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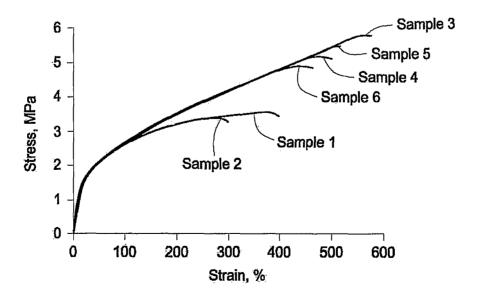
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(54) Title: ELASTOMERIC COMPOSITIONS



(57) Abstract: A composition comprising: (i) at least one low molecular weight polyolefm; (ii) at least one block copolymer obtainable by selectively hydrogenating a block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a mid-block prepared originally with an olefin and subsequently hydrogenated; (iii) at least one polypropylene; and (iv) at least one plastomer, wherein the plastomer is an ethylene based polymer having a density of 0.86 g/cc to about 0.910 g/cc or a propylene based polymer having a heat of fusion (Hf) of 70 J/g or less.





TITLE: ELASTOMERIC COMPOSITIONS

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#### PRIORITY CLAIM

[0001] This invention claims the benefit of and priority to USSN 60/699,718, filed July 15, 2005.

#### FIELD OF THE INVENTION

[0002] The invention relates to modification of compositions comprising hydrogenated block copolymers, particularly styrenic block copolymers, to make elastomeric compositions (i.e. "elastomeric-like compositions") with improved flexibility after prolonged heat-aging and/or cooling with less surface blooming.

# BACKGROUND OF THE INVENTION

[0003] Thermoplastic elastomers (TPEs) are phase-separated systems in which at room temperature, the dispersed phase is rigid (i.e. glassy and/or crystallized) and the matrix phase is soft and elastomeric. The rigid domains act as crosslinks for the elastomeric phase, which is analogous to chemical crosslinks in conventional vulcanized rubbers. However, the crosslinks of the rigid domain is often referred to as physical crosslinking because flow can occur when the TPE is processed at high temperatures. Usually, TPEs have two service temperatures due to this phase-separated structure. The lower service temperature depends on the glass transition temperature of the elastomeric phase, Tg1, whereas the upper service temperature depends on the glass transition temperature of the glassy phase, Tg2, and/or its melting point, Tm, if crystallizable. Thus, the application

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temperature window of the TPE is represented by  $\Delta T = T_{g2} - T_{g1} \text{ or } T_m - T_{g1}.$ 

[0004] A plasticizer can be used to reduce the stiffness and/or  $T_g$  of a polymer. As an added benefit, a plasticizer can also improve the processability of the polymer. Plasticizers are liquids of low volatility and good thermal stability. Plasticizers are typically organic esters, e.g., phthalates, trimellitates, and adipates for plasticizing poly(vinyl chloride) (PVC). Typically, plasticizer efficiency is proportional to the  $T_g$  of the polymer to be plasticized. In other words, the efficiency is greater when the polymer has a higher  $T_g$ .

Hydrogenated styrenic block copolymers, such as those having a [0005] saturated ethylene-butene-1 mid-block (i.e., SEBS), possess good thermal However, their use in certain processes, such as thermoforming stability. operations, is limited because of poor processability. This is thought to be a result of the high incompatibility of the styrene end-block and the EB mid-block even in the melt state. Therefore, despite its stability to high temperatures, ultraviolet light, or ozone, SEBS is seldom used alone. Some common compounding ingredients for SEBS are oils, polyethylene, polypropylene, and fillers. Oils make the products softer and also act as processing aids. Paraffinic oils are preferred because they are more compatible with the EB center block. Aromatic oils are generally avoided because they intrude into and plasticize the polystyrene domains. Blends with as high as 90% oil (5% SEBS and 5% wax) have been used as cable filling compounds, which occupy the voids in "bundled" telephone cables and prevent water seepage. Other applications include toys, hand exercising grips, etc.

[0006] Polypropylene (PP) is the preferred polymeric additive to SEBS because it ameliorates the aforementioned processability problem when used in conjunction with process oils. In injection molding or extrusion molding of useful parts, the PP/SEBS/oil mixture forms two co-continuous phases. The high melting-point PP phase enhances both the solvent-resistance and heat-resistance of the compounds. Additionally, the presence of SEBS improves the impact

resistance of PP, especially at low temperatures. Normally this would be accompanied by a loss in clarity because the added polymer forms a separate phase with a different refractive index. However, PP/SEBS blends are nearly as transparent as neat PP, probably because of matched refractive indices. In some applications, LLDPE is added to SEBS. Blends of LLDPE/SEBS with PP also retain the clarity of the neat PP and show improved impact resistance. These blends are mostly used to make blown film, where they have improved impact resistance and tear strength, especially in the seal area.

[0007] As a generalization, conditions for processing compounds based on SEBS by injection molding, blow molding, extrusion, etc. are processed under conditions suitable for PP. However, difficulties exist in using high levels of process oil in the blends to achieve lower values of hardness because the oil tends to bloom to the surface ("surface blooming") and/or emit from the polymers during service. Oils also have a yellowish appearance which detracts from the optical properties in the final product. Further, oils tend to emit a distinct odor which detracts from its use in closed or contained environments, such as automotive interiors.

[0008] Typically, mineral oils or synthetic oils are added as the processing oil or plasticizer to block copolymers including SEBS polymers to improve processability. Mineral oils are any petroleum-based oil that is derived from petroleum crude oil and subjected to refining steps, such as distillation, solvent processing, hydroprocessing, and/or dewaxing to achieve the final oil. This also includes petroleum-based oils that are extensively purified and/or modified through severe processing treatments. Examples of commercially available mineral oils include but are not limited to Drakeol from Penreco (USA), Paralux from Chevron (USA), Sunpar from Sunoco (USA), Plastol and Flexon from ExxonMobil (USA), Shellflex from Royal Dutch Shell (UK/Netherlands), and Diana from Idemitsu (Japan).

[0009] Other block copolymer blends have been proposed to improve processability and maintain thermal stability. For example, U.S. Patent No.

4,904,731 teaches polymeric compositions of a C2-C10 olefin polymer, a hydrogenated block copolymer, and an LLDPE, useful for shaped structures having good clarity and good impact strength. U.S. Patent No. 5,925,707 discloses oil gel compositions of styrene block copolymers, oil, and optionally a polyolefin wax and/or liquid extender. WO 02/31044 discloses a composition of SEBS, polypropylene, and a polydecene having a molecular weight of from about 400 and 1000 g/mol to make flexible products. Other references include U.S. Patent No. 4,132,698; U.S. Patent No. 4,960,820; WO 01/18109; WO 2004/014998; and EP 0300689.

[0010] There is a need, therefore, for an elastomeric block copolymer having improved flexibility after prolonged heat-aging and/or cooling with less surface blooming.

#### **SUMMARY OF THE INVENTION**

- [0011] A composition having surprisingly improved flexibility after prolonged heat-aging and/or cooling and/or decreased surface blooming, and methods for making the same are provided. In one or more embodiments, the composition comprises:
  - (i) at least one low molecular weight polyolefin;
- (ii) at least one block copolymer obtainable by selectively hydrogenating a block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a mid-block prepared originally with an olefin and subsequently hydrogenated;
  - (iii) at least one polypropylene; and
- (iv) at least one plastomer, wherein the plastomer is an ethylene based polymer having a density of 0.86 g/cc to about 0.910 g/cc or a propylene based polymer having a heat of fusion (Hf) of 70 J/g or less.

# BRIEF DESCRIPTION OF THE DRAWINGS

[0012] So that the manner in which the above recited features of the present invention can be understood in detail, a more particular description of the invention, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0013] Figure 1 is a stress-strain curve of illustrative blends according to one or more embodiments described. The blends correspond to samples 1-6 described in the Examples below.

[0014] Figure 2 is a graphical representation showing the relationship between the Vicat softening temperature and the  $T_{\rm g2}$  of the illustrative blends.

[0015] Figure 3 is a graphical representation showing weight losses of the illustrative blends in TGA at 150°C for 2 hr.

## **DETAILED DESCRIPTION**

claims defines a separate invention, which for infringement purposes is recognized as including equivalents to the various elements or limitations specified in the claims. Depending on the context, all references below to the "invention" can in some cases refer to certain specific embodiments only. In other cases it will be recognized that references to the "invention" will refer to subject matter recited in one or more, but not necessarily all, of the claims. Each of the inventions will now be described in greater detail below, including specific embodiments, versions and examples, but the inventions are not limited to these embodiments, versions or examples, which are included to enable a person having

ordinary skill in the art to make and use the inventions, when the information in this patent is combined with available information and technology.

[0017] In one or more embodiments, the composition comprises one or more low molecular weight polyolefins, selectively hydrogenated block copolymers, polypropylenes, and plastomers. Surprisingly, it has been discovered that the addition of the one or more low molecular weight polyolefins to a blend of one or more selectively hydrogenated block copolymers, polypropylenes, and plastomers provides for compositions having improved flexibility after prolonged heat-aging and/or cooling. The compositions also surprisingly have decreased surface blooming.

### Low Molecular Weight Polyolefins

[0018] The one or more low molecular weight polyolefins according to the present invention can be any polyolefin having a number-average molecular weight (Mn) of less than 21,000 g/mol. Such polyolefins include oligomers such as C5-C14 alphaolefins, including copolymers thereof, and oligomers of ethylene/butene-1 and isobutylene/butene-1. In one or more embodiments, the low molecular weight polyolefins can be or can include at least one non-functionalized plasticizer ("NFP").

[0019] In one or more embodiments above or elsewhere herein, the NFP is or includes an isoparaffin-rich hydrocarbon. In one or more embodiments above or elsewhere herein, the NFP is or includes a polyalphaolefin (PAO). In one or more embodiments above or elsewhere herein, the NFP is or includes a high purity hydrocarbon fluid. In one or more embodiments above or elsewhere herein, the NFP is or includes a Group III hydrocarbon oil (also called a Group III lubricant basestock or Group III mineral oil).

### Non-Functionalized Plasticizer (NFP)

[0020] A NFP is a hydrocarbon liquid, that is a liquid compound comprising carbon and hydrogen, which does not include to an appreciable extent functional

groups selected from hydroxide, aryls and substituted aryls, halogens, alkoxys, carboxylates, esters, carbon unsaturation, acrylates, oxygen, nitrogen, and carboxyl. By "appreciable extent", it is meant that these groups and compounds comprising these groups are not deliberately added to the NFP, and if present at all, are present at less than 5 wt% by weight of the NFP in one embodiment, more preferably less than 4 wt%, more preferably less than 3 wt%, more preferably less than 2 wt%, more preferably less than 1 wt%, more preferably less than 0.7 wt%, more preferably less than 0.5 wt%, more preferably less than 0.3 wt%, more preferably less than 0.1 wt%, more preferably less than 0.05 wt%, more preferably less than 0.01 wt%, more preferably less than 0.01 wt%, more preferably less than 0.01 wt%, based upon the weight of the NFP.

[0021] In one embodiment, aromatic moieties (including any compound whose molecules have the ring structure characteristic of benzene, naphthalene, phenanthrene, anthracene, etc.) are substantially absent from the NFP. By "substantially absent", it is meant that these compounds are not added deliberately to the compositions and if present at all, are present at less than 0.5 wt%, preferably less than 0.1 wt%.

[0022] In another embodiment, naphthenic moieties (including any compound whose molecules have a saturated ring structure such as would be produced by hydrogenating benzene, naphthalene, phenanthrene, anthracene, etc.) are substantially absent from the NFP. By "substantially absent", it is meant that these compounds are not added deliberately to the compositions and if present at all, are present at less than 0.5 wt%, preferably less than 0.1 wt%.

[0023] In another embodiment, the NFP is a hydrocarbon that does not contain olefinic unsaturation to an appreciable extent. By "appreciable extent of olefinic unsaturation" it is meant that the carbons involved in olefinic bonds account for less than 10% (preferably less than 8%, more preferably less than 6%, more preferably less than 4%, more preferably less than 2%, more preferably less than 1%, more preferably less than 0.7%, more preferably less than 0.5%, more preferably less than 0.3%, more preferably less than 0.1%, more preferably less

than 0.05%, more preferably less than 0.01%, more preferably less than 0.001%) of the total number of carbons. In some embodiments, the percent of carbons of the NFP involved in olefinic bonds is between 0.001 and 10% of the total number of carbon atoms in the NFP, preferably between 0.01 and 5%, preferably between 0.1 and 2%, more preferably less than 1%.

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[0024] Particularly preferred NFPs include isoparaffins, PAOs, Group III basestocks or mineral oils, high purity hydrocarbon fluids derived from a so-called Gas-To-Liquids processes, and mineral oils with a viscosity index greater than 100, pour point less than -20°C, specific gravity less than 0.86, and flash point greater than 200°C.

[0025] In another embodiment, the NFP comprises C6 to C200 paraffins, and C8 to C100 paraffins in another embodiment. In another embodiment, the NFP consists essentially of C6 to C200 paraffins, or essentially of C8 to C100 paraffins in another embodiment. In yet another embodiment, the NFP comprises C20 to C1500 paraffins, preferably C25 to C500 paraffins, preferably C25 to C500 paraffins, preferably C30 to C500 paraffins, preferably C40 to C500 paraffins, preferably C40 to C500 paraffins, preferably C30 to C150 paraffins, preferably C20 to C100 paraffins. In a preferred embodiment, the NFP comprises oligomers of C5 to C24 olefins.

#### Isoparaffins

In one embodiment of the present invention, the NFP is an isoparaffinrich hydrocarbon liquid with a pour point of -50°C or less (preferably -60°C or less) and a specific gravity of 0.84 or less (preferably 0.83 or less). By isoparaffin-rich is meant that the NFP comprises at least 50 wt% (preferably at least 60 wt%, preferably at least 70 wt%, preferably at least 80 wt%, preferably at least 90 wt%, preferably 100 wt%) of C6 to C150 (preferably C6 to C100, preferably C6 to C25, preferably C8 to C20) isoparaffins. Preferably the paraffin chains possess C1 to C10 alkyl branching along at least a portion of each paraffin chain. More preferably, the isoparaffins are saturated aliphatic hydrocarbons

whose molecules have at least one carbon atom bonded to at least three other carbon atoms or at least one side chain (i.e., a molecule having one or more tertiary or quaternary carbon atoms), wherein the number-average molecular weight is in the range of 100 to 1000 (preferably 120 to 500, preferably 150 to 300) g/mol.

[0027] In another embodiment, the isoparaffin-rich NFP has a kinematic viscosity at 25°C of 30 cSt or less (preferably 25 cSt or less, preferably 20 cSt or less, preferably 15 cSt or less) and a glass transition temperature (Tg) that cannot be determined by ASTM E 1356 or if it can be determined then the Tg according to ASTM E 1356 is preferably less than 0°C, more preferably less than -10 °C, more preferably less than -20 °C, more preferably less than -30 °C. Preferably the number-average molecular weight of the isoparaffin-rich NFP is in the range of 100 to 300 g/mol.

In another embodiment, the isoparaffin-rich NFP is a mixture of [0028] branched and normal paraffins having from 6 to 50 carbon atoms, and from 10 to 24 carbon atoms in another embodiment, in the molecule. The isoparaffin composition has a ratio of branch paraffin to n-paraffin ratio (branch paraffin:nparaffin) ranging from 0.5:1 to 9:1 in one embodiment, and from 1:1 to 4:1 in another embodiment. The isoparaffins of the mixture in this embodiment contain greater than 50 wt% (by total weight of the isoparaffin composition) mono-methyl species, for example, 2-methyl, 3-methyl, 4-methyl, 5-methyl or the like, with minimum formation of branches with substituent groups of carbon number greater than 1, such as, for example, ethyl, propyl, butyl or the like, based on the total weight of isoparaffins in the mixture. In one embodiment, the isoparaffins of the mixture contain greater than 70 wt% of the mono-methyl species, based on the total weight of the isoparaffins in the mixture. The isoparaffinic mixture boils within a range of from 100°C to 350°C in one embodiment, and within a range of from 110°C to 320°C in another embodiment. In preparing the different grades, the paraffinic mixture is generally fractionated into cuts having narrow boiling ranges, for example, 35°C boiling ranges. These branch paraffin/n-paraffin blends are described in, for example, US 5,906,727.

[0029] Suitable isoparaffin-rich hydrocarbon liquids are described in, for example, US 6197285, US 3818105 and US 3439088, and are commercially available under the tradename ISOPAR<sup>TM</sup> (ExxonMobil Chemical), some of which are summarized in Table B. Other suitable isoparaffin-rich hydrocarbon liquids are commercial available under the trade names SHELLSOL<sup>TM</sup> (Royal Dutch/Shell), SOLTROL<sup>TM</sup> (Chevron Phillips) and SASOL<sup>TM</sup> (Sasol Limited). The percentage of carbons in chain-type paraffinic structures (CP) in such liquids is close to 100% (95% or more).

Table A. ISOPAR™ Series Isoparaffins

	KV @ 25°C (cSt)	pour point (°C)	specific gravity	flash point (°C)	distillation range (°C)
ISOPAR G	1.5	-57	0.75	106	161-176
ISOPAR H	1.8	-63	0.76	127	178-188
ISOPAR K	1.9	-60	0.76	131	179-196
ISOPAR L	2.0	-57	0.77	144	188-207
ISOPAR M	3.8	-57	0.79	198	223-254
ISOPAR V	14.8	-63	0.82	266	272-311

[0030] In another embodiment the isoparaffin-rich NFP has one or more of the following properties: a distillation range (as determined by ASTM D 86) having a difference between the upper temperature and the lower temperature of 40 °C or less, preferably 30 °C or less, preferably 20 °C or less, preferably 10 °C or less, preferably between 6 and 40 °C; and or a glass transition temperature (Tg) determined by ASTM E1356 of less than 0°C, preferably less than -10°C, more preferably less than -20°C, more preferably less than -30°C, more preferably less than -50°C, or most preferably a Tg that can not be determined by ASTM E1356; and or a pour point (as determined by ASTM D 97) of -40 °C or less, preferably -50 °C or less, preferably -60 °C or less; and or a specific gravity (as determined by ASTM D 4052, 15.6/15.6°C) of less than 0.85, preferably less than 0.84,

preferably less than 0.83, preferably from 0.65 to 0.85, preferably from 0.70 to 0.84, preferably from 0.75 to 0.83, preferably from 0.800 to 0.840; and or a final boiling point (as determined by ASTM D 1160) of from 115 to 500°C, preferably from 200 to 450°C, preferably from 250 to 400°C; and or a number average molecular weight (Mn) between 2,000 and 100 g/mol, preferably between 1500 and 150, more preferably between 1000 and 200; and or a flash point as measured by ASTM D 56 of 0 to 150°C, and or a density (ASTM D4052, 15.6oC) of from 0.70 to 0.83 g/cm3; and or a kinematic viscosity (ASTM D445) of from 0.5 to 20

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## Polyalphaolefins

cSt at 25°C.

