



US 20170292047A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2017/0292047 A1**
(43) **Pub. Date: Oct. 12, 2017**

(54) **HEXENE-1 CONTAINING AMORPHOUS
POLYALPHAOLEFINS FOR IMPROVED
HOT MELT ADHESIVES**

(71) Applicant: **REXtac LLC**, Odessa, TX (US)

(72) Inventors: **Andres Sustic**, Odessa, TX (US); **John
Passmore**, Odessa, TX (US); **Nick
Fowler**, Odessa, TX (US); **John J.
DeCair**, Odessa, TX (US)

(21) Appl. No.: **15/486,115**

(22) Filed: **Apr. 12, 2017**

Related U.S. Application Data

(60) Provisional application No. 62/321,663, filed on Apr.
12, 2016.

Publication Classification

(51) **Int. Cl.**
C09J 123/22 (2006.01)
C09J 11/06 (2006.01)
(52) **U.S. Cl.**
CPC **C09J 123/22** (2013.01); **C09J 11/06**
(2013.01); **C09J 2205/114** (2013.01); **C09J**
2423/00 (2013.01); **C09J 2453/00** (2013.01);
C09J 2423/10 (2013.01)

(57) **ABSTRACT**

Propylene-co-hexene-1-co-butene-1 terpolymers, made either with or without an in-reactor-added organosilicon external donor, are used in the formulation of improved-performance, APAO-based, hot melt adhesives. The addition of an external donor during the manufacture of hexene-1 based amorphous polyalpha-olefins (APAO's) results in products having enhanced physical and mechanical properties compared to similar adhesive products made without the addition of the external donor.

HEXENE-1 CONTAINING AMORPHOUS POLYALPHAOLEFINS FOR IMPROVED HOT MELT ADHESIVES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/321,663, filed on Apr. 12, 2016, the contents of which are hereby incorporated by reference in their entirety.

FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not Applicable

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0003] The present invention generally relates to formulations suitable for use as hot-melt adhesives and pressure-sensitive adhesives. More particularly, it relates to APAO-based adhesives.

2. Description of the Related Art Including Information Disclosed Under 37 CFR 1.97 and 1.98

[0004] Amorphous poly-alpha-olefins (APAO) are produced by the (co-) polymerization of α -olefins, e.g. propylene or 1-butene with Ziegler-Natta catalysts. The (co-) polymers have an amorphous structure which makes them useful for the production of hot melt adhesives (HMAs).

[0005] U.S. Pat. No. 5,302,675, "High Tensile Strength Amorphous 1-Butene/Propylene Copolymers," describes a process for the production of propylene/1-butene copolymers comprising: reacting propylene and 1-butene monomers in the presence of a catalyst system comprising: (a) a solid supported catalyst component may be prepared by the method comprising: (i) co-communiting magnesium halide support base and aluminum trihalide in a molar ratio from about 8:0.5 to about 8:3 in the absence of added electron donor; and (ii) then co-communiting the product of step (i) in the absence of added electron donor with sufficient titanium tetrahalide to provide a molar ratio of magnesium halide to titanium tetrahalide from about 8:0.1 to about 8:1.0; (b) a trialkylaluminum co-catalyst, having from 1 to 9 carbon atoms in each alkyl group in an amount such that the Al-to-Ti ratio may be between about 50:1 and about 500:1; (c) an alkoxy silane component of the formula $R_n Si(OR')_{4-n}$ where $n=1-3$, R =aryl or alkyl and R' =C1-C3 alkyl in a sufficient quantity such that the molar ratio of organoaluminum co-catalyst to alkoxy silane is in the range from about 20:1 to about 45:1, said copolymer being characterized by a propylene content of 25 to 50 wt. %, a 1-butene content of 75 to 50 wt. % and a tensile strength of at least 300 psig.

