any one of claims 1-2, wherein said at least one first comonomer comprises ethylene.
4. The adhesive composition of any one of claims 1-3, wherein said propylene-based polymer comprises 90 wt% to 99 wt% of propylene-derived units and 10 wt% to 1 wt% of ethylene-derived units, based on the weight of said propylene-based polymer.
5. The adhesive composition of any one of claims 1-4, wherein said Brookfield viscosity measured by ASTM D-3236 at 190°C of said propylene-based polymer is from 250 to 25,000 mPa•sec.
6. The adhesive composition of any one of claims 1-5, wherein said characteristic time (t_c) of said propylene-based polymer is from 1 to 800 nanoseconds.
7. The adhesive composition of claim 1, wherein said at least one second comonomer is a C_3 to C_{20} alpha-olefin.
8. The adhesive composition of claim 7, wherein said ethylene-based polymer comprises 51 wt% to 99 wt% of ethylene-derived units and 49 wt% to 1 wt% of octene-derived units, based on the weight of the said ethylene-based polymer.
9. The adhesive composition of claim 1, wherein said first comonomer and said second comonomer are different, said first comonomer is ethylene, and said second comonomer is octene.
10. The adhesive composition of claim 9, further comprising one or more additives, said additives selected from the group consisting of a functionalized component, a tackifier component, a process oil component, a wax component, an antioxidant component, or a mixture thereof.
11. The adhesive composition of any one of claims 9-10, wherein said adhesive composition comprises 99 wt% to 1 wt% of said propylene-based polymer and 1 wt% to 99 wt% of said ethylene-based polymer, based on the weight of said adhesive composition.
12. The adhesive composition of any one of claims 9-11, wherein said adhesive composition has a melting temperature measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min is no more than 130°C.
13. The adhesive composition of any one of claims 9-12, wherein said adhesive composition has one or more of the following properties:

- (i) a Brookfield viscosity of 250 to 5000 mPa•sec measured by ASTM D-3236 at 177°C;
- (ii) a percent fiber tear at 25°C greater than or equal to 85%;
- (iii) a percent fiber tear at 2°C greater than or equal to 80%;
- (iv) a percent fiber tear at -18°C greater than or equal to 75%;
- (v) an adhesion set time of 6 seconds or less; and
- (vi) a melting temperature (T_m) of 130°C or less measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min.

14. An adhesive composition comprising:

(a) a propylene-based polymer comprising from 50 wt% to 100 wt% propylene-derived units and from 0 wt% to 50 wt% ethylene-derived units, said propylene-based polymer having a Brookfield viscosity in the range of 250 to 25,000 mPa•sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range of 60 to 150 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1000 nanoseconds;

(b) an ethylene-based polymer comprising from 50 wt% to 100 wt% ethylene-derived units and from 0 wt% to 50 wt% octene-derived units, said ethylene-based polymer having a Brookfield viscosity in the range of 250 to 50,000 mPa•sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range of 1 to 100 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1500 nanoseconds;

wherein said characteristic time (t_c) is defined by Equation 1:

$$t_c = \frac{BV}{\text{Density} \times \text{Heat of Fusion}} \quad (\text{Equation 1})$$

wherein said BV is the Brookfield viscosity of said propylene-based or said ethylene-based polymer measured by ASTM D-3236 at 190°C in units of mPa•sec, said Density is the density of said propylene-based or said ethylene-based polymer in units of g/cm³ at 23°C, and said Heat of Fusion is the heat of fusion of said propylene-based or said ethylene-based polymer in units of J/g.

15. A hot melt adhesive composition comprising:

(a) 40 wt% to 60 wt% of a propylene-based polymer based on the weight

of said hot melt adhesive, said propylene-based polymer comprising from 50 wt% to 100 wt% propylene-derived units, and 0 wt% to 50 wt% ethylene-derived units, said propylene-based polymer having a Brookfield viscosity in the range of 250 to 25,000 mPa•sec measured by ASTM D-3236 at 190°C, a heat of fusion in the range of 60 to 150 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1000 nanoseconds;

(b) 40 wt% to 60 wt% of an ethylene-based polymer based on the weight of said hot melt adhesive, said ethylene-based polymer comprising from 50 wt% to 100 wt% ethylene-derived units and from 0 wt% to 50 wt% octene-derived units, said ethylene-based polymer having a Brookfield viscosity in the range of 250 to 50,000 mPa•sec measured by ASTM D-3236 at 190°C, and a heat of fusion in the range of 1 to 100 J/g measured by differential scanning calorimetry at second melt with a heating rate of 10°C/min and a characteristic time (t_c) in the range from 1 to 1500 nanoseconds;

wherein said characteristic time (t_c) is defined by Equation 1:

$$t_c = \frac{BV}{\text{Density} \times \text{Heat of Fusion}} \quad (\text{Equation 1})$$

wherein said BV is the Brookfield viscosity of said propylene-based or said ethylene-based polymer measured by ASTM D-3236 at 190°C in units of mPa•sec, said Density is the density of said propylene-based or said ethylene-based polymer in units of g/cm³ at 23°C, and said Heat of Fusion is the heat of fusion of said propylene-based or said ethylene-based polymer in units of J/g; and

(c) at least one of a functionalized component, a tackier component, a process oil component, a wax component, an antioxidant component, or a mixture thereof.