[0031] In another embodiment of the present invention, the NFP comprises a polyalphaolefin (PAO) liquid with a pour point (as measured by ASTM D 97) of -10°C or less and a kinematic viscosity at 100°C (measured by ASTM D 445) of 3 cSt or more. PAO liquids are described in, for example, US 3,149,178; US 4,827,064; US 4,827,073; US 5,171,908; and US 5,783,531 and in Synthetic Lubricants and High-Performance Functional Fluids (Leslie R. Rudnick & Ronald L. Shubkin, ed. Marcel Dekker, Inc. 1999), p. 3-52.

[0032] PAO liquids can be conveniently prepared by the oligomerization of an alpha-olefin in the presence of a polymerization catalyst, such as a Friedel-Crafts catalyst (including, for example, AlCl3, BF3, and complexes of BF3 with water, alcohols, carboxylic acids, or esters), a coordination complex catalyst (including, for example, the ethylaluminum sesquichloride + TiCl4 system), or a homogeneous or heterogeneous (supported) catalyst more commonly used to make polyethylene and/or polypropylene (including, for example, Ziegler-Natta catalysts, metallocene or other single-site catalysts, and chromium catalysts).

[0033] In one embodiment, the PAO comprises C20 to C1500 (preferably C30 to C800, more preferably C35 to C400, most preferably C40 to C250) oligomers of  $\alpha$ -olefins. These oligomers are dimers, trimers, tetramers, pentamers, etc. of C3 to C24 (preferably C5 to C18, more preferably C6 to C14, even more preferably

C8 to C12, most preferably C10) branched or linear α-olefins, provided that C3 and C4 alpha-olefins are present at 10 wt% or less. In another embodiment, the PAO comprises C3 to C24 (preferably C5 to C18, more preferably C6 to C14, most preferably C8 to C12) linear alpha-olefins (LAOs), provided that C3 and C4 LAOs are present at 10 wt% or less. Suitable olefins include propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, and blends thereof. Oligomers of LAOs with only even carbon numbers between 6 and 18 (inclusive) are particularly preferred.

[0034] In one embodiment, a single LAO is used to prepare the oligomers. In this case, a preferred embodiment involves the oligomerization of 1-decene, and the PAO is a mixture of oligomers (including, for example, dimers, trimers, tetramers, pentamers, and higher) of 1-decene. In another embodiment, the PAO comprises oligomers of two or more C3 to C18 LAOs, to make 'bipolymer' or 'terpolymer' or higher-order copolymer combinations, provided that C3 and C4 LAOs are present at 10 wt% or less. In this case, a preferred embodiment involves the oligomerization of a mixture of 1-octene, 1-decene, and 1-dodecene, and the PAO is a mixture of oligomers (for example, dimers, trimers, tetramers, pentamers, and higher) of 1-octene/1-decene/1-dodecene 'terpolymer'.

[0035] In another embodiment, the PAO comprises oligomers of a single alpha-olefin species having a carbon number of 5 to 24 (preferably 6 to 18, more preferably 8 to 12, most preferably 10). In another embodiment, the NFP comprises oligomers of mixed alpha-olefins (i.e., involving two or more alpha-olefin species), each alpha-olefin having a carbon number of 3 to 24 (preferably 5 to 24, more preferably 6 to 18, most preferably 8 to 12), provided that alpha-olefins having a carbon number of 3 or 4 are present at 10 wt% or less. In a particularly preferred embodiment, the PAO comprises oligomers of mixed alpha-olefins (i.e., involving two or more alpha-olefin species) where the weighted average carbon number for the alpha-olefin mixture is 6 to 14 (preferably 8 to 12, preferably 9 to 11).

[0036] In another embodiment, the PAO comprises oligomers of one or more alpha-olefin with repeat unit formulas of

[0037]  $-[CHR-CH_2]-$ 

[0038] where R is a C3 to C18 saturated hydrocarbon branch. In a preferred embodiment, R is constant for all oligomers. In another embodiment, there is a range of R substituents covering carbon numbers from 3 to 18. Preferably, R is linear, i.e.,

[0039] R is  $(CH_2)nCH_3$ ,

[0040] where n is 3 to 17, preferably 4 to 11, and preferably 5 to 9. Optionally, R can contain one methyl or ethyl branch, i.e.,

[0041] R is  $(CH_2)m[CH(CH_3)](CH_2)zCH_3$  or R is  $(CH_2)x[CH(CH_2CH_3)](CH_2)yCH_3$ ,

[0042] where (m + z) is 1 to 15, preferably 1 to 9, preferably 3 to 7, and (x + y) is 1 to 14, preferably 1 to 8, preferably 2 to 6. Preferably m > z; more preferably m is 0 to 15, more preferably 2 to 15, more preferably 3 to 12, more preferably 4 to 9; and n is 0 to 10, preferably 1 to 8, preferably 1 to 6, preferably 1 to 4. Preferably x > y; more preferably x is 0 to 14, more preferably 1 to 14, more preferably 2 to 11, more preferably 3 to 8; and y is 0 to 10, preferably 1 to 8, preferably 1 to 6, preferably 1 to 4. Preferably, the repeat units are arranged in a head-to-tail fashion with minimal heat-to-head connections.

The PAO can be atactic, isotactic, or syndiotactic. In one embodiment, the PAO has essentially the same population of meso and racemic dyads, on average, making it atactic. In another embodiment, the PAO has more than 50% (preferably more than 60%, preferably more than 70%, preferably more than 80%, preferably more than 90%) meso dyads (i.e., [m]) as measured by 13C-NMR. In another embodiment, the PAO has more than 50% (preferably more than 60%, preferably more than 70%, preferably more than 80%, preferably more than 90%) racemic dyads (i.e., [r]) as measured by 13C-NMR. In one embodiment, [m]/[r]

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determined by 13C-NMR is between 0.9 and 1.1 in one embodiment, [m]/[r] is greater than 1 in another embodiment, and [m]/[r] is less than 1 in yet another embodiment.

[0044] The PAO liquid can be comprised of one or more distinct PAO components. In one embodiment, the NFP is a blend of one or more PAOs with different compositions (e.g., different alpha-olefin(s) were used to make the oligomers) and/or different physical properties (e.g., kinematic viscosity, pour point, viscosity index, and/or glass transition temperature).

[0045] In one embodiment of the present invention, the PAO or blend of PAOs has a number average molecular weight of from 100 to 20,000 g/mol (preferably 300 to 15,000 g/mol, preferably 400 to 10,000 g/mol, preferably 500 to 5,000 g/mol, preferably 600 to 3,000 g/mol, preferably 600 to 1,500 g/mol).

[0046] In a preferred embodiment, the PAO or blend of PAOs has a kinematic viscosity at 100°C of 3 cSt or more (preferably 5 cSt or more, preferably 6 cSt or more, preferably 8 cSt or more, preferably 10 cSt or more, preferably 20 cSt or more, preferably 30 cSt or more, preferably 40 cSt or more, preferably 100 or more, preferably 150 cSt or more). In another embodiment, the PAO or blend of PAOs has a kinematic viscosity at 100°C of 300 cSt or less (preferably 100 cSt or less). In another embodiment, the PAO has a kinematic viscosity at 100°C of 3 to 3,000 cSt (preferably 4 to 1,000 cSt, preferably 6 to 300 cSt, preferably 8 to 150 cSt, preferably 8 to 100 cSt, preferably 8 to 40 cSt). In another embodiment, the PAO or blend of PAOs has a kinematic viscosity at 100°C of 10 to 1000 cSt (preferably 10 to 300 cSt, preferably 10 to 100 cSt). In yet another embodiment, the PAO or blend of PAOs has a kinematic viscosity at 100°C of about 4 to 8 cSt.

[0047] In another preferred embodiment, the PAO or blend of PAOs has a Viscosity Index of 120 or more (preferably 130 or more, preferably 140 or more, preferably 150 or more, preferably 170 or more, preferably 190 or more, preferably 200 or more, preferably 250 or more, preferably 300 or more). In

another embodiment, the PAO or blend of PAOs has a viscosity Index of 120 to 350 (preferably 130 to 250).

- [0048] In yet another preferred embodiment, the PAO or blend of PAOs has a pour point of -10°C or less (preferably -20°C or less, preferably -25°C or less, preferably -30°C or less, preferably -35°C or less, preferably -40°C or less, preferably -50°C or less). In another embodiment, the PAO or blend of PAOs has a pour point of -15 to -70°C (preferably -25 to -60°C).
- [0049] In yet another preferred embodiment, the PAO or blend of PAOs has a glass transition temperature (Tg) of -40°C or less (preferably -50°C or less, preferably -60°C or less, preferably -70°C or less, preferably -80°C or less). In another embodiment, the PAO or blend of PAOs has a Tg of -50 to -120°C (preferably -60 to -100°C, preferably -70 to -90°C).
- [0050] In yet another preferred embodiment, the PAO or blend of PAOs has a flash point of 200°C or more (preferably 210°C or more, preferably 220°C or more, preferably 230°C or more), preferably between 240°C and 290°C.
- [0051] In yet another preferred embodiment, the PAO or blend of PAOs has a specific gravity (15.6/15.6°C) of 0.86 or less (preferably 0.855 or less, preferably 0.85 or less, preferably 0.84 or less).
- [0052] Particularly preferred PAOs and blends of PAOs are those having A) a flash point of 200°C or more (preferably 210°C or more, preferably 220°C or more, preferably 230°C or more); and B) a pour point less than -20°C (preferably less than -25°C, preferably less than -30°C, preferably less than -35°, preferably less than -40°C) and/or a kinematic viscosity at 100°C of 10 cSt or more (preferably 35 cSt or more, preferably 40 cSt or more, preferably 50 cSt or more).
- [0053] Further preferred PAOs or blends of PAOs have a kinematic viscosity at 100°C of at least 3 cSt (preferably at least 6 cSt, more preferably at least 8 cSt, most preferably at least 10 cSt, as measured by ASTM D445); a viscosity index of at least 120 (preferably at least 130, more preferably at least 140, most preferably

at least 150, as determined by ASTM D2270); a pour point of -10°C or less (preferably -20°C or less, more preferably -30°C or less, most preferably -40°C or less, as determined by ASTM D97); and a specific gravity (15.6/15.6°C) of 0.86 or less (preferably 0.855 or less, more preferably 0.85 or less, most preferably 0.84 or less, as determined by ASTM D 4052).

[0054] Desirable PAOs are commercially available as SpectraSyn™ and SpectraSyn Ultra™ from ExxonMobil Chemical in Houston, Texas (previously sold under the SHF and SuperSyn™ tradenames by ExxonMobil Chemical Company), some of which are summarized in Table B. Other useful PAOs include those sold under the tradenames Synfluid™ available from ChevronPhillips Chemical Company (Pasedena, Texas), Durasyn™ available from Innovene (Chicago, Illinois), Nexbase™ available from Neste Oil (Keilaniemi, Finland), and Synton™ available from Chemtura Corporation (Middlebury, Connecticut). For PAOs, the percentage of carbons in chain-type paraffinic structures (CP) is close to 100% (typically greater than 98% or even 99%).

Table B. SpectraSyn<sup>TM</sup> Series Polyalphaolefins

	KV @ 100°C, cSt	KV @ 40°C, cSt	VI	Pour Point, °C	Specific gravity	Flash Point, °C	APHA Color
Contracting Cross A	100 0, 000	19	126	-66	0.820	220	10
SpectraSyn 4	4	17	122	-60	0.820	228	10
SpectraSyn Plus 4	6	31	138	-57	0.827	246	10
SpectraSyn 6	_	30	140	<b>-</b> 54	0.827	246	10
SpectraSyn Plus 6	6	48	139	-48	0.833	260	10
SpectraSyn 8	8		137	-48	0.835	266	10
SpectraSyn 10	10	66		-36	0.850	281	10
SpectraSyn 40	39	396	147		0.853	283	60
SpectraSyn 100	100	1240	170	-30		> 265	10
SpectraSyn Ultra 150	150	1,500	218	-33	0.850		20
SpectraSyn Ultra 300	300	3,100	241	-27	0.852	> 265	
SpectraSyn Ultra 1000	1,000	10,000	307	-18	0.855	> 265	30

[0055] In some embodiments of the present invention, the PAO comprises oligomers of C4 olefins (including n-butene, 2-butene, isobutylene, and butadiene, and mixtures thereof) and up to 10 wt% of other olefins, having a kinematic viscosity at 100°C of 5 to 4000 cSt and a pour point of 10 to -60°C. Such a material is referred to as a "polybutenes" liquid when the oligomers comprise isobutylene and/or 1-butene and/or 2-butene. It is commonly used as an additive for polyolefins; e.g. to introduce tack or as a processing aid. The ratio of C4

olefin isomers can vary by manufacturer and by grade, and the material can or can not be hydrogenated after synthesis. In some cases, the polybutenes liquid is a polymer of a C4 raffinate stream. In other cases, it consists essentially of polyisobutylene or poly(n-butene) oligomers. Typically, the polybutenes liquid has a number-average molecular weight of less than 15,000 g/mol, and commonly less than 5,000 g/mol or even less than 1,000 g/mol. They are described in, for example, Synthetic Lubricants and High-Performance Functional Fluids (Leslie R. Rudnick & Ronald L. Shubkin, ed., Marcel Dekker 1999), p. 357-392.

[0056] Desirable polybutenes liquids are commercially available from a variety of sources including Innovene (Indopol grades) and Infineum (C-Series grades). When the C4 olefin is exclusively isobutylene, the material is referred to as "polyisobutylene" or PIB. Commercial sources of PIB include Texas Petrochemical (TPC Enhanced PIB grades). When the C4 olefin is exclusively 1-butene, the material is referred to as "poly-n-butene" or PNB. Properties of some liquids made from C4 olefin(s) are summarized in Table C. In general, grades with a flash point of 200°C or more also have a pour point greater than -10°C and/or a VI less than 120.

Table C. Commercial Examples of Oligomers of C4 olefin(s)

Grade	KV@	VI	Pour	Specific	Flash
	100°C,		Point, °C	gravity	Point, °C
	cSt				
TPC 137 (PIB)	6	132	-51	0.843	120
TPC 1105 (PIB)	220	145	-6	0.893	200
TPC 1160 (PIB)	660	190	+3	0.903	230
Innovene Indopol H-25	52	87	-23	0.869	150
Innovene Indopol H-50	108	90	-13	0.884	190
Innovene Indopol H-100	218	121	-7	0.893	210
Infineum C9945	11	74*	-34	0.854	170
Infineum C9907	78	103*	-15	0.878	204
Infineum C9995	230	131*	-7	0.888	212
Infineum C9913	630	174*	+10	0.888	240

<sup>\*</sup>Estimated based on the kinematic viscosity at 100°C and 38°C

[0057] This invention also relates to plasticized polyolefin compositions comprising one or more polyolefins, preferably polypropylene, and one or more

non-functionalized plasticizers where the non-functionalized plasticizer comprises a polyalphaolefin comprising oligomers of C5 to C18 olefins (preferably C6 to C14, more preferably C8 to C12, more preferably C10); having a kinematic viscosity of 5 cSt or more at 100°C (preferably 8 cSt or more, preferably 10 cSt or more at 100°C); a viscosity index of 120 or more (preferably 130 or more); and a

pour point of -10°C or less (preferably -20°C or less, preferably -30°C or less).

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[0058] This invention also relates to plasticized polypropylene compositions comprising polypropylene and one or more non-functionalized plasticizers where the non-functionalized plasticizer comprises oligomers of linear olefins having 5 to 18 carbon atoms (preferably 6 to 14 carbon atoms, more preferably 8 to 12 carbon atoms, more preferably 10 carbon atoms); a kinematic viscosity at 100 °C of 5 to 300 cSt (preferably 8 to 150 cSt, preferably 10 to 100 cSt); a viscosity index of 120 or more (more preferably 130 or more, more preferably 140 or more); and a pour point of -20 °C or less (more preferably -30 °C or less, more preferably -40 °C or less).

#### High Purity Hydrocarbon Fluids

[0059] In another embodiment, the nonfunctionalized plasticizer (NFP) is a high purity hydrocarbon fluid of lubricating viscosity comprising a mixture of C20 to C120 paraffins, 50 wt% or more being isoparaffinic hydrocarbons and less than 50 wt% being hydrocarbons that contain naphthenic and/or aromatic structures. Preferably, the mixture of paraffins comprises a wax isomerate lubricant base stock or oil, which includes: hydroisomerized natural and refined waxes, such as slack waxes, deoiled waxes, normal alpha-olefin waxes, microcrystalline waxes, and waxy stocks derived from gas oils, fuels hydrocracker bottoms, hydrocarbon raffinates, hydrocracked hydrocarbons, lubricating oils, mineral oils, polyalphaolefins, or other linear or branched hydrocarbon compounds with carbon number of about 20 or more; and hydroisomerized synthetic waxes, such as Fischer-Tropsch waxes (i.e., the high boiling point residues of Fischer-Tropsch synthesis, including waxy hydrocarbons); or mixtures thereof. Most preferred are lubricant base stocks or oils derived from

hydrocarbons synthesized in a Fischer-Tropsch process as part of an overall Gasto-Liquids (GTL) process.