[0006] U.S. Pat. Nos. 5,681,913, 5,637,665, and 5,714,554 each entitled "High Tensile Strength Amorphous 1-Butene/Propylene and Ethylene/Propylene Copolymers," describe amorphous propylene/1-butene and ethylene/propylene copolymers having increased tensile properties produced by the process comprising: reacting propylene and 1-butene monomers or ethylene and propylene monomers in the presence of a catalyst system comprising: (a) a solid sup-

ported catalyst component is prepared by the method comprising: (i) co-communiting magnesium halide support base and aluminum tri-halide in a molar ratio from about 8:0.5 to about 8:3 in the absence of added electron donor; and (ii) then co-communiting the product of step (i) in the absence of added electron donor with sufficient titanium tetra-halide to provide a molar ratio of magnesium halide to titanium tetrahalide from about 8:0.1 to about 8:1.0; (b) a trialkylaluminum co-catalyst, having from 1 to 9 carbon atoms in each alkyl group in an amount such that the Al-to-Ti ratio is between about 50:1 and about 500:1; and (c) an alkoxy silane component of the formula $R_n Si(OR')_{4-n}$ where $n=1-3$, R =aryl or alkyl and R' =C1-C3 alkyl.

[0007] U.S. Pat. No. 6,586,543, "Process for the Preparation of Substantially Amorphous Poly-Alpha-Olefins," describes a process for preparing a substantially amorphous poly- α -olefin, which includes: a) performing a solid catalyst and, optionally, a first amount of a trialkylaluminum cocatalyst, by contacting the catalyst and optionally the cocatalyst with at least one selected from the group including oxygen and a compound which includes active oxygen, to form a preformed catalyst, wherein the solid catalyst includes magnesium, aluminum and titanium, and wherein said trialkylaluminum cocatalyst includes 1 to 9 carbon atoms in each alkyl group; b) contacting the preformed catalyst with a second amount of the cocatalyst, wherein a molar ratio of trialkylaluminum to the titanium ranges from 40:1 to 700:1, to form a catalyst mixture; c) polymerizing, in the liquid phase, with the catalyst mixture, an olefin or an olefin mixture at a temperature between 30° and 160° C., to produce the poly- α -olefin.

[0008] U.S. Pat. No. 4,309,522, "Process for the production of extensively amorphous butene-1-propene-ethene terpolymers having a high softening point," describes a process for preparing an extensively amorphous butene-1-propene-ethene terpolymer having a high softening point that comprises low-pressure solution polymerizing butene-1, propene and ethene by contacting these monomers with a catalytically effective amount of a mixed catalyst of a thermally unstable crystalline $TiCl_3$ -0.30 to 0.35 $AlCl_3$ and a trialkyl aluminum or dialkyl aluminum hydride, each having alkyl groups of 2-4 carbon atoms, the atomic ratio of Al:Ti being 0.8-4.0.

[0009] U.S. Pat. No. 4,322,514, "Process for preparing a copolymer," describes a process for preparing a non- or low-crystalline soft copolymer, characterized in that 50 to 98 mole % of propylene, 0.2 to 30 mole % of ethylene and 0.2 to 45 mole % of a straight-chained α -olefin having not less than four carbon atoms are copolymerized using a catalyst, said catalyst comprising (1) a solid substance containing magnesium and titanium and (2) an organometallic compound.

[0010] U.S. Pat. No. 4,826,939, "Highly amorphous olefin terpolymer," describes highly amorphous olefin terpolymers from propylene, 1-hexene, and ethylene in which the ethylene units are incorporated in the polymer chain in a highly random manner, and a process for producing such terpolymers.

[0011] U.S. Pat. No. 4,847,340, "Novel propylene polymerization process," describes a process for the production of substantially amorphous copolymers consisting essentially of ethylene and propylene which comprises reacting from about 70 to about 96.5 wt. % propylene and from about 3.5 to about 30 wt. % ethylene at a temperature between about

130° F. and about 175° F. and at a reactor pressure sufficient to maintain propylene in the liquid phase, in the presence of from about 0.7 to about 3.0 mol % hydrogen based on the monomer feed to the process and employing as catalyst a composition of: (a) a solid catalyst component produced by the method comprising: (i) co-comminuting magnesium halide support base and aluminum trihalide in a molar ratio from about 8:0.5 to about 8:3 in the absence of added electron donor and (ii) then co-comminuting the product of step (i) in the absence of added electron donor with sufficient titanium tetrahalide to provide a molar ratio of magnesium halide to titanium tetrahalide from about 8:0.4 to about 8:1.

[0012] U.S. Pat. No. 3,954,697, "Poly(higher-1-olefin-co-propylene) copolymers as hot-melt, pressure-sensitive adhesives" describes a hot melt, pressure sensitive adhesive comprising an amorphous propylene/higher 1-olefin copolymer containing 40 to 60 mole percent higher 1-olefin having a melt viscosity range at 190° C. of 10,000 cp. to 75,000 cp., a density of 0.85 to 0.86 grs/cc, a glass transition temperature of -30° to -45° C., and having no melting point measurable by Differential Scanning Calorimetry, wherein said higher 1-olefin is a member of the group consisting of 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene.

[0013] U.S. Pat. No. 4,072,812, "Poly(higher-1-olefin/propylene) copolymers as hot-melt pressure-sensitive adhesives", describes a hot melt, pressure sensitive adhesive comprising an amorphous propylene/higher 1-olefin copolymer containing 40 to 60 mole percent higher 1-olefin having a melt viscosity range at 190° C. of 10,000 cps. to 75,000 cps., a density of 0.85 to 0.86 grs/cc, a glass transition temperature of -30° to -45° C., and having no melting point measurable by Differential Scanning Calorimetry, wherein said higher 1-olefin is at least two members of the group consisting of 1-hexene, 1-heptene, 1-octene, 1-nonene and 1-decene.

[0014] U.S. Pat. No. 4,169,116, "Blends of substantially amorphous olefin copolymers and compatible tackifying resins useful as hot-melt, pressure-sensitive adhesives", describes an adhesive composition capable of being used as a hot-melt, pressure-sensitive adhesive comprising a blend of (1) about 95 to 50 weight percent of a substantially amorphous olefin copolymer containing at least one C₃ to C₅ linear alpha-olefin and 40 to 60 mole percent of at least one higher alpha-olefin of 6 to 10 carbon atoms, said copolymer having a melt viscosity of >76,000 to 1,000,000 centipoise at 190° C., and (2) 5 to 50 weight percent of at least one compatible tackifying resin.

[0015] U.S. Pat. No. 4,210,570, "Blends of substantially amorphous olefin copolymers, compatible tackifying resins and plasticizing oils useful as hot melt, pressure-sensitive adhesives", describes an adhesive composition capable of being used as a hot-melt, pressure-sensitive adhesive comprising a blend of (1) about 98 to 25 weight percent of a substantially amorphous or semicrystalline olefin copolymer containing at least one C₃ to C₅ linear alpha-olefin and 15 to 60 mole percent of at least one higher linear alpha-olefin of 6 to 10 carbon atoms, said copolymer having a melt viscosity of 5,000 to 1,000,000 centipoise at 190° C., (2) 1 to 60 weight percent of at least one compatible tackifying resin, and (3) 1 to 25 weight percent plasticizing oil.

[0016] U.S. Pat. No. 4,288,358, "Blends of propylene/1-butene or 1-pentene/higher alpha-olefin copolymers, compatible tackifying resins and plasticizing oils useful as hot-melt, pressure-sensitive adhesives," describes an adhe-

sive composition capable of being used as a hot-melt, pressure-sensitive adhesive comprising a blend of (1) about 98 to 25 weight percent of an olefin copolymer containing 10-65 mole % propylene, 15-75 mole % of either 1-butene or 1-pentene and 3 to 14 mole percent of at least one higher linear alpha-olefin of 6 to 10 carbon atoms, said copolymer having a melt viscosity of 10,000 to 1,000,000 centipoise at 190° C., (2) 1 to 60 weight percent of at least one compatible tackifying resin, and (3) 1 to 25 weight percent plasticizing oil.