In one embodiment, the mixture of paraffins has a naphthenic content [0060] of less than 40 wt%, preferably less than 30 wt%, preferably less than 20 wt%, preferably less than 15 wt%, preferably less than 10 wt%, preferably less than 5 wt%, preferably less than 2 wt%, preferably less than 1 wt% (based on the total weight of the hydrocarbon mixture); and/or a normal paraffins content of less than 5 wt%, preferably less than 4 wt%, preferably less than 3 wt%, preferably less than 1 wt% (based on the total weight of the hydrocarbon mixture); and/or an aromatic content of 1 wt% or less, preferably 0.5 wt% or less; and/or a saturates level of 90 wt% or higher, preferably 95 wt% or higher, preferably 98 wt% or higher, preferably 99 wt% or higher; and/or the percentage of carbons in chaintype paraffinic structures (CP) of 80% or more, preferably 90% or more, preferably 95% or more, preferably 98% or more; and/or a branched paraffin:normal paraffin ratio greater than about 10:1, preferably greater than 20:1, preferably greater than 50:1, preferably greater than 100:1, preferably greater than 500:1, preferably greater than 1000:1; and/or sidechains with 4 or more carbons making up less than 10% of all sidechains, preferably less than 5%, preferably less than 1%; and/or sidechains with 1 or 2 carbons making up at least 50% of all sidechains, preferably at least 60%, preferably at least 70%, preferably at least 80%, preferably at least 90%, preferably at least 95%, preferably at least 98%; and/or a sulfur content of 300 ppm or less, preferably 100 ppm or less, preferably 50 ppm or less, preferably 10 ppm or less (where ppm is on a weight basis); and/or a nitrogen content of 300 ppm or less, preferably 100 ppm or less, preferably 50 ppm or less, preferably 10 ppm or less (where ppm is on a weight basis); and/or a number-average molecular weight of 300 to 1800 g/mol, preferably 400 to 1500 g/mol, preferably 500 to 1200 g/mol, preferably 600 to 900 g/mol; and/or a kinematic viscosity at 40°C of 10 cSt or more, preferably 25 cSt or more, preferably between about 50 and 400 cSt; and/or a kinematic viscosity at 100°C ranging from 2 to 50 cSt, preferably 3 to 30 cSt, preferably 5 to 25 cSt, preferably 6 to 20 cSt, more preferably 8 to 16 cSt; and/or a viscosity index (VI)

of 80 or greater, preferably 100 or greater, preferably 120 or greater, preferably 130 or greater, preferably 140 or greater, preferably 150 or greater, preferably 160 or greater, preferably 180 or greater; and/or a pour point of -5°C or lower, preferably -10°C or lower, preferably -15°C or lower, preferably -20°C or lower, preferably -20°C or lower, preferably -25°C or lower, preferably -30°C or lower; and/or a flash point of 200°C or more, preferably 220°C or more, preferably 240°C or more, preferably 260°C or more; and/or a specific gravity (15.6°C/15.6°C) of 0.86 or less, preferably 0.85 or less, preferably 0.84 or less; and/or an aniline point of 120°C or more; and/or a bromine number of 1 or less.

In a preferred embodiment, the mixture of paraffins comprises a GTL [0061] base stock or oil. GTL base stocks and oils are fluids of lubricating viscosity that are generally derived from waxy synthesized hydrocarbons, that are themselves derived via one or more synthesis, combination, transformation, and/or rearrangement processes from gaseous carbon-containing compounds and hydrogen-containing compounds as feedstocks, such as: hydrogen, carbon dioxide, carbon monoxide, water, methane, ethane, ethylene, acetylene, propane, propylene, propyne, butane, butylenes, and butynes. Preferably, the feedstock is "syngas" (synthesis gas, essentially CO and H2) derived from a suitable source, such as natural gas and/or coal. GTL base stocks and oils include wax isomerates, comprising, for example, hydroisomerized synthesized waxes, hydroisomerized Fischer-Tropsch (F-T) waxes (including waxy hydrocarbons and possible analogous oxygenates), or mixtures thereof. GTL base stocks and oils can further comprise other hydroisomerized base stocks and base oils. Particularly preferred GTL base stocks or oils are those comprising mostly hydroisomerized F-T waxes and/or other liquid hydrocarbons obtained by a F-T synthesis process.

[0062] The synthesis of hydrocarbons, including waxy hydrocarbons, by F-T can involve any suitable process known in the art, including those involving a slurry, a fixed-bed, or a fluidized-bed of catalyst particles in a hydrocarbon liquid. The catalyst can be an amorphous catalyst, for example based on a Group VIII metal such as Fe, Ni, Co, Ru, and Re on a suitable inorganic support material, or a crystalline catalyst, for example a zeolitic catalyst. The process of making a

lubricant base stock or oil from a waxy stock is characterized as a hydrodewaxing process. A hydrotreating step, while typically not required for F-T waxes, can be performed prior to hydrodewaxing if desired. Some F-T waxes can benefit from removal of oxygenates while others can benefit from oxygenates treatment prior to hydrodewaxing. The hydrodewaxing process is typically conducted over a catalyst or combination of catalysts at high temperatures and pressures in the presence of hydrogen. The catalyst can be an amorphous catalyst, for example based on Co, Mo, W, etc. on a suitable oxide support material, or a crystalline catalyst, for example a zeolitic catalyst such as ZSM-23 and ZSM-48 and others disclosed in US patents 4,906,350, often used in conjunction with a Group VIII metal such as Pd or Pt. This process can be followed by a solvent and/or catalytic dewaxing step to lower the pour point of the hydroisomerate. Solvent dewaxing involves the physical fractionation of waxy components from the hydroisomerate. Catalytic dewaxing converts a portion of the hydroisomerate to lower boiling hydrocarbons; it often involves a shape-selective molecular sieve, such as a zeolite or silicoaluminophosphate material, in combination with a catalytic metal component, such as Pt, in a fixed-bed, fluidized-bed, or slurry type process at high temperatures and pressures in the presence of hydrogen.

[0063] Useful catalysts, processes, and compositions for GTL base stocks and oils, Fischer-Tropsch hydrocarbon derived base stocks and oils, and wax isomerate hydroisomerized base stocks and oils are described in, for example, US Patents 2,817,693; 4,542,122; 5,545,674; 4,568,663; 4,621,072; 4,663,305; 4,897,178; 4,900,407; 4,921,594; 4,923,588; 4,937,399; 4,975,177; 5,059,299; 5,158,671; 5,182,248; 5,200,382; 5,290,426; 5,516,740; 5,580,442; 5,885,438; 5,935,416; 5,935,417; 5,965,475; 5,976,351; 5,977,425; 6,025,305; 6,080,301; 6,090,989; 6,096,940; 6,103,099; 6,165,949; 6,190,532; 6,332,974; 6,375,830; 6,383,366; 6,475,960; 6,620,312; and 6,676,827; European Patents EP 324528, EP 532116, EP 532118, EP 537815, EP 583836, EP 666894, EP 668342, EP 776959; WPO patent applications WO 97/31693, WO 99/20720, WO 99/45085, WO 02/64710, WO 02/64711, WO 02/70627, WO 02/70629, WO 03/33320; and British Patents 1,350,257; 1,390,359; 1,429,494; and 1,440,230. Particularly

favorable processes are described in European Patent Applications EP 464546 and EP 464547. Processes using Fischer-Tropsch wax feeds are described in US 4,594,172; 4,943,672; 6,046,940; 6,103,099; 6,332,974; 6,375,830; and 6,475,960.

[0064] Desirable GTL-derived fluids are expected to become broadly available from several commercial sources, including Chevron, ConocoPhillips, ExxonMobil, Sasol, SasolChevron, Shell, Statoil, and Syntroleum.

[0065] This invention also relates to plasticized polyolefin compositions comprising one or more polyolefins and one or more non-functionalized plasticizers, where one or more NFP is a high purity hydrocarbon fluid derived from a GTL process comprising a mixture of paraffins of carbon number ranging from about C20 to C100, a molar ratio of isoparaffins:n-paraffins greater than about 50:1, the percentage of carbons in paraffinic structures (CP) of 98% or more, a pour point ranging from about -20 to -60°C, and a kinematic viscosity at 100°C ranging from about 6 to 20 cSt.

[0066] As used herein, the following terms have the indicated meanings: "naphthenic" describes cyclic (mono-ring and/or multi-ring) saturated hydrocarbons (i.e., cycloparaffins) and branched cyclic saturated hydrocarbons; "aromatic" describes cyclic (mono-ring and/or multi-ring) unsaturated hydrocarbons and branched cyclic unsaturated hydrocarbons; "hydroisomerized" describes a catalytic process in which normal paraffins and/or slightly branched isoparaffins are converted by rearrangement into more branched isoparaffins (also known as "isodewaxing"); "wax" is a hydrocarbonaceous material existing as a solid at or near room temperature, with a melting point of 0°C or above, and consisting predominantly of paraffinic molecules, most of which are normal paraffins; "slack wax" is the wax recovered from petroleum oils such as by solvent dewaxing, and can be further hydrotreated to remove heteroatoms.

#### Group III basestocks or mineral oils

[0067] In another embodiment, the NFP comprises a Group III hydrocarbon oil (also called a Group III lubricant basestock or Group III mineral oil). Preferably

the NFP has a saturates levels of 90% or more (preferably 92% or more, preferably 94% or more, preferably 95% or more, preferably 98% or more); and a sulfur content less than 0.03% (preferably between 0.001 and 0.01%); and a VI of 120 or more (preferably 130 or more). Preferably the Group III hydrocarbon oil has a kinematic viscosity at 100°C of 3 to 50, preferably 4 to 40 cSt, preferably 6 to 30 cSt, preferably 8 to 20; and/or a number average molecular weight of 300 to 5,000 g/mol, preferably 400 to 2,000 g/mol, more preferably 500 to 1,000 g/mol. Preferably the Group III hydrocarbon oil has a pour point of -10°C or less, a flash point of 200°C or more, and a specific gravity (15.6°C/15.6°C) of 0.86 or less.

[0068] Desirable Group III basestocks are commercially available from a number of sources and include those described in Table D. The percentage of carbons in chain-type paraffinic structures (CP) in such liquids is greater than 80%.

Table D. Commercially available Group III Basestocks

	KV@	VI	Pour	Specific	Flash
	100°C,		Point,	gravity	Point,
	cSt		°C		°C
UCBO 4R <sup>1</sup>	4.1	127	-18	0.826	216
UCBO 7R <sup>1</sup>	7.0	135	-18	0.839	250
Nexbase 3043 <sup>2</sup>	4.3	124	-18	0.831	224
Nexbase 3050 <sup>2</sup>	5.1	126	-15	0.835	240
Nexbase 3060 <sup>2</sup>	6.0	128	-15	0.838	240
Nexbase 3080 <sup>2</sup>	8.0	128	-15	0.843	260
Yubase YU-4 <sup>3</sup>	4.2	122	-15	0.843	230
Yubase YU-6 <sup>3</sup>	6.5	131	-15	0.842	240
Yubase YU-8 <sup>3</sup>	7.6	128	-12	0.850	260
Ultra-S 4 <sup>4</sup>	4.3	123	-20	0.836	220
Ultra-S 6 <sup>4</sup>	5.6	128	-20	0.839	234
Ultra-S 8 4	7.2	127	-15	0.847	256
VHVI 4 <sup>5</sup>	4.6	128	-21	0.826	
VHVI 8 <sup>5</sup>	8.0	127	-12	0.850	248
Visom 4 <sup>6</sup>	4.0				210
Visom 6 <sup>6</sup>	6.6	148	-18	0.836	250

- i) Available from ChevronTexaco (USA).
- ii) Available from Neste Oil (Finland).
- iii) Available from SK Corp (South Korea).

- iv) Available from ConocoPhillips (USA) / S-Oil (South Korea).
- v) Available from PetroCanada (Canada).
- vi) Available from ExxonMobil (USA).

#### General Characteristics of Useful NFPs

[0069] In preferred embodiments, the NFP has a kinematic viscosity at 100°C (KV100) of 4 cSt or more, preferably 5 cSt or more, preferably 6 to 5000 cSt, preferably 8 to 3000 cSt, preferably 10 to 1000 cSt, preferably 12 to 500 cSt, preferably 15 to 350 cSt, preferably 35 to 300 cSt, preferably 40 to 200 cSt, preferably 8 to 300 cSt, preferably 6 to 150 cSt, preferably 10 to 100 cSt, preferably less than 50 cSt, wherein a desirable range can be any combination of any lower KV100 limit with any upper KV100 limit described herein. In other embodiments, the NFP has a kinematic viscosity at 100°C of less than 2 cSt.

[0070] In preferred embodiments, the NFP has a pour point of -10°C or less, preferably -20°C or less, preferably -30°C or less, preferably -40°C or less, preferably -40°C or less, preferably -40°C or less, preferably -10 to -100°C, preferably -15 to -80°C, preferably -15 to -75°C, preferably -20 to -70°C, preferably -25 to -65°C, preferably greater than -120°C, wherein a desirable range can be any combination of any lower pour point limit with any upper pour point limit described herein. In another embodiment, the NFP has a pour point of less than -30°C when the kinematic viscosity at 40°C is from 0.5 to 200 cSt. Most mineral oils, which typically include aromatic moieties and other functional groups, have a pour point of from 10 to -20°C in the same kinematic viscosity range.

[0071] In a preferred embodiment, the NFP has a glass transition temperature (Tg) of -40°C or less (preferably -50°C or less, preferably -60°C or less, preferably -70°C or less, preferably -80°C or less, preferably -45 to -120°C, preferably -65 to -90°C, wherein a desirable range can be any combination of any lower Tg limit with any upper Tg limit described herein.

[0072] In preferred embodiments, the NFP has a Viscosity Index (VI) of 90 or more, preferably 100 or more, preferably 110 or more, preferably 120 or more,

preferably 130 or more, preferably 115 to 350, preferably 135 to 300, preferably 140 to 250, preferably 150 to 200, preferably 125 to 180, wherein a desirable range can be any combination of any lower VI limit with any upper VI limit described herein.

[0073] In preferred embodiments, the NFP has a flash point of 200°C or greater, preferably 210° or greater, preferably 230°C or greater, preferably 200 to 350°C, preferably 210 to 300°C, preferably 215 to 290°C, preferably 220 to 280°C, preferably 240 to 280°C, wherein a desirable range can be any combination of any lower flash point limit with any upper flash point limit described herein.

[0074] In preferred embodiments, the NFP has a specific gravity of 0.86 or less, preferably 0.855 or less, preferably 0.84 or less, preferably 0.78 to 0.86, preferably 0.79 to 0.855, preferably 0.80 to 0.85, preferably 0.81 to 0.845, preferably 0.82 to 0.84, wherein a desirable range can be any combination of any lower specific gravity limit with any upper specific gravity limit described herein.

[0075] In preferred embodiments, the NFP has a number-average molecular weight (Mn) of 250 g/mol or more, preferably 300 g/mol or more, preferably 500 g/mol or more, preferably 300 to 21,000 g/mol, preferably 300 to 10,000 g/mol, preferably 400 to 5,000 g/mol, preferably 500 to 3,000 g/mol, preferably 10 kg/mol or less, preferably 5 kg/mol or less, preferably 2 kg/mol or less, preferably 1 kg/mol or less, wherein a desirable range can be any combination of any lower Mn limit with any upper Mn limit described herein.

[0076] In preferred embodiments, the NFP has a low degree of color, such as typically identified as "water white", "prime white", "standard white", or "bright and clear," preferably an APHA color of 100 or less, preferably 80 or less, preferably 60 or less, preferably 20 or less, as determined by ASTM D1209.

[0077] In other embodiments, any NFP can have an initial boiling point (ASTM D1160) of from 300 to 600°C in one embodiment, and from 350 to 500°C in another embodiment, and greater than 400°C in yet another embodiment.

[0078] Any of the NFP's for use in the present invention can be described by any embodiment described herein, or any combination of the embodiments described herein. For example, in one embodiment, the NFP is a C6 to C200 paraffin having a pour point of less than -25°C. Alternately, the NFP comprises an aliphatic hydrocarbon having a kinematic viscosity of from 0.1 to 1000 cSt at 100°C. Alternately, the NFP is selected from isoparaffins and PAOs and blends thereof having from 8 to 25 carbon atoms.

In another embodiment, the NFP of the present invention comprises [0079] C25 to C1500 paraffins, and C30 to C500 paraffins in another embodiment, and has a flash point of 200°C or more and a pour point of -10°C or less and a viscosity index of 120 or more. Alternately the NFP comprises C25 to C1500 paraffins, preferably C30 to C500 paraffins, and has a flash point of 200°C or more and a pour point of -20°C or less. Alternately the NFP comprises C25 to C1500 paraffins, preferably C30 to C500 paraffins, and has a flash point of 200°C or more and a kinematic viscosity at 100°C of 35 cSt or more. In another embodiment, the NFP consists essentially of C35 to C300 paraffins, preferably the NFP consists essentially of C40 to C250 paraffins, and has a flash point of 200°C or more and a pour point of -10°C or less and a viscosity index of 120 or more. Alternately the NFP consists essentially of C35 to C300 paraffins, preferably C40 to C250 paraffins, and has a flash point of 200°C or more and a pour point of -20°C or less. Alternately the NFP consists essentially of C35 to C300 paraffins, preferably C40 to C250 paraffins, and has a flash point of 200°C or more and a kinematic viscosity at 100°C of 35 cSt or more. Alternately the NFP has a flash point of 200°C or more and a pour point of -20°C or less. Alternately the NFP has a flash point of 200°C or more and a kinematic viscosity at 100°C of 35 cSt or more.

[0080] In a preferred embodiment, any NFP described herein has a flash point of 200°C or more (preferably 210°C or more) and a pour point of -20°C or less (preferably -25°C or less, more preferably -30°C or less, more preferably -35°C or less, more preferably -45°C or less, more preferably -50°C or less).

[0081] In another preferred embodiment, the NFP has a flash point of 220°C or more (preferably 230°C or more) and a pour point of -10°C or less (preferably -25°C or less, more preferably -30°C or less, more preferably -35°C or less, more preferably -45°C or less, more preferably -50°C or less).

[0082] In another preferred embodiment, the NFP has a kinematic viscosity at 100°C of 35 cSt or more (preferably 40 cSt or more, preferably 50 cSt or more, preferably 60 cSt or more) and a specific gravity (15.6/15.6°C) of 0.87 or less (preferably 0.865 or less, preferably 0.86 or less, preferably 0.855 or less) and a flash point of 200°C or more (preferably 230°C or more).