[0017] U.S. Pat. No. 4,826,939, "Highly amorphous olefin terpolymer", describes an amorphous, pressure-sensitive terpolymer comprising repeating units from about 0.1 to about 10 percent by weight ethylene, from about 30 to about 78 percent by weight propylene, and from 20 to 70 percent by weight 1-hexene, the terpolymer having a ring-and-ball softening point of from about 75° C. to about 120° C., a melt viscosity of from about 100 to about 100,000 cps at 190° C., no DSC melting point, and a 180° peel strength of at least about 1.2 pounds/inch. Also described is a process for producing an amorphous, pressure-sensitive terpolymer having no DSC melting point comprising continuously polymerizing a mixture of from about 0.1 to about 10 percent by weight ethylene, from about 30 to about 78 percent by weight propylene, and from about 20 to about 70 percent by weight 1-hexene, in the presence of a catalyst comprising an anionic coordination catalyst and in a solvent medium, at a temperature of from about 140° C. to about 250° C. and at a pressure of about 100 to about 5,000 pounds per square inch gauge.

[0018] The contents of each of the above-listed patents is hereby incorporated by reference in its entirety.

BRIEF SUMMARY OF THE INVENTION

[0019] Propylene-co-hexene-1 copolymers, optionally containing 1-butene monomer to form propylene-co-hexene-1-co-butene-1 terpolymers, are made using a supported Ziegler-Natta catalyst either with or without an in-reactor added organosilicon external donor.

[0020] Copolymers and terpolymers according to the invention may be used in the formulation of improved-performance APAO-based hot melt adhesives.

DETAILED DESCRIPTION OF THE INVENTION

[0021] Due to the compositional nature of propylene-co-hexene-1 copolymer APAOs, and optionally propylene-co-hexene-1-co-butene-1 terpolymers, each of the comonomers adds a unique set of properties to the APAO, which may be enhanced, or changed, by the addition of an external organosilicon donor.

[0022] The use of these APAO copolymers and terpolymers, may add unique properties when used as components in hot melt adhesive formulations such as those used preferentially in pressure-sensitive adhesives and also in such applications as in personal hygiene products (e.g. diapers, feminine hygiene, elastic attachment, etc.), in assembly, construction, lamination, footwear and other applications that require such properties as permanent tackiness, controllable open time, low-temperature flexibility, good temperature resistance and other such desirable properties.

[0023] An HMA according to the present invention may be made up of a propylene-co-hexene-1 copolymer APAO

with a hexene-1 content of about 10 wt. %, more preferably, about 25 wt. %, much more preferably with about 30 wt. % and most preferably with about 50 wt. % by weight but it may contain up to 90 wt. %. This copolymer may be utilized in an unformulated form, that is, as-obtained from the reactor APAO. When applied, or coated, as a hot melt, or cast from an organic solvent solution, onto a substrate typically such as stock paper or a plastic film or any other porous or non-porous substrate (the primary substrate) by any of the commercially known and used coating methods, the subject of this invention bonds strongly, forming a destructive bond to the primary substrate.

[0024] Pressure sensitive applications (PSA's) require good adhesion to a variety of substrates, but such adhesion should be reversible and no adhesive should be transferred to the surface or secondary substrate or substrates onto which the primary substrate coated with the HMA subject of this invention, may be applied. This copolymer exhibits this type of PSA properties. Such types of pressure sensitive adhesives may be considered for removable applications such as removable tapes and labels. The addition of another monomer component such as butene-1, results in a propylene-co-hexene-1-co-butene-1 terpolymer APAO with an even broader envelope of PSA- and other HMA-properties and performance. The terpolymer may have a butene-1 content of up to 40 wt. %; however, it should preferably have about 5 to 25 wt. % and most preferably 5 to 10 wt. % by weight. Moreover, the addition of a so-called external donor of the organosilicon class, such as for example cyclohexylmethyldimethoxysilane (CMDMS), or phenyltriethoxysilane (PES), imparts certain unique characteristics to the physical and mechanical properties of the copolymer and also to the terpolymer, properties that reflect favorably in the final performance of the hot melt adhesive containing it.