[0083] In another preferred embodiment, the NFP has a) a flash point of 200°C or more, b) a specific gravity of 0.86 or less, and c1) a pour point of -10°C or less and a viscosity index of 120 or more, or c2) a pour point of -20°C or less, or c3) a kinematic viscosity at 100°C of 35 cSt or more.

[0084] In another preferred embodiment, the NFP has a specific gravity (15.6/15.6°C) of 0.85 or less (preferably between 0.80 and 0.85) and a kinematic viscosity at 100°C of 3 cSt or more (preferably 4 or more, preferably 5 cSt or more, preferably 8 cSt or more, preferably 10 cSt or more, preferably 15 cSt or more, preferably 20 cSt or more) and/or a number-average molecular weight (Mn) of at least 280 g/mol.

[0085] In another preferred embodiment, the NFP has a specific gravity (15.6/15.6°C) of 0.86 or less (preferably between 0.81 and 0.855, preferably between 0.82 and 0.85) and a kinematic viscosity at 100°C of 5 cSt or more (preferably 6 or more, preferably 8 cSt or more, preferably 10 cSt or more, preferably 12 cSt or more, preferably 15 cSt or more, preferably 20 cSt or more) and/or a number-average molecular weight (Mn) of at least 420 g/mol.

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[0086] In another preferred embodiment, the NFP has a specific gravity (15.6/15.6°C) of 0.87 or less (preferably between 0.82 and 0.87) and a kinematic viscosity at 100°C of 10 cSt or more (preferably 12 cSt or more, preferably 14 cSt or more, preferably 16 cSt or more, preferably 20 cSt or more, preferably 30 cSt or more, preferably 40 cSt or more) and/or a number-average molecular weight (Mn) of at least 700 g/mol.

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[0087] In another preferred embodiment, the NFP has a specific gravity (15.6/15.6°C) of 0.88 or less (preferably 0.87 or less, preferably between 0.82 and 0.87) and a kinematic viscosity at 100°C of 15 cSt or more (preferably 20 cSt or more, preferably 25 cSt or more, preferably 30 cSt or more, preferably 40 cSt or more) and/or a number-average molecular weight (Mn) of at least 840 g/mol.

[0088] In another preferred embodiment the NFP has a kinematic viscosity at 100°C of 3 to 3000 cSt, preferably 6 to 300 cSt, more preferably 8 to 100 cSt; and a number average molecular weight (Mn) of 300 to 21,000 g/mol, preferably 500 to 5,000 g/mol, more preferably 600 to 3,000 g/mol.

[0089] In another preferred embodiment the NFP has a kinematic viscosity at 100°C of 3 to 500 cSt, preferably 6 to 200 cSt, more preferably 8 to 100 cSt, more preferably 3 to 25 cSt; and a number average molecular weight (Mn) of 300 to 10,000 g/mol, preferably 400 to 5,000 g/mol, more preferably 500 to 2,500 g/mol, more preferably 300 to 1,200 g/mol.

[0090] In another preferred embodiment the NFP has a kinematic viscosity at 100°C of 3 to 100 cSt, preferably 4 to 50 cSt, more preferably 6 to 25 cSt, more preferably 3 to 15 cSt; and a number average molecular weight (Mn) of 300 to 3,000 g/mol, preferably 350 to 2,000 g/mol, more preferably 400 to 1,000 g/mol, more preferably 300 to 800 g/mol.

[0091] In another preferred embodiment, the NFP has a pour point of -25°C or less, preferably between -30°C and -90°C, and a kinematic viscosity in the range of from 20 to 5000 cSt at 40°C. In another preferred embodiment, the NFP has a pour point of -25°C or less and a Mn of 400 g/mol or greater. Most mineral oils,

which typically include functional groups, have a pour point of from 10°C to -25°C at the same viscosity and molecular weight ranges.

[0092] In another preferred embodiment the NFP has kinematic viscosity at 100°C of 3 cSt or greater, preferably 6 cSt or greater, more preferably 8 cSt or greater, and one or more of the following properties:

a pour point of -10°C or less, preferably -20°C or less, preferably -30°C or less, preferably -40°C or less; and/or, a Viscosity Index of 120 or greater; and/or, a low degree of color, such as typically identified as "water white", "prime white", "standard white", or "bright and clear," preferably an APHA color of 100 or less, preferably 80 or less, preferably 60 or less, preferably 40 or less, preferably 20 or less, preferably 15 or less as determined by ASTM D1209; and/or a flash point of 200°C or more, preferably 220°C or more, preferably 240°C or more; and/or a specific gravity (15.6°C) of less than 0.86.

[0094] Most mineral oils at the same viscosity range have a pour point greater than -20°C or an APHA color of greater than 20 or a specific gravity (15.6°C) of 0.86 or more.

or more and one or more of the following properties: a pour point of -10°C or less, preferably -20°C or less, preferably -30°C or less, preferably -40°C or less; and/or, a kinematic viscosity at 100°C of 3 cSt or greater, preferably 6 cSt or greater, preferably 8 cSt or greater, preferably 10 cSt or greater; and/or, a low degree of color, such as typically identified as "water white", "prime white", "standard white", or "bright and clear," preferably an APHA color of 100 or less, preferably 80 or less, preferably 60 or less, preferably 40 or less, preferably 20 or less, preferably 15 or less, as determined by ASTM D1209; and/or a flash point of 200°C or more, preferably 220°C or more, preferably 240°C or more; and/or a specific gravity (15.6°C) of less than 0.86.

[0096] Most mineral oils have a Viscosity Index of less than 120.

[0097] In another preferred embodiment, the NFP has a pour point of -20°C or less, preferably -30°C or less, and one or more of the following properties: a kinematic viscosity at 100°C of 3 cSt or greater, preferably 6 cSt or greater, preferably 8 cSt or greater, preferably 10 cSt or more; and/or, a Viscosity Index of 120 or greater, preferably 130 or greater; and/or, a low degree of color, such as typically identified as "water white", "prime white", "standard white", or "bright and clear," preferably APHA color of 100 or less, preferably 80 or less, preferably 60 or less, preferably 40 or less, preferably 20 or less, preferably 15 or less as determined by ASTM D 1209; a flash point of 200°C or more, preferably 220°C or more, preferably 240°C or more; and/or a specific gravity (15.6°C) of less than 0.86.

[0098] Most mineral oils have a kinematic viscosity at 100°C of less than 6 cSt, or an APHA color of greater than 20, or a flash point less than 200°C when their pour point is less than -20°C.

In another preferred embodiment the NFP has a glass transition [0099] temperature (Tg) that cannot be determined by ASTM E 1356 or, if it can be determined, then the Tg according to ASTM E 1356 is less than 0°C, preferably less than -10°C, more preferably less than -20°C, more preferably less than -30°C, more preferably less than -40°C, and, preferably, also has one or more of the following properties: an initial boiling point as determined by ASTM D 1160 greater than 300°C, preferably greater than 350°C, preferably greater than 400°C; and/or a pour point of -10°C or less, preferably -15°C or less, preferably -25°C or less, preferably -35°C or less, preferably -45°C or less; and/or a specific gravity (ASTM D 4052, 15.6/15.6oC) of less than 0.88, preferably less than 0.86, preferably less than 0.84, preferably from 0.80 to 0.88, preferably from 0.82 to 0.86; and/or a final boiling point as determined by ASTM D1160 of from 300oC to 800oC, preferably from 400oC to 700oC, preferably greater than 500oC; and/or a weight average molecular weight (Mw) between 30,000 and 400 g/mol preferably between 15,000 and 500 g/mol, more preferably between 5,000 and 600 g/mol; and/or a number average molecular weight (Mn) between 10,000 and 400 g/mol, preferably between 5,000 and 500 g/mol, more preferably between

2,000 and 600 g/mol; and/or a flash point as measured by ASTM D 92 of 200°C or greater; and/or a specific gravity (15.6°C) of less than 0.86.

[00100] In certain particularly preferred embodiments, the NFP has a specific gravity of 0.86 or less (preferably 0.855 or less, preferably 0.85 or less), and one or more of the following: a VI of 120 or more (preferably 135 or more, preferably 140 or more), and/or a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more).

[00101] In certain particularly preferred embodiments, the NFP has a pour point of -10°C or less (preferably -15°C or less, preferably -20°C or less, preferably -25°C or less), a VI of 120 or more (preferably 135 or more, preferably 140 or more), and optionally a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more).

[00102] In certain particularly preferred embodiments, the NFP has a pour point of -20°C or less (preferably -25°C or less, preferably -30°C or less, preferably -40°C or less) and one or more of the following: a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more), and/or a VI of 120 or more (preferably 135 or more, preferably 140 or more), and/or a KV100 of 4 cSt or more (preferably 6 cSt or more, preferably 8 cSt or more, preferably 10 cSt or more), and/or a specific gravity of 0.86 or less (preferably 0.855 or less, preferably 0.85 or less).

[00103] In certain particularly preferred embodiments, the NFP has a KV100 of 4 cSt or more (preferably 5 cSt or more, preferably 6 cSt or more, preferably 8 cSt or more, preferably 10 cSt or more), a specific gravity of 0.86 or less (preferably 0.855 or less, preferably 0.85 cSt or less), and a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more).

[00104] In a preferred embodiment, the NFP has a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more), a pour point of -10°C or less (preferably -15°C or less, preferably -20°C or less, preferably -25°C or less), a specific gravity of 0.86 or less (preferably 0.855 or less, preferably 0.85 or less),

a KV100 of 4 cSt or more (preferably 5 cSt or more, preferably 6 cSt or more, preferably 8 cSt or more, preferably 10 cSt or more), and optionally a VI of 100 or more (preferably 120 or more, preferably 135 or more).

[00105] In a preferred embodiment, the NFP has a KV100 of 35 cSt or more (preferably 40 or more) and a specific gravity of 0.86 or less (preferably 0.855 or less), and optionally one or more of the following: a flash point of 200°C or more (preferably 220°C or more, preferably 240°C or more), and/or a pour point of -10°C or less (preferably -15°C or less, preferably -20°C or less, preferably -25°C or less).

[00106] In a preferred embodiment, the NFP has a flash point of 200°C or more (preferably 210°C or more, preferably 220°C or more), a pour point of -10°C or less (preferably -20°C or less, preferably -30°C or less), and a KV100 of 6 cSt or more (preferably 8 cSt or more, preferably 10 cSt or more, preferably 15 cSt or more).

[00107] In a preferred embodiment, the NFP has a pour point of -40°C or less (preferably -50°C or less) and a specific gravity of 0.84 or less (preferably 0.83 or less).

[00108] In a preferred embodiment, the percentage of carbons in chain-type paraffins (CP) for any NFP is at least 80% (preferably at least 85%, more preferably at least 90%, even more preferably at least 95%, even more preferably at least 98%, most preferably at least 99%).

[00109] Preferred compositions of the present invention can be characterized in that the glass transition temperature (Tg) of the composition decreases by at least 1°C (preferably at least 2°C, preferably at least 3°C, preferably at least 4°C, preferably at least 5°C, preferably at least 6°C, preferably at least 7°C, preferably at least 8°C, preferably at least 9°C, preferably at least 10°C) for every 1 wt% of NFP present in the composition, while the peak melting and crystallization temperatures of the polyolefin remain within 5°C (preferably within 4°C,

preferably within 3°C, preferably within 2°C) of their values for the unplasticized polyolefin.

[00110] Preferred compositions of the present invention can be characterized in that the glass transition temperature (Tg) of the plasticized composition is at least 2°C (preferably at least 4°C, preferably at least 6°C, preferably at least 8°C, preferably at least 10°C, preferably at least 12°C, preferably at least 15°C, preferably at least 20°C, preferably at least 30°C) lower than that of the unplasticized polyolefin, while the peak melting and crystallization temperatures of the polyolefin remain within 5°C (preferably within 4°C, preferably within 3°C, preferably within 2°C) of their values for the unplasticized polyolefin.

[00111] Preferred compositions of the present invention can be characterized in that the glass transition temperature (Tg) of at least one propylene polymer in the composition decreases by at least 1°C (preferably at least 2°C, preferably at least 3°C, preferably at least 5°C, preferably at least 6°C, preferably at least 7°C, preferably at least 8°C, preferably at least 9°C, preferably at least 9°C, preferably at least 10°C) for every 1 wt% of NFP present in the composition, while the peak melting and crystallization temperatures of the polyolefin remain within 5°C (preferably within 4°C, preferably within 3°C, preferably within 2°C) of their values for the unplasticized polyolefin.

[00112] Preferred compositions of the present invention can be characterized in that the glass transition temperature (Tg) of at least one propylene polymer in the plasticized composition is at least 2°C (preferably at least 4°C, preferably at least 6°C, preferably at least 8°C, preferably at least 10°C, preferably at least 12°C, preferably at least 15°C, preferably at least 20°C, preferably at least 25°C, preferably at least 30°C) lower than that of the unplasticized polyolefin, while the peak melting and crystallization temperatures of the polyolefin remain within 5°C (preferably within 4°C, preferably within 3°C, preferably within 2°C) of their values for the unplasticized polyolefin.

[00113] Preferred compositions of the present invention can be characterized in that the plasticized composition decreases less than 3% (preferably less than 2%, preferably less than 1%) in weight when permanence of the NFP is determined by ASTM D1203 (0.25 mm thick sheet, 300 hours in dry 70°C oven). Weight loss here refers to the reduction in weight in excess of that measured for the unplasticized composition under the same test conditions.

[00114] Preferred NFP's of this invention are characterized in that, when blended with the polyolefin to form a plasticized composition, the NFP is miscible with the polyolefin as indicated by no change in the number of tan-delta peaks in the Dynamic Mechanical Thermal Analysis (DMTA) trace as compared to the unplasticized polyolefin DMTA trace (the "trace" is the plot of tan-delta vs temperature). Lack of miscibility is indicated by an increase in the number of tan-delta peaks in DMTA trace over those in the unplasticized polyolefin.

[00115] For purpose of this invention and the claims thereto, unless otherwise noted, the following tests shown in Tables E-G should be used for the indicated property:

Table E. Polyolefin Characterization Test Methods

A CITINA TO 1000 (1000C/2 16 lcg)			
ASTM D 1238 (190°C/2.16 kg)			
ASTM D 1238 (230°C/2.16 kg)			
ASTM D 1505			
DMTA (see Experimental			
Methods)			
DSC (see Experimental Methods)			
DSC (see Experimental Methods)			
DSC (see Experimental Methods)			
DSC (see Experimental Methods)			
SEC-3D (see Experimental			
Methods)			
SEC-3D (see Experimental			
Methods)			
ASTM D 1601 (135°C in decalin)			

Table F. Mechanical Property Test Methods

Tensile Properties	ASTM D 638		
Heat Deflection Temperature	ASTM D 648 (66 psi)		
Vicat Softening Temperature	ASTM D 1525 (200 g)		
Gardner Impact Strength	ASTM D 5420		
Izod Impact Strength	ASTM D 256 (A)		
1% Secant Flexural Modulus	ASTM D 790 (A)		
Rockwell Hardness	ASTM D 785 (R scale)		

Table G. NFP Property Test Methods

Kinematic Viscosity (KV)	ASTM D 445			
Viscosity Index (VI)	ASTM D 2270			
Pour Point	ASTM D 97			
Specific Gravity and Density	ASTM D 4052 (15.6/15.6°C)			
Flash Point	ASTM D 92			
M <sub>n</sub>	GC (if KV100 of 10 cSt or less) or GPC			
<b>.</b>	(if KV100 is more than 10 cSt) (see			
	Experimental Methods)			
Glass Transition Temperature (Tg)	ASTM 1356			
Branch Paraffin: N-paraffin ratio	<sup>13</sup> C-NMR (see Experimental Methods)			
Wt% mono-methyl species	<sup>13</sup> C-NMR (see Experimental Methods)			
% side chains with X number of carbons	<sup>13</sup> C-NMR (see Experimental Methods)			
Boiling/ Distillation Range	ASTM D 1160			
Carbon Type Composition (C <sub>A</sub> , C <sub>N</sub> , C <sub>P</sub> )	ASTM D 2140 (see Experimental			
,	Methods)			
Saturates Content	ASTM D 2007			
Sulfur Content	ASTM D 2622			
Nitrogen Content	ASTM D 4629			
Bromine Number	ASTM D 1159 (or ASTM D 2710 if so			
	directed by ASTM D 1159)			
Aniline Point	ASTM D 611			
Color	ASTM D 1209 (APHA Color)			

#### Selectively hydrogenated block copolymers

[00116] The selectively hydrogenated block copolymers according to the present invention can be characterized as having: (i) terminal polymeric blocks of a vinyl aromatic monomer; and (ii) a central polymeric block which can be obtained by preparing the block copolymer using an olefin, preferably a conjugated diolefin, and subsequently selectively hydrogenating said central polymeric block.

[00117] In a preferred embodiment the end-blocks of these copolymers are polymer blocks of styrene. Other vinyl aromatic hydrocarbons, including alphamethyl styrene, various alkyl-substituted styrenes, alkoxy-substituted styrenes, vinyl naphthalene, vinyl toluene and the like, can be substituted for styrene.

[00118] The midblock is at least one olefin, preferably a conjugated diolefin which is subsequently hydrogenated. By "subsequently hydrogenated" is meant that the conjugated diolefin midblock is selectively hydrogenated after incorporation into the polymer. Suitable hydrogenated block copolymers can be prepared by techniques per se well-known in the art, such as those described in the aforementioned U.S. Patent No. 4,904,731, and references incorporated therein. A particularly preferred midblock comprises, consists essentially of, or consists of ethylene/butene-1 copolymer or ethylene/propylene copolymer.

[00119] In addition to selectively hydrogenated SEBS, other block copolymers which can be selectively hydrogenated to provide useful components include SIS (styrene-isoprene-styrene), SBS (styrene-butadiene-styrene), and star-branched SIS and SBS compounds, all of which are per se well-known in the art.

[00120] In an embodiment, block copolymers which can be hydrogenated to form the hydrogenated block copolymers useful as midblocks in the polymeric composition of this invention will have the following general formula: Bx -(A-B)y -Az, where A is a poly(monoalkenyl) block and B is a poly(conjugated diene) block; x and z are, independently, integers equal to 0 or 1; y is a whole number from 1 to about 25; provided, however, that  $z + y \ge 2$ .

[00121] In general, while not critical to the characterization, each polymeric block A can have the same or a different weight average molecular weight within the range from about 4,000 to about 50,000 and each polymeric block B can have the same or a different weight average molecular weight within the range from about 10,000 to about 200,000. In a preferred embodiment, each polymeric block A will have approximately the same weight average molecular weight within the

range from about 5, 000 to about 10,000 and each polymeric block B will have approximately the same weight average molecular weight within the range from about 25, 000 to about 100,000.

[00122] In general, the block copolymers useful in the present invention can be hydrogenated using any of the methods known in the prior art to be suitable for such hydrogenation. In an embodiment, the conditions used to hydrogenate the block copolymers useful in this invention can be selected to insure that at least 50%, preferably at least 80% and most preferably at least 95% of the ethylenic unsaturation remaining in the conjugated diolefin polymer blocks after preparation is saturated as a result of the hydrogenation. The hydrogenation conditions will also be selected so as to insure that less than 20%, preferably less than 10% and most preferably less than 5% of the aromatic unsaturation in the monoalkenyl aromatic hydrocarbon polymer blocks is hydrogenated. Suitable hydrogenation methods are well-known in the art, such as discussed in the aforementioned U.S. Patent No. 4,904,731 (as well as numerous other references such as Statutory Invention Registration US H1956 H), and the aforementioned conditions can be selected by one of ordinary skill in the art in possession of this disclosure.

[00123] Specific examples of selectively hydrogenated block copolymers useful in the present invention include the KRATON® G polymers commercially available from Shell.

### Polypropylene

[00124] The polypropylene component of the blend is selected from polypropylene homopolymer, polypropylene copolymers, and blends thereof. The homopolymer can be atactic polypropylene, isotactic polypropylene, syndiotactic polypropylene and blends thereof. The copolymer can be a random copolymer, a statistical copolymer, a block copolymer, and blends thereof. In a preferred embodiment the polypropylene is at least one atactic homopolymer or copolymer of propylene.

[00125] As used herein, the term "polypropylene" means a polymer made of at least 50% propylene units, preferably at least 70% propylene units, more preferably at least 80% propylene units, even more preferably at least 90% propylene units, even more preferably at least 95% propylene units or 100% propylene units.

[00126] The method of making the polypropylene is not critical, as it can be made by slurry, solution, gas phase or other suitable processes, and by using catalyst systems appropriate for the polymerization of polyolefins, such as Ziegler-Natta-type catalysts, metallocene-type catalysts, other appropriate catalyst systems or combinations thereof.

[00127] In a preferred embodiment the propylene is a homopolymer or copolymer made using Zeigler Natta catalysts. In another embodiment the propylene polymers are made using metallocene catalysts. Such catalysts are well known in the art, and are described in, for example, Ziegler Catalysts (Gerhard Fink, Rolf Mülhaupt and Hans H. Brintzinger, eds., Springer-Verlag 1995); Resconi et al., *Selectivity in Propene Polymerization with Metallocene Catalysts*, 100 CHEM. REV. 1253-1345 (2000); and I, II METALLOCENE-BASED POLYOLEFINS (Wiley & Sons 2000).

[00128] It will be recognized by one of ordinary skill in the art that other preferred embodiments include combinations of embodiments specified herein, e.g., for the polypropylene, a preferred embodiment includes an atactic propylene homopolymer made using a Zeigler Natta catalyst.

[00129] Preferred propylene homopolymers and copolymers useful in this invention typically can also be described by one or more of the following characteristics: (a) an Mw of 30,000 to 2,000,000 g/mol preferably 50,000 to 1,000,000, more preferably 90,000 to 500,000, as measured by GPC as described below in the test methods; (b) an Mw/Mn of 1 to 40, preferably 1.6 to 20, more preferably 1.8 to 10, more preferably 1.8 to 3 as measured by GPC as described below in the test methods; (c) a Tm (second melt) of 30 to 200°C, preferably 30 to

185°C, preferably 50 to 175, more preferably 60 to 170 as measured by the DSC method described below in the test methods; (d) a crystallinity of 5 to 80%, preferably 10 to 70, more preferably 20 to 60% as measured by the DSC method described below in the test methods; (e) a glass transition temperature (Tg) of -40°C to 20°C, preferably -20°C to 10°C, more preferably -10°C to 5°C as measured by the DMTA method described below in the test methods; (f) a heat of fusion (Hf) of 180 J/g or less, preferably 20 to 150 J/g, more preferably 40 to 120 J/g as measured by the DSC method described below in the test methods; (g) a crystallization temperature (Tc) of 15 to 120°C, preferably 20 to 115 °C, more preferably 25 to 110°C, preferably 60 to 145°C, as measured by the method described below in the test methods; (h) a heat deflection temperature of 45 to 140°C, preferably 60 to 135°C, more preferably 75 to 125°C as measured by the method described below in the test methods; (i) a Rockwell hardness (R scale) of 25 or more, preferably 40 or more, preferably 60 or more, preferably 80 or more, preferably 100 or more, preferably from 25 to 125; (j) a percent crystallinity of at least 30%, preferably at least 40%, alternatively at least 50%, as measured by the method described below in the test methods; (k) a percent amorphous content of at least 50%, alternatively at least 60%, alternatively at least 70 %, even alternatively between 50 and 95%, or 70% or less, preferably 60% or less, preferably 50% or less as determined by subtracting the percent crystallinity from 100; and (1) a branching index (g') of 0.2 to 2.0, preferably 0.5 to 1.5, preferably 0.7 to 1.1, as measured by the method described below.

[00130] In an embodiment, the polypropylene is a propylene homopolymer. In one preferred embodiment the propylene homopolymer has a molecular weight distribution (Mw/Mn) of up to 40, preferably ranging from 1.5 to 10, and from 1.8 to 7 in another embodiment, and from 1.9 to 5 in yet another embodiment, and from 2.0 to 4 in yet another embodiment. In another embodiment the propylene homopolymer has a Gardner impact strength, tested on 0.125 inch disk at 23°C, that can range from 20 in-lb to 1000 in-lb in one embodiment, and from 30 in-lb to 500 in-lb in another embodiment, and from 40 in-lb to 400 in-lb in yet another embodiment. In yet another embodiment, the 1% secant flexural modulus can

range from 100 MPa to 2300 MPa, and from 200 MPa to 2100 MPa in another embodiment, and from 300 MPa to 2000 MPa in yet another embodiment, wherein a desirable polypropylene can exhibit any combination of any upper flexural modulus limit with any lower flexural modulus limit. The melt flow rate (MFR) (ASTM D 1238, 230°C, 2.16 kg) of preferred propylene polymers range from 0.1 dg/min to 2500 dg/min in one embodiment, and from 0.3 to 500 dg/min in another embodiment.

[00131] In an embodiment, the polypropylene homopolymer or propylene copolymer useful in the present invention has some level of isotacticity. Thus, in one embodiment, a polypropylene comprising isotactic polypropylene is a useful polymer in the invention of this patent, and similarly, highly isotactic polypropylene is useful in another embodiment. As used herein, "isotactic" is defined as having at least 10% isotactic pentads according to analysis by <sup>13</sup>C-NMR as described in the test methods below. As used herein, "highly isotactic" is defined as having at least 60% isotactic pentads according to analysis by <sup>13</sup>C-NMR. In a desirable embodiment, the polypropylene is a polypropylene homopolymer having at least 85% isotacticity, and at least 90% isotacticity in yet another embodiment.

[00132] In another embodiment, the polypropylene comprises a polypropylene homopolymer having at least 85% syndiotacticity, and at least 90% syndiotacticity in yet another embodiment. As used herein, "syndiotactic" is defined as having at least 10% syndiotactic pentads according to analysis by <sup>13</sup>C-NMR as described in the test methods below. As used herein, "highly syndiotactic" is defined as having at least 60% syndiotactic pentads according to analysis by <sup>13</sup>C-NMR.

[00133] In another embodiment the polypropylene comprises a propylene homopolymer that is isotactic, highly isotactic, syndiotactic, highly syndiotactic, atactic, or mixtures thereof. Atactic polypropylene is defined to be less than 10% isotactic or syndiotactic pentads. Preferred atactic polypropylenes typically have an Mw of 20,000 up to 1,000,000.

[00134] Preferred propylene polymers that are useful in this invention include those sold under the tradenames ACHIEVE™ and ESCORENE™ by ExxonMobil Chemical Company in Houston, Texas.

[00135] In another embodiment of the invention, the polypropylene is a propylene copolymer, either random, or block, of propylene derived units and units selected from ethylene and C<sub>4</sub> to C<sub>20</sub> α-olefin derived units, typically from ethylene and  $C_4$  to  $C_{10}$   $\alpha$ -olefin derived units in another embodiment. The ethylene or C<sub>4</sub> to C<sub>20</sub> α-olefin derived units are present from 0.1 wt% to 50 wt% of the copolymer in one embodiment, and from 0.5 to 30 wt% in another embodiment, and from 1 to 15 wt% in yet another embodiment, and from 0.1 to 5 wt% in yet another embodiment, wherein a desirable copolymer comprises ethylene and C<sub>4</sub> to C<sub>20</sub> α-olefin derived units in any combination of any upper wt% limit with any lower wt% limit described herein. The propylene copolymer will have a weight average molecular weight of from greater than 8,000 g/mol in one embodiment, and greater than 10,000 g/mol in another embodiment, and greater than 12,000 g/mol in yet another embodiment, and greater than 20,000 g/mol in yet another embodiment, and less than 1,000,000 g/mol in yet another embodiment, and less than 800,000 in yet another embodiment, wherein a desirable copolymer can comprise any upper molecular weight limit with any lower molecular weight limit described herein.

[00136] Particularly desirable propylene copolymers have a molecular weight distribution (Mw/Mn) ranging from 1.5 to 10, and from 1.6 to 7 in another embodiment, and from 1.7 to 5 in yet another embodiment, and from 1.8 to 4 in yet another embodiment. The Gardner impact strength, tested on 0.125 inch disk at 23°C, of the propylene copolymer can range from 20 in-lb to 1000 in-lb in one embodiment, and from 30 in-lb to 500 in-lb in another embodiment, and from 40 in-lb to 400 in-lb in yet another embodiment. In yet another embodiment, the 1% secant flexural modulus of the propylene copolymer ranges from 100 MPa to 2300 MPa, and from 200 MPa to 2100 MPa in another embodiment, and from 300 MPa to 2000 MPa in yet another embodiment, wherein a desirable polypropylene can exhibit any combination of any upper flexural modulus limit with any lower

flexural modulus limit. The melt flow rate (MFR) (ASTM D 1238, 230°C, 2.16 kg) of propylene copolymer ranges from 0.1 dg/min to 2500 dg/min in one embodiment, and from 0.3 to 500 dg/min in another embodiment.

[00137] In another embodiment the polypropylene can be a propylene copolymer comprising propylene and one or more other monomers selected from the group consisting of ethylene and C<sub>4</sub> to C<sub>20</sub> linear, branched or cyclic monomers, and in some embodiments is a C<sub>4</sub> to C<sub>12</sub> linear or branched alphaolefin, preferably butene, pentene, hexene, heptene, octene, nonene, decene, dodecene, 4-methyl-pentene-1, 3-methyl pentene-1, 3,5,5-trimethyl-hexene-1, and the like. The monomers can be present at up to 50 weight %, preferably from 0 to 40 weight %, more preferably from 0.5 to 30 weight %, more preferably from 2 to 30 weight %, more preferably from 5 to 20 weight %.

[00138] Preferred linear alpha-olefins useful as comonomers for the propylene copolymers useful in this invention include C3 to C8 alpha-olefins, more preferably 1-butene, 1-hexene, and 1-octene, even more preferably 1-butene. Preferred linear alpha-olefins useful as comonomers for the butene copolymers useful in this invention include C<sub>3</sub> to C<sub>8</sub> alpha-olefins, more preferably propylene, 1-hexene, and 1-octene, even more preferably propylene. Preferred branched alpha-olefins include 4-methyl-1-pentene, 3-methyl-1-pentene, and 3,5,5trimethyl-1-hexene, 5-ethyl-1-nonene. Preferred aromatic-group-containing monomers contain up to 30 carbon atoms. Suitable aromatic-group-containing monomers comprise at least one aromatic structure, preferably from one to three, more preferably a phenyl, indenyl, fluorenyl, or naphthyl moiety. The aromaticgroup-containing monomer further comprises at least one polymerizable double bond such that after polymerization, the aromatic structure will be pendant from the polymer backbone. The aromatic-group containing monomer can further be substituted with one or more hydrocarbyl groups including but not limited to C1 to C10 alkyl groups. Additionally two adjacent substitutions can be joined to form a ring structure. Preferred aromatic-group-containing monomers contain at least one aromatic structure appended to a polymerizable olefinic moiety. Particularly preferred aromatic monomers include styrene, alpha-methylstyrene,

para-alkylstyrenes, vinyltoluenes, vinylnaphthalene, allyl benzene, and indene, especially styrene, paramethyl styrene, 4-phenyl-1-butene and allyl benzene.

[00139] Non-aromatic cyclic group containing monomers are also preferred. These monomers can contain up to 30 carbon atoms. Suitable non-aromatic cyclic group containing monomers preferably have at least one polymerizable olefinic group that is either pendant on the cyclic structure or is part of the cyclic structure. The cyclic structure can also be further substituted by one or more hydrocarbyl groups such as, but not limited to, C1 to C10 alkyl groups. Preferred non-aromatic cyclic group containing monomers include vinylcyclohexane, vinylcyclohexene, vinylnorbornene, ethylidene norbornene, cyclopentadiene, cyclopentene, cyclohexene, cyclobutene, vinyladamantane and the like.

[00140] In another embodiment the propylene component comprises a random copolymer, also known as an "RCP," comprising propylene and up to 20 mole % of ethylene or a  $C_4$  to  $C_{20}$  olefin, preferably up to 20 mole % ethylene.

[00141] In another embodiment, the polypropylene component comprises an impact copolymer (ICP) or block copolymer. Propylene impact copolymers are commonly used in a variety of applications where strength and impact resistance are desired such as molded and extruded automobile parts, household appliances, luggage and furniture. Propylene homopolymers alone are often unsuitable for such applications because they are too brittle and have low impact resistance particularly at low temperature, whereas propylene impact copolymers are specifically engineered for applications such as these.

[00142] A typical propylene impact copolymer contains at least two phases or components, e.g., a homopolymer component and a copolymer component. The impact copolymer can also comprise three phases such as a PP/EP/PE combination with the PP continuous and a dispersed phase with EP outside and PE inside the dispersed phase particles. These components are usually produced in a sequential polymerization process wherein the homopolymer produced in a first reactor is transferred to a second reactor where copolymer is produced and

incorporated within the matrix of the homopolymer component. The copolymer component has rubbery characteristics and provides the desired impact resistance, whereas the homopolymer component provides overall stiffness.

[00143] Another important feature of ICP's is the amount of amorphous polypropylene they contain. In certain embodiments, it is useful to characterize ICPs according to the invention as having low amorphous polypropylene, preferably less than 3% by weight, more preferably less than 2% by weight, even more preferably less than 1% by weight and most preferably there is no measurable amorphous polypropylene. Percent amorphous polypropylene is determined by the method described below.

[00144] Preferred impact copolymers can be a reactor blend (in situ blend) or a post reactor (ex-situ) blend. In one embodiment, a suitable impact copolymer comprises from 40% to 95% by weight Component A and from 5% to 60% by weight Component B based on the total weight of the impact copolymer; wherein Component A comprises propylene homopolymer or copolymer, the copolymer comprising 10% or less by weight ethylene, butene, hexene or octene comonomer; and wherein Component B comprises propylene copolymer, wherein the copolymer comprises from 5% to 70% by weight ethylene, butene, hexene and/or octene comonomer, and from about 95% to about 30% by weight propylene. In one embodiment of the impact copolymer, Component B consists essentially of propylene and from about 30% to about 65% by weight ethylene. In another embodiment, Component B comprises ethylene-propylene copolymers, ethylenepropylene-diene terpolymers, ethylene-acrylate copolymers, ethylene-vinyl acetate, styrene-butadiene copolymers, ethylene-acrylic ester copolymers, polybutadiene, polyisoprene, natural rubber, isobutylene, hydrocarbon resin (the hydrocarbon resin being characterized by a molecular weight less than 5000, a  $T_{\rm g}$ of about 50 to 100°C and a softening point, Ring and Ball, as measured by ASTM E-28, of less than about 140°C), rosin ester, and mixtures thereof. In another embodiment, Component B has a molecular weight distribution of less than 3.5. In yet another embodiment, Component B has a weight average molecular weight of at least 20,000. Impact copolymers have been previously disclosed in, for example, U.S. Pat. Nos. 6,342,566 and 6,384,142.

[00145] Component B is most preferably a copolymer consisting essentially of propylene and ethylene although other propylene copolymers, ethylene copolymers or terpolymers can be suitable depending on the particular product properties desired. For example, propylene/butene, hexene or octene copolymers, and ethylene/butene, hexene or octene copolymers can be used, and propylene/ethylene/hexene-1 terpolymers can be used. In a preferred embodiment though, Component B is a copolymer comprising at least 40% by weight propylene, more preferably from about 80% by weight to about 30% by weight propylene, even more preferably from about 70% by weight to about 35% by weight propylene. The comonomer content of Component B is preferably in the range of from about 20% to about 70% by weight comonomer, more preferably from about 30% to about 65% by weight comonomer, even more preferably from about 35% to about 60% by weight comonomer. Most preferably Component B consists essentially of propylene and from about 20% to about 70% ethylene, more preferably from about 30% to about 65% ethylene, and most preferably from about 35% to about 60% ethylene.

[00146] For other Component B copolymers, the comonomer contents will need to be adjusted depending on the specific properties desired. For example, for ethylene/hexene copolymers, Component B should contain at least 17% by weight hexene and at least 83% by weight ethylene.

[00147] Component B, preferably has a narrow molecular weight distribution Mw/Mn, i.e., lower than 5.0, preferably lower than 4.0, more preferably lower than 3.5, even more preferably lower than 3.0 and most preferably 2.5 or lower. These molecular weight distributions should be obtained in the absence of visbreaking or peroxide or other post reactor treatment molecular weight tailoring. Component B preferably has a weight average molecular weight (Mw as determined by GPC) of at least 100,000, preferably at least 150,000, and most preferably at least 200,000.