[0025] Co-adjuvants may form a part of the subject HMA, such as tackifiers, preferably the type considered compatible with APAO polymers. Such tackifiers are of the partially and fully hydrogenated C5, hydrogenated C5-C9, and hydrogenated DCPD-type resins but may be any other tackifier which, by its chemical nature, is compatible with the APAO terpolymer. Yet other components may be polyethylene, maleic anhydride grafted polyethylene, Fischer-Tropsch paraffinic waxes and metallocene waxes. These, as well as other similar compatible waxes, have the effect of controlling the melt viscosity and also controlling the rate of set of the HMA. Also, so-called liquid plasticizers such as mineral, paraffinic or naphthenic oils, may be used in the terpolymer-based formulation to add such properties as melt viscosity control, tackiness and controllable open time. Also, components such as anti-oxidants and UV stabilizers may be added as co-adjuvants. Other compatible polymers which may be included in the formulation of the subject HMA include, for example, hydrogenated styrene block copolymers of the SEBS and SEPS type and polyethylenes such as LLDPE of melt indices (MIs) of typically more than 500 dg/min. Also used, preferably as the minor component, may be the so-called metallocene polyethylenes which are known in the art as mPEs and whose composition consists of ethylene copolymerized with such alpha-olefins as 1-butene or 1-hexene or 1-octene. Metallocene polypropylenes (mPP), of the appropriate molecular weight so as to be compatible with the subject APAO terpolymer, may also be added as a minor component.

[0026] Both the propylene-co-hexene-1 copolymer and propylene-co-butene-1-co-hexene-1 terpolymer may be made according to the teachings of U.S. Pat. No. 4,847,340, whereby they are made at a temperature between about 130° F. and about 175° F. and at a reactor pressure sufficient to maintain propylene in the liquid phase (in the absence of any added solvent), and in the presence of from about 0.7 to about 3.0 mol % hydrogen based on the monomer feed. The hydrogen concentration present during the manufacture of the subject copolymers and terpolymers may be adjusted so that their melt viscosity, measured at 375° F., is less than 3500 cps, preferably less than 3000 cps.

[0027] The use of the propylene-hexene-1 and propylene-co-hexene-1-co-butene-1 APAOs made in the presence of the externally added organosilicon when used either unformulated or, alternatively, properly formulated with the above-named co-adjuvants, at concentrations of 0 to up to 25 wt. % of tackifier(s), or between 0 to about 15 wt. % of the above-mentioned wax(es), or between 0 and 25 wt. % of the above mentioned oil(s), will result in hot melt adhesives with enhanced properties for use in pressure-sensitive adhesives, and also in personal hygiene products (e.g. diapers, feminine hygiene, elastic attachment, etc.), in assembly, and other such applications.

[0028] The above-named co-adjuvants may interact with the long polymeric chains of the propylene-co-hexene-1 and propylene-co-hexene-1-butene-1 APAOs made in the presence of the externally added organosilicon in such a way as to result in an HMA with a lower, yet desirable, melt viscosity which results in better wetting and penetration of various substrates, porous, or non-porous, resulting in a higher degree of adhesive bonding. Also, the interaction of the multiple components results in a higher, yet controllable, tackiness for such applications which demand a certain degree of tackiness and pressure sensitive adhesiveness. Other interactions will become obvious to the user.

[0029] A hot-melt adhesive according to the invention may comprise: a) an APAO copolymer or terpolymer, preferably made in the presence of an externally added donor; b) a tackifier; and optionally, c) a wax component of the type(s) described above and d) a liquid plasticizer such as mineral oil or a naphthenic oil.

Experimental Conditions

[0030] Several propylene-co-hexene-1 copolymerization and propylene-co-butene-1-co-hexene-1 terpolymerization reactions were carried out either in the absence or in the presence of an external donor. External donors such as phenyltriethoxysilane (PES or A-Donor, CAS No. 780-69-8) or cyclohexylmethyldimethoxysilane (CMDMS or C-Donor, CAS No. 17865-32-6) were used. Other silane-based external donors such as diphenyldimethoxysilane (B-Donor, CAS No. 6843-66-9), diisobutyldimethoxy silane (CAS No. 17980-32-4), dicyclopentylmethoxy silane (DDMS or D-Donor, CAS No. 126990-35-0) and diisopropylmethoxy silane (DPMS or P-Donor, CAS No. 18230-61-0) may also be used. Yet other less-common silane-based donors may also be used for the reactions in the subject matter.