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[00148] Component B preferably has an intrinsic viscosity greater than 1.00 dl/g, more preferably greater than 1.50 dl/g and most preferably greater than 2.00 dl/g. The term "intrinsic viscosity" or "IV" is used conventionally herein to mean the viscosity of a solution of polymer such as Component B in a given solvent at a given temperature, when the polymer composition is at infinite dilution.

According to the ASTM standard test method D 1601-78, IV measurement involves a standard capillary viscosity measuring device, in which the viscosity of a series of concentrations of the polymer in the solvent at the given temperature are determined. For Component B, decalin is a suitable solvent and a typical temperature is 135°C. From the values of the viscosity of solutions of varying concentrations, the "value" at infinite dilution can be determined by extrapolation.

Component B preferably has a composition distribution breadth index [00149] (CDBI) of greater than 60%, more preferably greater than 65%, even more preferably greater than 70%, even more preferably greater than 75%, still more preferably greater than 80%, and most preferably greater than 85%. CDBI defines the compositional variation among polymer chains in terms of ethylene (or other comonomer) content of the copolymer as a whole. A measure of composition distribution is the "Composition Distribution Breadth Index" ("CDBI") as defined in U.S. Patent 5,382,630 which is hereby incorporated by reference. CDBI is defined as the weight percent of the copolymer molecules having a comonomer content within 50% of the median total molar comonomer content. The CDBI of a copolymer is readily determined utilizing well known techniques for isolating individual fractions of a sample of the copolymer. One such technique is Temperature Rising Elution Fraction (TREF), as described in Wild, et al., <u>J. Poly.</u> Sci., Poly. Phys. Ed., vol. 20, p. 441 (1982) and U.S. Patent No. 5,008,204, which are incorporated herein by reference.

[00150] Component B of the ICPs preferably has low crystallinity, preferably less than 10% by weight of a crystalline portion, more preferably less than 5% by weight of a crystalline portion. Where there is a crystalline portion of Component B, its composition is preferably the same as or at least similar to (within 15% by

weight) the remainder of Component B in terms of overall comonomer weight percent.

[00151] The preferred melt flow rate or MFR of these ICP's depends on the desired end use but is typically in the range of from about 0.2 dg/min to about 200 dg/min, more preferably from about 5 dg/min to about 100 dg/min. Significantly, high MFRs, i.e., higher than 50 dg/min are obtainable. The ICP preferably has a melting point (Tm) of at least 145°C, preferably at least 150°C, more preferably at least 152°C, and most preferably at least 155°C.

[00152] The ICPs comprise from about 40% to about 95% by weight Component A and from about 5% to about 60% by weight Component B, preferably from about 50% to about 95% by weight Component A and from about 5% to about 50% Component B, even more preferably from about 60% to about 90% by weight Component A and from about 10% to about 40% by weight Component B. In the most preferred embodiment, the ICP consists essentially of Components A and B. The overall comonomer (preferably ethylene) content of the total ICP is preferably in the range of from about 2% to about 30% by weight, preferably from about 5% to about 25% by weight, even more preferably from about 5% to about 15% by weight comonomer.

[00153] In another embodiment a preferred impact copolymer composition is prepared by selecting Component A and Component B such that their refractive indices (as measured by ASTM D 542-00) are within 20 % of each other, preferably within 15 %, more preferably 10%, even more preferably within 5% of each other. This selection produces impact copolymers with outstanding clarity. In another embodiment a preferred impact copolymer composition is prepared by selecting a blend of Component A and an NFP, and a blend of Component B and an NFP such that refractive indices of the blends (as measured by ASTM D 542-00) are within 20 % of each other, preferably within 15 %, more preferably 10%, even more preferably within 5% of each other.

[00154] In yet another embodiment, the Gardner impact strength, tested on 0.125 inch disk at -29°C, of the propylene impact copolymer ranges from 20 in-lb to 1000 in-lb, and from 30 in-lb to 500 in-lb in another embodiment, and from 40 in-lb to 400 in-lb in yet another embodiment. Further, the 1% secant flexural modulus of the propylene impact copolymer can range from 100 MPa to 2300 MPa in one embodiment, and from 200 MPa to 2100 MPa in another embodiment, and from 300 MPa to 2000 MPa in yet another embodiment, wherein a desirable polypropylene can exhibit any combination of any upper flexural modulus limit with any lower flexural modulus limit. The melt flow rate (MFR) (ASTM D 1238, 230°C, 2.16 kg) of desirable homopolymers ranges from 0.1 dg/min to 2500 dg/min in one embodiment, and from 0.3 to 500 dg/min in another embodiment.

[00155] In another embodiment polymers that are useful in this invention include homopolymers and random copolymers of propylene having a heat of fusion as determined by Differential Scanning Calorimetry (DSC) of less than 50 J/g, a melt index (MI) of less than 20 dg/min and or an MFR of 20 dg/min or less, and contains stereoregular propylene crystallinity preferably isotactic stereoregular propylene crystallinity. In another embodiment the polymer is a random copolymer of propylene and at least one comonomer selected from ethylene,  $C_4$ - $C_{12}$   $\alpha$ -olefins, and combinations thereof. Preferably the random copolymers of propylene comprises from 2 wt% to 25 wt% polymerized ethylene units, based on the total weight of the polymer; has a narrow composition distribution; has a melting point (Tm) of from 25°C to 120°C, or from 35°C to 80°C; has a heat of fusion within the range having an upper limit of 50 J/g or 25 J/g and a lower limit of 1 J/g or 3 J/g; has a molecular weight distribution Mw/Mn of from 1.8 to 4.5; and has a melt index (MI) of less than 20 dg/min, or less than 15 dg/min. The intermolecular composition distribution of the copolymer is determined by thermal fractionation in a solvent. A typical solvent is a saturated hydrocarbon such as hexane or heptane. The thermal fractionation procedure is described below. Typically, approximately 75% by weight, preferably 85% by weight, of the copolymer is isolated as one or two adjacent, soluble fractions with the balance of the copolymer in immediately preceding or succeeding fractions.

Each of these fractions has a composition (wt% comonomer such as ethylene or other  $\alpha$ -olefin) with a difference of no greater than 20% (relative), preferably 10% (relative), of the average weight % comonomer of the copolymer. The copolymer has a narrow composition distribution if it meets the fractionation test described above.

[00156] A particularly preferred polymer useful in the present invention is an elastic polymer with a moderate level of crystallinity due to stereoregular propylene sequences. The polymer can be: (A) a propylene homopolymer in which the stereoregularity is disrupted in some manner such as by regio-inversions; (B) a random propylene copolymer in which the propylene stereoregularity is disrupted at least in part by comonomers; or (C) a combination of (A) and (B).

[00157] In one embodiment, the polymer further includes a non-conjugated diene monomer to aid in vulcanization and other chemical modification of the blend composition. The amount of diene present in the polymer is preferably less than 10% by weight, and more preferably less than 5% by weight. The diene can be any non-conjugated diene which is commonly used for the vulcanization of ethylene propylene rubbers including, but not limited to, ethylidene norbornene, vinyl norbornene, and dicyclopentadiene.

[00158] In one embodiment, the polymer is a random copolymer of propylene and at least one comonomer selected from ethylene, C<sub>4</sub>-C<sub>12</sub> α-olefins, and combinations thereof. In a particular aspect of this embodiment, the copolymer includes ethylene-derived units in an amount ranging from a lower limit of 2%, 5%, 6%, 8%, or 10% by weight to an upper limit of 20%, 25%, or 28% by weight. This embodiment will also include propylene-derived units present in the copolymer in an amount ranging from a lower limit of 72%, 75%, or 80% by weight to an upper limit of 98%, 95%, 94%, 92%, or 90% by weight. These percentages by weight are based on the total weight of the propylene and ethylene-derived units; i.e., based on the sum of weight percent propylene-derived units and weight percent ethylene-derived units being 100%. The ethylene

composition of a polymer can be measured as follows. A thin homogeneous film is pressed at a temperature of about  $150^{\circ}$ C or greater, then mounted on a Perkin Elmer PE 1760 infrared spectrophotometer. A full spectrum of the sample from  $600 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$  is recorded and the monomer weight percent of ethylene can be calculated according to the following equation: Ethylene wt % =  $82.585 - 111.987X + 30.045 \text{ X}^2$ , wherein X is the ratio of the peak height at  $1155 \text{ cm}^{-1}$  and peak height at either  $722 \text{ cm}^{-1}$  or  $732 \text{ cm}^{-1}$ , whichever is higher. The concentrations of other monomers in the polymer can also be measured using this method.

[00159] Comonomer content of discrete molecular weight ranges can be measured by Fourier Transform Infrared Spectroscopy (FTIR) in conjunction with samples collected by GPC. One such method is described in Wheeler and Willis, Applied Spectroscopy, 1993, vol. 47, pp. 1128-1130. Different but similar methods are equally functional for this purpose and well known to those skilled in the art.

[00160] Comonomer content and sequence distribution of the polymers can be measured by <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C NMR), and such method is well known to those skilled in the art.

[00161] In one embodiment, the polymer is a random propylene copolymer having a narrow composition distribution. In another embodiment, the polymer is a random propylene copolymer having a narrow composition distribution and a melting point of from 25°C to 110°C. The copolymer is described as random because for a polymer comprising propylene, comonomer, and optionally diene, the number and distribution of comonomer residues is consistent with the random statistical polymerization of the monomers. In stereoblock structures, the number of block monomer residues of any one kind adjacent to one another is greater than predicted from a statistical distribution in random copolymers with a similar composition. Historical ethylene-propylene copolymers with stereoblock structure have a distribution of ethylene residues consistent with these blocky structures rather than a random statistical distribution of the monomer residues in

the polymer. The intramolecular composition distribution (i.e., randomness) of the copolymer can be determined by <sup>13</sup>C NMR, which locates the comonomer residues in relation to the neighboring propylene residues. The intermolecular composition distribution of the copolymer is determined by thermal fractionation in a solvent. A typical solvent is a saturated hydrocarbon such as hexane or heptane. Typically, approximately 75% by weight, preferably 85% by weight, of the copolymer is isolated as one or two adjacent, soluble fractions with the balance of the copolymer in immediately preceding or succeeding fractions. Each of these fractions has a composition (wt% comonomer such as ethylene or other  $\alpha$ olefin) with a difference of no greater than 20% (relative), preferably 10% (relative), of the average weight % comonomer of the copolymer. The copolymer has a narrow composition distribution if it meets the fractionation test described above. To produce a copolymer having the desired randomness and narrow composition, it is beneficial if (1) a single-site metallocene catalyst is used which allows only a single statistical mode of addition of the first and second monomer sequences and (2) the copolymer is well-mixed in a continuous flow stirred tank polymerization reactor which allows only a single polymerization environment for substantially all of the polymer chains of the copolymer.

[00162] The crystallinity of the polymers can be expressed in terms of heat of fusion. Embodiments of the present invention include polymers having a heat of fusion, as determined by DSC, ranging from a lower limit of 1.0 J/g, or 3.0 J/g, to an upper limit of 50 J/g, or 10 J/g. Without wishing to be bound by theory, it is believed that the polymers of embodiments of the present invention have generally isotactic, crystallizable propylene sequences, and the above heats of fusion are believed to be due to the melting of these crystalline segments.

[00163] The crystallinity of the polymer can also be expressed in terms of crystallinity percent. The thermal energy for the highest order of polypropylene is estimated at 207 J/g. That is, 100% crystallinity is equal to 207 J/g. Preferably, the polymer has a polypropylene crystallinity within the range having an upper limit of 65%, 40%, 30%, 25%, or 20%, and a lower limit of 1%, 3%, 5%, 7%, or 8%.

"melting point," as used herein, is the highest peak highest meaning the largest amount of polymer being reflected as opposed to the peak occurring at the highest temperature among principal and secondary melting peaks as determined by DSC, discussed above. In one embodiment of the present invention, the polymer has a single melting point. Typically, a sample of propylene copolymer will show secondary melting peaks adjacent to the principal peak, which are considered together as a single melting point. The highest of these peaks is considered the melting point. The polymer preferably has a melting point by DSC ranging from an upper limit of 110°C, 105°C, 90°C, 80°C, or 70°C, to a lower limit of 0°C, 20°C, 25°C, 30°C, 35°C, 40°C, or 45°C.

[00165] In an embodiment, the polypropylene used in the invention have a weight average molecular weight (Mw) within the range having an upper limit of 5,000,000 g/mol, 1,000,000 g/mol, or 500,000 g/mol, and a lower limit of 10,000 g/mol, 20,000 g/mol, or 80,000 g/mol, and a molecular weight distribution Mw/Mn (MWD), sometimes referred to as a "polydispersity index" (PDI), ranging from a lower limit of 1.5, 1.8, or 2.0 to an upper limit of 40, 20, 10, 5, or 4.5, with a range of from any upper limit to any lower limit being contemplated as preferred embodiments. In one embodiment, the polymer has a Mooney viscosity, ML(1+4) @ 125°C, of 100 or less, 75 or less, 60 or less, or 30 or less. Mooney viscosity, as used herein, can be measured as ML(1+4) @ 125°C according to ASTM D1646, unless otherwise specified.

[00166] The polymers used in embodiments of the present invention can have a tacticity index (m/r) ranging from a lower limit of 4 or 6 to an upper limit of 8, 10, or 12. The tacticity index, expressed herein as "m/r", is determined by <sup>13</sup>C nuclear magnetic resonance (NMR). The tacticity index m/r is calculated as defined in H. N. Cheng, *Macromolecules*, 17, 1950 (1984). The designation "m" or "r" describes the stereochemistry of pairs of contiguous propylene groups, "m" referring to meso and "r" to racemic. An m/r ratio of 0 to less than 1.0 generally describes a syndiotactic polymer, and an m/r ratio of 1.0 an atactic material, and an m/r ratio of greater than 1.0 an isotactic material. An isotactic material

theoretically can have a ratio approaching infinity, and many by-product atactic polymers have sufficient isotactic content to result in ratios of greater than 50.

[00167] In one embodiment, the polymer has isotactic stereoregular propylene crystallinity. The term "stereoregular" as used herein means that the predominant number, i.e. greater than 80%, of the propylene residues in the polypropylene or in the polypropylene continuous phase of a blend, such as impact copolymer exclusive of any other monomer such as ethylene, has the same 1,2 insertion and the stereochemical orientation of the pendant methyl groups is the same, either meso or racemic.

[00168] An ancillary procedure for the description of the tacticity of the propylene units of embodiments of the current invention is the use of triad tacticity. The triad tacticity of a polymer is the relative tacticity of a sequence of three adjacent propylene units, a chain consisting of head to tail bonds, expressed as a binary combination of m and r sequences. It is usually expressed for copolymers of the present invention as the ratio of the number of units of the specified tacticity to all of the propylene triads in the copolymer. The triad tacticity (mm fraction) of a propylene copolymer can be determined from a <sup>13</sup>C NMR spectrum of the propylene copolymer as described in WO 2004/014997.

### Plastomer

[00169]. In one or more embodiments, the plastomer is or includes one or more copolymers comprising at least 50 wt% ethylene, and having up to 50 wt %, preferably 1 to 35 weight %, even more preferably 1 to 6 weight % of a C3-C20 comonomer. The plastomer can also include termonomers and tetramonomers which can be one or more of the C3 to C20 olefins, any C4 to C20 linear, cyclic or branched dienes or trienes and any styrenic monomers such as styrene, alphamethyl styrene, or para-methyl styrene. Preferred examples include butadiene, pentadiene, cyclopentadiene, hexadiene, cyclohexadiene, heptadiene, octadiene, nonadiene, norbornene, vinyl norbornene, ethylidene norbornene, isoprene and heptadiene.

polymerizable olefin monomer and are preferably a linear, branched or cyclic olefin, even more preferably an alpha-olefin. Examples of suitable olefins include propylene, butene, isobutylene, pentene, isopentene, cyclopentene, hexene, isohexene, cyclohexene, heptene, isoheptene, cycloheptene, octene, isooctene, cyclooctene, nonene, cyclononene, decene, isodecene, dodecene, isodecene, 4-methyl-pentene-1, 3-methyl-pentene-1, and 3,5,5-trimethyl hexene-1. Suitable monomers also include dienes, trienes, and styrenic monomers. Preferred examples include styrene, alpha-methyl styrene, para-alkyl styrene (such as paramethyl styrene), hexadiene, norbornene, vinyl norbornene, ethylidene norbornene, butadiene, isoprene, heptadiene, octadiene, and cyclopentadiene. Preferred comonomers for the copolymer of ethylene are propylene, butene, hexene and/or octene.

[00171] The plastomer preferably has a composition distribution breadth index (CDBI) above 90%, even more preferably above 95%. In another preferred embodiment, the plastomer has a density of 0.86 to 0.925 g/cm<sup>3</sup> and a CDBI of over 90%, preferably between 95% and 99%. In another embodiment, the plastomer has a melt flow rate at 190°C of 0.1 to 100 dg/min, preferably 0.5 to 50 dg/min, more preferably 0.8 to 30 dg/min. In one or more embodiments, the plastomer has a density ranging from a low of 0.86 g/cm<sup>3</sup>, 0.87 g/cm<sup>3</sup>, or 0.88 g/cm<sup>3</sup> to a high of 0.90 g/cm<sup>3</sup>, 0.91 g/cm<sup>3</sup>, 0.92 g/cm<sup>3</sup>, or 0.925 g/cm<sup>3</sup>.

[00172] Composition Distribution Breadth Index (CDBI) is a measure of the composition distribution of monomer within the polymer chains. The CDBI can be measured by the procedure described in PCT publication WO 93/03093, published Feb. 18, 1993 including that fractions having a weight average molecular weight (Mw) below 15,000 are ignored when determining CDBI. For purposes of this invention, a homopolymer is defined to have a CDBI of 100%.

[00173] In a preferred embodiment, the plastomer can include metallocene polyethylenes (mPE's). The mPE homopolymers or copolymers may be produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination

with an activator of alumoxane and/or a non-coordinating anion in solution, slurry, high pressure or gas phase. The catalyst and activator may be supported or unsupported and the cyclopentadienyl rings by may substituted or unsubstituted. Several commercial products produced with such catalyst/activator combinations are commercially available from ExxonMobil Chemical Company in Baytown, Texas under the tradename EXACT™. For more information on the methods and catalysts/activators to produce such mPE homopolymers and copolymers see WO 94/26816; WO 94/03506; EPA 277,003; EPA 277,004; U.S. Pat. No. 5,153,157; U.S. Pat. No. 5,198,401; U.S. Pat. No. 5,240,894; U.S. Pat. No. 5,017,714; CA 1,268,753; U.S. Pat. No. 5,324,800; EPA 129,368; U.S. Pat. No. 5,264,405; EPA 520,732; WO 92 00333; U.S. Pat. No. 5,096,867; U.S. Pat. No. 5,507,475; EPA 426 637; EPA 573 403; EPA 520 732; EPA 495 375; EPA 500 944; EPA 570 982; WO91/09882; WO94/03506 and U.S. Pat. No. 5,055,438.

[00174] In one or more embodiments, the plastomer is or includes one or more Exact<sup>TM</sup> Plastomers. Exact<sup>TM</sup> Plastomers are available from ExxonMobil Chemical Company. Illustrative Exact<sup>TM</sup> Plastomers and respective, representative physical properties include:

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	EXACT <sup>TM</sup>	Composition	Density	Melt-Index	DSC-Melting
	Plastomer	Composition	(g/cm3)	(dg/min)	Peak
ļ	Grades		()		(°C),10°C/min
1	3024	Ethylene/butene	0.905	4.5	98
1.	3035	Ethylene/butene	0.900	3.5	88
2.	3128	Ethylene/butene	0.900	1.2	92
3.	4006	Ethylene/butene	0.880	10	60
4.		Ethylene/butene	0.888	2.2	70
5.	4011 4033	Ethylene/butene	0.880	0.8	60
6.		Ethylene/butene	0.873	4.5	55
7.	4049	Ethylene/hexene	0.900	16.5	96
8.	3040 3131	Ethylene/hexene	0.900	3.5	95
9.		Ethylene/hexene	0.900	1.2	96
10.	3132 3139	Ethylene/hexene	0.900	7.5	95
11.	4056	Ethylene/hexene	0.883	2.2	72
12.	4151	Ethylene/hexene	0.895	2.2	89
13.	0201	Ethylene/octene	0.902	1.1	95
14.	0201	Ethylene/octene  Ethylene/octene	0.902	3.0	95
15.		Ethylene/octene  Ethylene/octene	0.902	10	96
16.	0210	Ethylene/octene	0.902	30	95
17.	5061	Ethylene/octene	0.868	0.5	53
18.	5062	Ethylene/octene	0.860	0.5	43
19.	5101	Ethylene/octene	0.902	1.1	98
20.	5171	Ethylene/octene	0.870	1.0	55
21.	5171	Ethylene/octene	0.882	1.1	73
22.		Ethylene/octene	0.860	3.0	36
23.	5361	Ethylene/octene	0.870	5.0	64
24.	8201	Ethylene/octene	0.882	1.1	67
25.	8201	Ethylene/octene  Ethylene/octene	0.882	3.0	73
26.	8203	Ethylene/octene	0.882	10	67
27.	8210	Ethylene/octene	0.882	30	77
28.	8230	Emylene/octene	0.002		

[00175] In one or more embodiments, the plastomer has a heat of fusion less than 70 J/g. In one or more embodiments, the plastomer has a heat of fusion less than 69 J/g or less than 68 J/g, or less than 67 J/g, or less than 66 J/g, or less than 65 J/g. In one or more embodiments, the plastomer has a heat of fusion ranging from a low of 40 J/g, 45 J/g, or 50 J/g to a high of 60 J/g, 65 J/g, or 70 J/g.

### Fillers/additives

[00176] In certain embodiments, the elastomeric-like composition can include fillers, additives, and the like. Suitable fillers include titanium dioxide, calcium

carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads or glass fibers, mineral aggregates, talc, clay, wollastonite, and the like. In a preferred embodiment, the fillers described above can be present at 20 wt% or less (based upon the weight of the composition), preferably 10 wt% or less, preferably 5 wt% or less, preferably between 0.5 and 5 wt%. In another embodiment, the composition does not comprise calcium carbonate. By does not comprise is meant that the calcium carbonate is present at less than 0.5 weight %, preferably less than 0.01 wt%.

[00177] The polymeric composition of this invention can further comprise typical additives per se known in the art such antioxidants, adjuvants, and/or adhesion promoters. Preferred antioxidants include phenolic antioxidants, such as Irganox 1010, Irganox, 1076 both available from Ciba-Geigy. Other preferred additives include block, antiblock, pigments, processing aids, UV stabilizers, neutralizers, lubricants, surfactants and/or nucleating agents can also be present in one or more than one layer in the films. Other preferred additives include polydimethylsiloxane, dyes, waxes, calcium stearate, carbon black, low molecular weight resins and glass beads. Preferred 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 Saret 633 from Sartomer), polyphenylene oxide, oxidized polyolefins, acid modified polyolefins, and anhydride modified polyolefins.

[00178] In another embodiment the polymeric composition can be combined with less than 3 wt. % anti-oxidant, less than 3 wt. % flow improver, less than 10 wt. % wax, and or less than 3 wt. % crystallization aid.

[00179] Other optional components that can be combined with the compositions disclosed include other additives such as surfactants, fillers, color masterbatches, and the like.

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[00180] An important subclass of "fillers" or "additives" includes nanoclays. In embodiments the compositions disclosed can include a nanoclay (the combination

of a polymer and a nanoclay is referred to as a nanocomposite).

[00181] The organoclay can comprise one or more of ammonium, primary alkylammonium, secondary alkylammonium, tertiary alkylammonium, quaternary alkylammonium, phosphonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines or sulfides or sulfonium derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines or sulfides.

[00182] The organoclay can be selected from one or more of montmorillonite, sodium montmorillonite, calcium montmorillonite, magnesium montmorillonite, nontronite, beidellite, volkonskoite, laponite, hectorite, saponite, sauconite, magadite, kenyaite, sobockite, svindordite, stevensite, vermiculite, halloysite, aluminate oxides, hydrotalcite, illite, rectorite, tarosovite, ledikite and/or florine mica.

[00183] The organoclay is preferably present in the nanocomposite at from 0.1 to 50 wt%, based on the total weight of the nanocomposite.

[00184] While preferred amounts of certain specific filler/additives and certain classes of filler/additives have been suggested above, more generally (absent specific directions otherwise given herein) the compositions of this invention can optionally have one or more fillers/additives, preferably in the amount of less than 30 weight%, or less than 25 wt. %, or less than 20 wt. %, or less than 15 wt. %, preferably less than 10 wt. %, more preferably less than 5 wt. %, or in other embodiments less than 2 wt %, or less than 1 wt %, based upon the total weight of the various components and the total weight of the filler/additives. While not critical to the characterization of a "composition comprising a filler/additive", which means that one or more fillers and/or additives are added, a lower limit can be 100 ppm, 500 ppm, 1000 ppm, 0.01 wt %, 0.1 wt %, or similar amounts. In some cases it can be preferable for there to be no fillers/additives, or in other cases preferred embodiments can be directed to the absence of specific fillers/additives,

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e.g., some preferred embodiments have no carbonates, no inorganic fillers, and so on. Filler/additives in the nature of unavoidable impurities can of course be present in the case where no filler/additives are purposefully added but in some embodiments it can be useful to further purify ingredients to avoid filler/additives as much as possible. One of ordinary skill in the art, in possession of the present disclosure, can determine the nature and amount of these optional ingredients by routine experimentation.

## Blending of the components

[00185] The components can be blended using conventional equipment and methods, such a by blending the individual components and subsequently melt mixing in a mixer, or by mixing the components together directly in a mixer, such as a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder including a compounding extruder and a side-arm extruder used directly or indirectly downstream of a polymerization process. The composition can then be extruded into pellets. The blending per se would be well within the skill of the ordinary artisan. The pellets can then be used in the final process, e.g., thermoformed or otherwise molded or extruded into a product, such as a film, sheet, or other article described.

[00186] In one or more embodiments, the blend comprises at least one low molecular weight polyolefin in an amount of about 1.0 wt% to about 90 wt%, based on the total weight of the composition. In one or more embodiments, the blend comprises at least one low molecular weight polyolefin in an amount of about 5.0 wt% to about 50 wt%, based on the total weight of the composition. Preferably, the blend comprises at least one low molecular weight polyolefin in an amount of about 10 wt% to about 30 wt%, based on the total weight of the composition

[00187] In one or more embodiments, the blend comprises at least one selectively hydrogenated block copolymer in an amount of about 1.0 wt% to about 90 wt%, preferably of from about 10 wt% to about 30 wt%, preferably of about 50

wt% to 70 wt%, based on the total weight of the composition. Preferably, the at least one selectively hydrogenated block copolymer is or includes a block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a central polymeric block prepared originally with a conjugated diolefin and subsequently hydrogenated.

[00188] In one or more embodiments, the blend comprises at least one polypropylene in the amount of about 1.0 wt% to about 90 wt%, preferably of about 5.0 wt% to about 50 wt%, preferably of about 10 wt% to about 30 wt%, based on the total weight of the composition.

[00189] In one or more embodiments, the blend comprises at least one plastomer in the amount of about 1.0 wt% to about 90 wt%, preferably of about 5.0 wt% to about 50 wt%, preferably of about 10 wt% to about 30 wt%, based on the total weight of the composition. In one or more embodiments, the blend comprises at least one plastomer in the amount of less than 50 wt%, less than 40 wt%, less than 30 wt%, less than 25 wt%, less than 20 wt%, less than 15 wt%, less than 10 wt%, less than 5 wt%, less than 3 wt%, or less than 2 wt%.

[00190] In one or more embodiments, the blend comprises about 5 wt% to about 50 wt% of at least one low molecular weight polyolefin; about 10 wt% to about 30 wt% of at least one selectively hydrogenated block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a central polymeric block prepared originally with a conjugated diolefin and subsequently hydrogenated; about 5.0 wt% to about 50 wt% of at least one polypropylene; and about 5.0 wt% to about 50 wt% of at least one plastomer.

[00191] In one or more embodiments, the blend comprises about 10 wt% to about 30 wt% of at least one low molecular weight polyolefin; about 50 wt% to about 70 wt% of at least one selectively hydrogenated block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a central polymeric block prepared originally with a conjugated diolefin and subsequently

hydrogenated; about 10 wt% to about 30 wt% of at least one polypropylene; and about 10 wt% to about 30 wt% of at least one plastomer.

# Experimental Methods

Dynamic Mechanical Thermal Analysis (DMTA)

[00192] The glass transition temperature (Tg) can be measured using dynamic mechanical thermal analysis (DMTA). This test provides information about the small-strain mechanical response (relaxation behavior) of a sample as a function of temperature over a temperature range that includes the glass transition region and the visco-elastic region prior to melting.

[00193] Typically, samples are tested using a three point bending configuration (TA Instruments DMA 2980). A solid rectangular compression molded bar is placed on two fixed supports; a movable clamp applied a periodic deformation to the sample midpoint at a frequency of 1 Hz and amplitude of 20 µm. The sample is initially cooled to -130°C then heated to 60°C at a heating rate of 3°C/min. In some cases, compression molded bars are tested using other deformation configurations, namely dual cantilever bending and tensile elongation (Rheometrics RSAII). The periodic deformation under these configurations is applied at a frequency of 1 Hz and strain amplitude of 0.05%. The sample is cooled to -130°C and then heated to 60°C at a rate of 2°C/min. The slight difference in heating rates does not influence the glass transition temperature measurements significantly.

[00194] The output of these DMTA experiments is the storage modulus (E') and loss modulus (E"). The storage modulus measures the elastic response or the ability of the material to store energy, and the loss modulus measures the viscous response or the ability of the material to dissipate energy. Tan-delta is the ratio of E"/E' and gives a measure of the damping ability of the material. The beginning of the broad glass transition ( $\beta$ - relaxation) is identified as the extrapolated tangent to the tan-delta peak. In addition, the peak temperature and area under the peak are also measured to more fully characterize the transition from glassy to visco-

elastic region. Thus the glass transition temperature is the peak temperature associated with the  $\beta$ - relaxation peak.

# Differential Scanning Calorimetry (DSC)

[00195] Crystallization temperature (Tc) and melting temperature (Tm) are measured using Differential Scanning Calorimetry (DSC) using commercially available equipment such as a TA Instruments 2920 DSC. Typically, 6 to 10 mg of molded polymer or plasticized polymer is sealed in an aluminum pan and loaded into the instrument at room temperature. Melting data (first heat) is acquired by heating the sample to at least 30°C above its melting temperature, typically 220°C for polypropylene, at a heating rate of 10°C/min. The sample is held for at least 5 minutes at this temperature to destroy its thermal history. Crystallization data are acquired by cooling the sample from the melt to at least 50°C below the crystallization temperature, typically -50°C for polypropylene, at a cooling rate of 20°C/min. The sample is held at this temperature for at least 5 minutes, and finally heated at 10°C/min to acquire additional melting data (second heat). The endothermic melting transition (first and second heat) and exothermic crystallization transition are analyzed for onset of transition and peak temperature. The melting temperatures reported are the peak melting temperatures from the second heat unless otherwise specified. For polymers displaying multiple peaks, the melting point (or melting temperature) is defined to be the peak melting temperature (i.e., associated with the largest endothermic calorimetric response in that range of temperatures) from the DSC melting trace; likewise, the crystallization temperature is defined to be the peak crystallization temperature (i.e., associated with the largest exothermic calorimetric response in that range of temperatures) from the DSC crystallization trace.

[00196] Areas under the DSC curve are used to determine the heat of transition (heat of fusion,  $H_f$ , upon melting or heat of crystallization,  $H_c$ , upon crystallization), which can be used to calculate the degree of crystallinity (also called the percent crystallinity). The percent crystallinity (X%) is calculated using the formula: [area under the curve (in J/g) / H° (in J/g)] \* 100, where H° is the

heat of fusion for the homopolymer of the major monomer component. These values for H° are to be obtained from the *Polymer Handbook, Fourth Edition*, published by John Wiley and Sons, New York 1999, except that a value of 290 J/g is used as the equilibrium heat of fusion (H°) for 100% crystalline polyethylene, a value of 140 J/g is used as the equilibrium heat of fusion (H°) for 100% crystalline polybutene, and a value of 207 J/g (H°) is used as the heat of fusion for a 100% crystalline polypropylene.

[00197] Crystallization half time at  $125^{\circ}$ C was measured on a Perkin Elmer Pyris I DSC. The sample was melted at  $200^{\circ}$ C for 10 min; cooled to  $160^{\circ}$ C at  $150^{\circ}$ C/min and then to  $140^{\circ}$ C at  $40^{\circ}$ C/min; held at  $140^{\circ}$ C for 45 min; heated again to  $200^{\circ}$ C at  $150^{\circ}$ C/min and held there for 10 min; cooled to  $145^{\circ}$ C at  $150^{\circ}$ C/min and then to  $125^{\circ}$ C at  $40^{\circ}$ C/min; and held at  $125^{\circ}$ C for 45 min to acquire crystallization data. The crystallization half-time is the time required for half of the final crystallinity to develop, as measured by  $\Delta$ Hc; that is, if the final  $\Delta$ H<sub>c</sub> after 45 min is X J/g, the crystallization half time is the time required for  $\Delta$ H<sub>c</sub> to reach X/2 J/g. Crystallization half time at  $140^{\circ}$ C was measured identically except the final temperature was  $140^{\circ}$ C instead of  $125^{\circ}$ C.

### Size-Exclusion Chromatography of Polymers (SEC-3D)

[00198] Molecular weight (weight-average molecular weight, Mw, number-average molecular weight, Mn, and molecular weight distribution, Mw/Mn or MWD) can be determined using a High Temperature Size Exclusion Chromatograph (either from Waters Corporation or Polymer Laboratories), equipped with a differential refractive index detector (DRI), an online light scattering (LS) detector, and a viscometer. Experimental details not described below, including how the detectors were calibrated, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, Macromolecules, Volume 34, Number 19, 6812-6820, (2001).

[00199] Three Polymer Laboratories PLgel 10mm Mixed-B columns are preferably used. The nominal flow rate is 0.5 cm<sup>3</sup>/min, and the nominal injection volume is 300 µL. The various transfer lines, columns and differential

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refractometer (the DRI detector) are contained in an oven maintained at 135°C. Solvent for the SEC experiment is prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent grade 1, 2, 4 trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.7 µm glass pre-filter and subsequently through a 0.1 µm Teflon filter. The TCB is then degassed with an online degasser before entering the SEC. Polymer solutions are prepared by placing 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 hours. 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 ranges 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 can be purged. Flow rate in the apparatus is then increased to 0.5 ml/minute, and the DRI is allowed to stabilize for 8-9 hours before injecting the first sample. The LS laser is turned on 1 to 1.5 hours before running samples.

[00200] 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 light scattering (LS) analysis. Units on parameters throughout this description of the SEC method are such that concentration is expressed in g/cm<sup>3</sup>, molecular weight is expressed in g/mole, and intrinsic viscosity is expressed in dL/g.

[00201] The light scattering detector can be 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):

$$\frac{K_{o}c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_{2}c$$

Here,  $\Delta R(\theta)$  is the measured excess Rayleigh scattering intensity at scattering angle  $\theta$ , c is the polymer concentration determined from the DRI analysis,  $A_2$  is the second virial coefficient [for purposes of this invention and the claims thereto,  $A_2 = 0.0006$  for propylene polymers and 0.001 otherwise],  $P(\theta)$  is the form factor for a monodisperse random coil (M.B. Huglin, LIGHT SCATTERING FROM POLYMER SOLUTIONS, Academic Press, 1971), and  $K_0$  is the optical constant for the system:

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

in which  $N_A$  is 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. For purposes of this invention and the claims thereto (dn/dc) = 0.104 for propylene polymers and 0.1 otherwise.

[00202] A high temperature Viscotek Corporation viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, can be used to determine specific viscosity. 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,  $\eta_s$ , 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:

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

where c is concentration and was determined from the DRI output.