[0031] The polymerization reactions were carried out in an Autoclave Engineers™ 1-L autoclave typically at 70° C. and for one hour. Before running a reaction, the autoclave was cleaned of any residual polymer from any previous reaction using an organic solvent such as heptane to assure a clean reactor. The agitator/mixer assembly was placed on top of

the autoclave which was then tightened securely. The autoclave was then heated, or baked, at 150° C., under a dry nitrogen atmosphere for about one hour, and then the autoclave was cooled to about 40° C., still under a nitrogen blanket. The temperature was controlled with a Julabo GmbH temperature control unit. A more detailed description of the polymerization process is described for example in U.S. Pat. Nos. 5,681,913, 5,637,665, 5,714,554 and/or 5,302,675. Once the reactor reached the set temperature, a mineral oil slurry of the catalyst, pre-contacted with the alkyl aluminum co-catalyst, TEA, was dosed into the reactor, followed by the monomers [propylene (CAS No. 115-07-1), butene-1 (CAS No. 106-98-9) and hexene-1 (CAS No. 592-41-6)], and by the hydrogen gas. The reaction was started by turning on the agitator and typically the reactions were quite exothermic but the Julabo unit was efficient in controlling the reaction temperature. The order of addition of the reactants may be varied to a certain extent, but the catalyst/cocatalyst mixture was always introduced first. After the prescribed reaction time, for example 1 hour, the agitator was stopped, the temperature of the Julabo unit was reduced and the autoclave was slowly depressurized to remove any unreacted reactants. Due to the high productivity, in grams of polymer produced per gram of catalyst, no catalyst deactivation, other than exposure to the atmosphere, was required. Once decompressed, the top was removed and the polymer was harvested from the reactor. Other polymerization reaction temperatures as low as 40° C. and as high as 90° C. may also be used. Reaction times may range from 5 minutes to as long as three hours. The reactions were performed in the absence of any added organic solvent because the liquefied monomers a) serve to remove the high exothermal heat of polymerization reaction, and b) serve as the suspension medium for the formed polymeric products.

[0032] The propylene monomer used was of very high purity, typically 99.99%+propylene with the remaining components being low-molecular-weight saturated hydrocarbons. This type of propylene is known in the trade as PGP or polymer grade propylene. Other propylene grades such as CGP, or chemical grade propylene, typically made up of at least 90+% propylene with the balance consisting of inert hydrogenated hydrocarbons may also be used. RGP, or refinery grade propylene, wherein the propylene content is usually 65-75%, propane is 20-30%, with the balance

butane/butylene (BB) and ethylene/ethane may also be used but it gives quite low polymer yields.

[0033] The butene-1 monomer used was high purity plant butene or it may be from what is called bottled, in small tanks, butene-1, with purities typically over 99+%. The hexene-1 used in the reactions was high purity (>97%) from vendors such as Sigma-Aldrich.

[0034] TABLE 1 shows 22 polymerization reactions that were run varying the amounts of monomers, external donor (as represented by the F2/F3 ratio), or the alkyl aluminum-to-donor ratio, and the hydrogen pressure to control the melt viscosity or molecular weight of the produced polymers. Total reaction volume was targeted at 700 ml. The reaction variables were chosen using a full factorial design of experiment, DoE, generated by Minitab 15 DoE software which covered a broad spectrum of factors or reaction variables.

TABLE 1

Example	C3=, ml	C4=, ml	C6=, ml	H ₂ , psi	F2/F3
1	300	0	400	60	400
2	375	75	250	90	200
3	150	150	400	120	400
4	375	75	250	90	200
5	150	150	400	60	400
6	450	150	100	60	0
7	150	150	400	120	0
8	150	150	400	60	0
9	450	150	100	120	400
10	450	150	100	60	400
11	375	75	250	90	200
12	300	0	400	60	0
13	375	75	250	90	200
14	375	75	250	90	200
15	300	0	400	120	400
16	375	75	250	90	200
17	300	0	400	120	0
18	300	0	100	120	0
19	300	0	100	60	0
20	450	150	100	120	0
21	600	0	100	60	400
22	600	0	100	120	400

TABLE 2

Physical and mechanical characterization of the polymerization products.									
Example	C4=, %	C6=, %	MV, cps	NP, dmm	RBSP, ° F.	OT, sec	RBT, cm	TS, psi	SAFT, ° F.
1	NA	49.2	1530	82	233	PSA	3 ± 1.6	Too Soft	110 ± 3
2	2.4	29.7	1248	42	253	PSA	1.8 ± 0.3	59 ± 3	149 ± 4
3	19.8	47.9	1147	TS	TS	PSA	2.0 ± 0.5	Too Soft	<85
4	2.2	28.2	1150	39	254	100	3.0 ± 1.2	25 ± 1.4	149 ± 2
5	10.6	9.4	4738	166	131	PSA	1.9 ± 0.4	Too Soft	<85
6	14.4	11.3	1855	31	254	150	24 ± 1.7	86 ± 3	184 ± 6
7	13.4	11.5	440	TS	TS	PSA	1.4 ± 0.2	Too Soft	83 ± 3
8	19.6	47.0	1500	~187	TS	PSA	1.2 ± 0.3	Too Soft	88 ± 3
9	10.4	10.2	1010	23	269	30	>30	183 ± 8	222 ± 12
10	12.4	9.8	4250	17	267	40	>30	323 ± 18	235 ± 6
11	4.4	26.9	718	42	254	100	16 ± 2.9	50 ± 2	154 ± 3
12	NA	57.2	1313	145	212	PSA	1.1 ± 0.3	Too Soft	176 ± 4
13	4.5	28.7	7275	36	259	240	2.3 ± 0.2	1.7 ± 0.1	158 ± 6
14	4.9	32.4	905	62	237	PSA	1.8 ± 0.8	29 ± 1	133 ± 4
15	NA	55.7	400	~286	144	PSA	2.5 ± 1.1	Too Soft	87 ± 3
16	4.7	31.5	800	70	232	PSA	1.4 ± 0.2	19 ± 0.4	123 ± 3

TABLE 2-continued

Physical and mechanical characterization of the polymerization products.									
Example	C4=, %	C6=, %	MV, cps	NP, dmm	RBSP, ° F.	OT, sec	RBT, cm	TS, psi	SAFT, ° F.
17	NA	50.1	520	155	215	Too Soft	1.6 ± 0.4	Too Soft	110 ± 4
18	NA	14.5	845	13	278	10	>30	110 ± 9	245 ± 6
19	NA	13.0	13000	15	285	10	>30	495 ± 29	256 ± 8
20	13.6	11.5	750	36	251	100	>30	60 ± 3	188 ± 5
21	NA	11.2	20750	8	290	Too Thick	>30	880 ± 70	275 ± 2
22	NA	13.5	980	13	280	10	>30	236 ± 18	254 ± 3

[0035] The concentration of incorporated butene-1 in the polymers (C4=, %), as well as the concentration of hexene-1 (C6=, %), was obtained using a proprietary FTIR spectroscopic test method. The melt viscosity, MV, was typically determined at 375° F. (190° C.), as per the ASTM D-3236 test method. The needle penetration, NP, was determined at 72 to 75° F., as per the ASTM D-1321 test method, while the ring and ball softening point, RBSP, was determined as per ASTM E-28. The open time, OT, as per ASTM D-4497, and the rolling ball tack, RBT, as per a modified ASTM D-3121 test. The tensile strength, TS, was determined as per ASTM D-638, and finally the shear adhesion failure temperature as per a modified TMHM-32 test.

EXAMPLES

Example 1

[0036] An Autoclave Engineers™ 1-L autoclave, properly conditioned as described above, to which calculated amounts of catalyst, co-catalyst and external donor, e.g. PES (targeting a F2/F3 of 400) were added, was loaded with 300 ml of propylene and 400 ml of hexene-1 and with 60 psi of hydrogen overpressure. The reaction was started and after an hour, it was stopped, unreacted monomers were vented and a soft solid product was recovered. The properties are described in Table 2 and according to a test commonly used in the pressure sensitive industry, the RBT of about 2 to 4 cm would give this product PSA properties.

Example 2

[0037] The same procedure as described in Example 1 was followed targeting a F2/F3 of 200, but adding 375 ml of propylene, 75 ml of butene-1, 250 ml of hexene-1 and 90 psi of hydrogen. The reaction was started, allowed to proceed for an hour, then stopped, unreacted monomers were vented and a somewhat harder solid than that of Example 1 was recovered. The properties are presented in Table 2 and a RBT of about 1.5 to 2 cm would give this product PSA properties.

Example 9

[0038] The same procedure as described in Example 1 was followed targeting a F2/F3 of 400, but adding 150 ml of propylene, 150 ml of butene-1, 400 ml of hexene-1 and 120 psi of hydrogen. The reaction was started, allowed to proceed for an hour, then stopped, unreacted monomers were vented and a somewhat harder solid than that of Example 1 was recovered. The properties are presented in Table 2 and a RBT of over 30 cm does not give it PSA properties.

[0039] The data presented in the above tables indicates that different polymer properties are obtained when using different reaction variables.

[0040] The foregoing presents particular embodiments of a system embodying the principles of the invention. Those skilled in the art will be able to devise alternatives and variations which, even if not explicitly disclosed herein, embody those principles and are thus within the scope of the invention. Although particular embodiments of the present invention have been shown and described, they are not intended to limit what this patent covers. One skilled in the art will understand that various changes and modifications may be made without departing from the scope of the present invention as literally and equivalently covered by the following claims.

What is claimed is:

1. A hot-melt formulation comprising:

- a propylene-co-hexene-1-co-butene-1 terpolymer made using a supported Ziegler-Natta catalyst, at a process temperature between about 130° F. and about 175° F. and at a reactor pressure sufficient to maintain propylene in the liquid phase (in the absence of any added solvent) and the hydrogen concentration present during the manufacture of the subject terpolymers is adjusted so that their melt viscosity, measured at 190° C., is less than 3500 cps, preferably less than 3000 cps, optionally in the presence of an organo-silane external donor and optionally with,
- a tackifier; and/or
- a styrenic block copolymer; and/or
- a high melt flow index metallocene or single-site catalyzed polyethylene; and/or
- a high melt flow rate polypropylene, either a homopolymer or random copolymer, of varying degrees of crystallinity or isotacticity, functionalized or without any polar functionality; and/or
- a wax component; and/or
- a liquid plasticizer.

2. The hot-melt formulation of claim 1 wherein the copolymer is made in the presence of an externally-added organosilicon donor.

3. The hot-melt formulation of claim 8 wherein the terpolymer is made in the presence of an externally-added organosilicon donor.

4. The hot-melt formulation of claim 1 comprising a propylene-co-hexene-1 copolymer with a boiling heptane insolubility of less than 20 wt. %.

5. The hot-melt formulation of claim 1 comprising a propylene-co-hexene-1 copolymer manufactured in the absence of any added solvent

6. The hot-melt formulation of claim 1 wherein the liquid plasticizer comprises a naphthenic oil.

7. The hot-melt formulation of claim 8 wherein the liquid plasticizer comprises a naphthenic oil.

8. The hot-melt formulation of claim 1 wherein the liquid plasticizer comprises a paraffinic oil.

9. The hot-melt formulation of claim 8 wherein the liquid plasticizer comprises a paraffinic oil.

10. The hot-melt formulation of claim 1 wherein the wax component comprises a paraffinic wax.

11. The hot-melt formulation of claim 8 wherein the wax component comprises a paraffinic wax.

12. The hot-melt formulation of claim 1 wherein the wax component comprises a metallocene wax.

13. The hot-melt formulation of claim 2 wherein the wax component comprises a metallocene wax.

14. The hot-melt formulation of claim 1 wherein the terpolymer is made at a process temperature between about 130° F. and about 175° F. and at a reactor pressure sufficient to maintain propylene in the liquid phase (in the absence of any added solvent).

15. The hot-melt formulation of claim 1 wherein the hydrogen concentration present during the manufacture of the terpolymer is adjusted such that its melt viscosity, measured at 375° F., is less than 3500 cps.

16. The hot-melt formulation of claim 1 wherein the hydrogen concentration present during the manufacture of the terpolymer is adjusted such that its melt viscosity, measured at 375° F., is less than 3000 cps.

* * * * *