[00203] The branching index (g') can be calculated using the output of the SEC-DRI-LS-VIS method as follows. The average intrinsic viscosity,  $[\eta]_{avg}$ , of the sample is calculated by:

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

where the summations are over the chromotographic slices, i, between the integration limits. The branching index g' is defined as:

$$g' = \frac{[\eta]_{avg}}{kM_v^{\alpha}}$$

where, for purpose of this invention and claims thereto,  $\alpha = 0.695$  for ethylene, propylene, and butene polymers; and k = 0.000579 for ethylene polymers, k = 0.000262 for propylene polymers, and k = 0.000181 for butene polymers.  $M_v$  is the viscosity-average molecular weight based on molecular weights determined by LS analysis.

# 13C-NMR spectroscopy

[00204] Polymer microstructure can be determined by <sup>13</sup>C-NMR spectroscopy, including the concentration of isotactic and syndiotactic diads ([m] and [r]), triads ([mm] and [rr]), and pentads ([mmmm] and [rrrr]). Samples can be dissolved in d<sub>2</sub>-1, 1, 2, 2-tetrachloroethane. Spectra are recorded at 125°C using a NMR spectrometer of 75 or 100 MHz. Polymer resonance peaks are referenced to mmmm = 21.8 ppm. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York 1969 and J. Randall in "Polymer Sequence Determination, <sup>13</sup>C-NMR Method", Academic Press, New York, 1977. The percent of methylene sequences of two in length, %(CH<sub>2</sub>)<sub>2</sub>, were calculated as follows: the integral of the methyl carbons between 14-18 ppm (which are equivalent in concentration to the number of methylenes in sequences of two in length) divided by the sum of the integral of the methylene sequences of one in length between 45-49 ppm and the integral of the methyl carbons between 14-18 ppm, times 100. This is a minimum calculation for the amount of methylene groups contained in a sequence of two or more since methylene sequences of greater than two have been excluded. Assignments were based on H. N. Cheng and J. A. Ewen, Makromol. Chem. 1989, 190, 1931.

### Fluid Properties

[00205] Pour Point is preferably measured by ASTM D 97.

[00206] Kinematic Viscosity (KV) is preferably measured by ASTM D 445.

[00207] Specific gravity is preferably determined by ASTM D 4052, at the temperature specified.

[00208] Viscosity index (VI) is preferably determined by ASTM D 2270.

[00209] Color can be determined on the APHA scale by ASTM D 1209. Note that an APHA color of 100 corresponds to a Saybolt color (ASTM D 156) of about +10; an APHA color of 20 corresponds to a Saybolt color of about +25; and an APHA color of 0 corresponds to a Saybolt color of about +30.

[00210] Carbon type composition can be determined by ASTM D 2140, and gives the percentage of aromatic carbons (CA), naphthenic carbons (CN), and paraffinic carbons (CP) in the fluid. Specifically, CA is the wt% of total carbon atoms in the fluid that are in aromatic ring-type structures; C<sub>N</sub> is the wt% of total carbon atoms in the fluid that are in saturated ring-type structures; and CP is the wt% of total carbon atoms in the fluid that are in paraffinic chain-type structures. ASTM D 2140 involves calculating a "Viscosity Gravity Constant" (VGC) and "Refractivity Intercept" (RI) for the fluid, and determining the carbon type composition from a correlation based on these two values. However, this method is known to fail for highly paraffinic oils, because the VGC and RI values fall outside the correlation range. Therefore, for purposes of this invention, the following protocol is used: If the calculated VGC (ASTM D 2140) for a fluid is 0.800 or greater, the carbon type composition including C<sub>P</sub> is determined by ASTM D 2140. If the calculated VGC (ASTM D 2140) is less than 0.800, the fluid is considered to have CP of at least 80%. If the calculated VGC (ASTM D 2140) is less than 0.800 but greater than 0.765, then ASTM D 3238 is used to determine the carbon type composition including C<sub>P</sub>. If application of ASTM D

3238 yields unphysical quantities (e.g., a negative  $C_A$  value), then  $C_P$  is defined to be 100%. If the calculated VGC (ASTM D 2140) for a fluid is 0.765 or less, then  $C_P$  is defined to be 100%.

### Number-Average Molecular Weight (Mn)

[00211] The number-average molecular weight (M<sub>n</sub>) can be determined by one of two methods. For samples having a kinematic viscosity at 100°C of 10 cSt or less, Gas Chromatography (GC) with a mass spectrometer detector is preferred. Such GC method is generally described in "Modern Practice of Gas Chromatography", R.L. Grob and E.F. Barry, Wiley-Interscience, 3rd Edition (July 1995). For samples having a kinematic viscosity at 100°C of more than 10 cSt, Gel Permeation Chromatography (GPC) using polystyrene standards is preferred. Such GPC method is generally described in "Modern Size Exclusion Liquid Chromatographs", W.W. Yan, J.J. Kirkland, and D.D. Bly, J. Wiley & Sons (1979).

#### Permanence

[00212] Permanence of the NFP can be determined by ASTM D1203, by measuring the weight loss from the plasticized composition in the form of a 0.25 mm thick sheet, after 300 hours in dry 70°C oven. Permanence is 100% minus the Corrected %weight loss, where Corrected %weight loss = (%weight loss for the plasticized composition) - (%weight loss for the unplasticized composition under the same test conditions), % weight loss = 100x(W-Wo)/Wo, W = weight after drying and Wo is the weight before drying. The unplasticized composition is the same composition as the plasticized composition but without NFP added.

### Methods for determining NFP content in blend

[00213] The preferred method to determine the NFP content (weight percent basis) in a blend is the Extraction method. Otherwise, the CRYSTAF method is used, unless the CRYSTAF soluble fraction for the unplasticized polyolefin is greater than 30% in which case the NMR method is used. In event of conflict between the Extraction method and the Crystaff method for the NMR method, the

Extraction method is preferred. All these methods are solution methods. The latter two involve constructing a model based on a calibration curve (or set of calibration curves) of measured parameter(s) as a function of modifier concentration. The calibration blends are prepared using the same polymer and modifier as the blend(s) under investigation but at known modifier concentrations. This set of calibrants should number at least five, and include the neat polymer as well as at least one modifier concentration above the maximum for the blend(s) under investigation but not greater than 50 weight percent modifier. The blend(s) under investigation are analyzed under the same conditions as the calibrants, and the modifier content determined by applying the model.

#### Extraction method

[00214] This method involves Soxhlet extraction, wherein at least a majority of the NFP is extracted with refluxing n-heptane. Analysis of the base polymer is also required because it can contain low molecular weight and/or amorphous material that is soluble in refluxing n-heptane. The level of plasticizer in the blend is determined by correcting its extractables level, in weight percent, by the extractables level for the base polymer, as described below.

[00215] The Soxhlet extraction apparatus consists of a 400 ml Soxhlet extractor, with a widened overflow tube (to prevent siphoning and to provide constant flow extraction); a metal screen cage fitted inside the main Soxhlet chamber; a Soxhlet extraction thimble (Whatman, single thickness, cellulose) placed inside the screen cage; a condenser with cooling water and drain; and a one-neck 1000 ml round bottom flask with appropriately sized stir bar and heating mantle.

[00216] The procedure is as follows. Dry the Soxhlet thimbles in a 95°C oven for about 60 minutes. Weigh the dry thimble directly after removal from oven; record this weight as A: Thimble Weight Before, in g. Weigh out 15-20 grams of sample (either in pellet or ground pellet form) into the thimble; record as B: Polymer Weight, in g. Place the thimble containing the polymer in the Soxhlet apparatus. Pour about 300 ml of HPLC-grade n-heptane into the round bottom

flask with stir bar and secure the flask on the heating mantle. Connect the round bottom flask, the Soxhlet, and the condenser in series. Pour more n-heptane down through the center of the condenser into the Soxhlet main chamber until the solvent level is just below the top of the overflow tube. Turn on the cooling water to the condenser. Turn on the heating mantle and adjust the setting to generate a rolling boil in the round bottom flask and maintain a good reflux. Allow to reflux for 16 hours. Turn the heat off but leave the cooling system on. Allow the system to cool down to room temperature. Disassemble the apparatus. Remove the thimble and rinse with a small amount of fresh n-heptane. Allow to air dry in the laboratory hood, followed by oven drying at 95°C for 90 minutes. Weigh the thimble containing the polymer directly after removal from oven; record as C: Polymer/Thimble Weight After, in g.

[00217] The quantity of extract is determined by calculating the weight loss from the sample, W= (A+B-C), in g. The extractables level, E, in weight percent, is then calculated by E=100(W/B). The plasticizer content in the blend, P, in weight percent, is calculated by P=E(blend)-E(base polymer).

### Crystallization Analysis Fractionation (CRYSTAF)

[00218] This method involves dissolving a sample in a solvent at high temperature, then cooling the solution slowly to cause fractionation of the sample based on solubility. For semi-crystalline samples, including blends, solubility depends primarily on crystallizability: portions of the sample that are more crystalline will precipitate out of solution at a higher temperature than portions of the sample that are less crystalline. The relative amount of sample in solution as a function of temperature is measured using an infrared (IR) detector to obtain the cumulative solubility distribution. The soluble fraction (SF) is defined as the IR signal at the lowest temperature divided by the IR signal when all the sample is dissolved at high temperature, and corresponds to the weight fraction of sample that has not crystallized.

[00219] In the case of a NFP in a thermoplastic polyolefin, the NFP is mostly or entirely amorphous and therefore contributes predominantly or exclusively to the SF. Thus, the SF will be larger for blends with higher NFP content. This relationship is exploited to determine the NFP content of a blend of known composition (polymer and NFP types) but unknown concentration. A calibration curve that describes the trend in SF as a function of NFP content is developed by making a series of blends of known concentration using the same polymer and NFP directly in the CRYSTAF vessels, and then running these blends under the same operating conditions as used for blends of unknown concentration. This series of a minimum of five calibrants must include the neat (unplasticized) polymer, and at least one NFP concentration above and one NFP concentration below the concentration of the unknown sample(s) in order to reliably apply the calibration curve to the unknown sample(s). Typically, a linear fit of the calibration points is found to provide a good representation of the SF as a function of NFP content (i.e.,  $R^2 > 0.9$ ); if necessary, a quadratic fit is used to improve the representation of the trend (i.e.,  $R^2 > 0.9$ ); if a quadratic fit is still insufficient then more calibrants are run to increase the density of points in the range of interest, and the fit is limited to a narrow enough range that a robust representation of the trend in the range of interest is achieved (i.e.,  $R^2 > 0.9$ ). This calibration curve is applied to the SF values measured for the blend(s) under investigation to calculate their respective fluid contents.

[00220] A typical CRYSTAF procedure is as follows. A commercial CRYSTAF 200 instrument (Polymer Char S.A., Valencia, Spain) with five stirred stainless steel vessels of 60 mL volume is used. Approximately 30 mg of sample are dissolved for 60 min at 160°C in 30 mL of 1,2-dichlorobenzene stabilized with 2g/4L of butylated hydroxytoluene. The solution is equilibrated for 45 min at 100°C. The crystallization process is carried out by lowering the temperature of the vessels from 100°C to 30°C at a rate of 0.2 °C/min. A dual wavelength infrared detector with a heated flow through cell maintained at 150°C is used to measure the polymer concentration in solution at regular intervals during the crystallization

cycle; the measuring wavelength is 3.5  $\mu m$  and the reference wavelength is 3.6  $\mu m$ .

[00221] If the soluble fraction for the unplasticized polyolefin is greater than 30% when analyzed in 1,2-dichlorobenzene as described above, then phenyl ether should be used as the solvent. In this case, the temperatures must be adjusted in the CRYSTAF protocol: the dissolution temperature is 160°C, the equilibration temperature is 160°C, the temperature scan is 160°C to 80°C, and the detector is maintained at 180°C. Otherwise, the protocol is identical. If the soluble fraction of the unplasticized polyolefin is still greater than 30%, then the NMR method should be used.

Nuclear Magnetic Resonance (NMR)

[00222] Another method to determine the amount of NFP in a blend is hightemperature solution-phase <sup>13</sup>C nuclear magnetic resonance (HTS-CNMR). The composition is determined using the reference spectra of the neat polymer and neat NFP, as well as spectra for a set of calibration blends (i.e., prepared from the neat polymer and NFP at known wt% NFP). The spectra are analyzed to determine a set of one or more diagnostic resonances or clusters of resonances that increase or decrease in strength monotonically with increasing NFP content. The corresponding peaks are integrated and their fractional contribution to the total integral calculated as a function of NFP content (weight %) to generate a set of calibration curves. A chemometrics model is developed using these calibration curves to provide a method to calculate the NFP content. The number of diagnostic resonances is chosen to allow the model to predict NFP content with a precision of 1 wt% or better over the calibration range. For a general description of chemometrics and how to develop a chemometrics model, see Chemometric Techniques for Quantitative Analysis by Richard Kramer (Marcel Dekker, 1998). The blend(s) of unknown concentration are then run following the same HTS-CNMR procedure as used for the calibrants, and the results analyzed according to the model to determine the weight % NFP.

[00223] A typical HTS-CNMR procedure is as follows. Samples are prepared in 1,1,2,2-tetrachloroethane- $d_2$ , with chromium acetylacetonate [Cr(acac)<sub>3</sub>] added as a relaxation agent to accelerate data acquisition. The Cr(acac)<sub>3</sub> concentration in the stock solvent is approximately 15 mg/ml. Sample concentrations are between 10 and 15 weight %. Free induction decays of 15,000 transients are accumulated at a temperature of 120°C on a Varian UnityPlus 500 using a 10mm broadband probe. Spectra are acquired with a 90° carbon excitation pulse, and inverse-gated WALTZ-16 proton decoupling. An acquisition time of approximately 1 second and recycle delay of 3.5 seconds are used to allow quantitative integration. Solvent choice and sample concentration can be adjusted to accommodate different solubility and to minimize spectral interference based on the specific composition of the blend. See *Carbon-13 NMR Spectroscopy: High-Resolution Methods and Applications in Organic Chemistry and Biochemistry*, 3rd edition, Eberhard Breitmaier and Wolfgang Voelter (VCH, 1990) for a general description of CNMR techniques.

#### Articles

[00224] Compositions according to the present invention are particularly useful in wire and cable insulation. The compositions according to the present invention are particularly useful for such applications because *inter alia* they are easily processed and thermally stable without using an appreciable amount of antioxidant, which can affect resistivity of insulation.

[00225] Compositions according to the invention are also particularly useful in formed goods for use in the food and medical industries. The compositions according to the present invention are particularly useful for such applications because *inter alia* they are readily injection molded and can also be readily extruded into films. The compositions have essentially no taste and do not require nitrosamines (or vulcanizing agents) or phthalate plasticizers (and thus in preferred embodiments the compositions do not contain these ingredients) and furthermore because of this the parts made of these compositions are relatively "clean-burning." The compositions are also stable to electromagnetic radiation,

particularly gamma-radiation (and thus also do not require stabilization agents with respect to electromagnetic radiation).

[00226] Compositions according to the invention are also particularly useful in flexible formed decorative and structural automotive parts such as instrument panels, seat material, bumper parts, and the like. The compositions are particularly useful for such applications because *inter alia* the compositions are readily injection molded and can also be readily extruded into films, and because of their stability to electromagnetic radiation, particularly UV radiation, without the necessity of stabilizers.

[00227] Compositions according to the invention are also particularly useful in extruded components for automotive uses. The compositions are particularly useful for such applications because *inter alia* the compositions possess both high service (greater than 150°C) and low service (less than 0°C and down to -50°C) temperatures. Illustrative components requiring high and low service temperatures include but are not limited to hoses, belts, gaskets, and other parts located in close vicinity of the engine. Other similar components include industrial conveyor belts, industrial hoses such as for air, water, steam and nitrogen, piping gaskets, seals, and electrical cables.

[00228] The compositions according to the invention are also particularly useful in components requiring low temperature flexibility (i.e. tension set or compression set down to -40°C and/or -50°C). Illustrative components include but are not limited to wiper blades, brake parts, weatherseals, building profiles, and transmission belts.

[00229] The compositions according to the invention are also particularly useful in components requiring UV stability. The compositions according to the invention are also particularly useful in co-extruded components having at least one colored component requiring UV stability. Illustrative components include but are not limited to weatherseals, weatherseal profiles, glass run channels,

beltline seals, lower sash seals, plugs, grommets, body to door seals, wiper blades, etc.

[00230] The compositions according to the invention are useful for the fabrication of parts made by using standard polymer processing techniques like extrusion, co-extrusion, injection molding, co-injection molding, rotational molding, blow molding, co-blow molding, calendaring and thermoforming. More specifically, the compositions according to the invention described are useful for making vehicle parts such as weather seals, brake parts such as cups, coupling disks, and diaphragm cups, boots such as constant velocity joints and rack and pinion joints, tubing, sealing gaskets, parts of hydraulically or pneumatically operated apparatus, o-rings, pistons, valves, valve seats, valve guides, and other elastomeric polymer based parts or elastomeric polymers combined with other materials such as metal/plastic combination materials. Also contemplated are transmission belts including V-belts, toothed belts with truncated ribs containing fabric faced V's, ground short fiber reinforced V's or molded gum with short fiber flocked V's.

[00231] In one or more embodiments, the compositions described can be at least partially adhered or otherwise at least partially attached to a second component or substrate to form a composite structure. The second component can be a thermoplastic elastomer or thermoplastic vulcanizate. The second component can also be, or include, a thermoset rubber, thermoplastic, or thermoplastic rubber. In one or more embodiments, two or more elastomeric structures are at least partially adhered or otherwise at least partially attached to one another by extrusion, injection molding, blow molding, or compression molding techniques to form a composite structure. Illustrative composite structures include, but are not limited to, molded corners, molded end caps, glass run channels, trunk seals, tailgate seals, cowl seals, gap fillers, glass encapsulation, cut line seals, door seals, hood-to-radiator seals, roof line seals, rocker panels, sashes, and belt-line seals. A particular belt-line seal is shown and described in U.S. Pat. No. 6,368,700 which is incorporated by reference in that regard. Other particular automotive seals can be found at http://www.santoprene.com.

[00232] In one or more embodiments, the compositions described can be at least partially adhered to a glass substrate, such as for glass encapsulation. Illustrative uses for glass encapsulation include windshield seals, sunroof seals, rear window seals, side window seals, and quarterlight seals, for example. Preferably, the composition is extruded using techniques known in the art to form an extruded elastomeric profile or gasket. This extruded profile or gasket is then adhered to the glass substrate.

# Specific Embodiments

[00233] Preferred embodiments of the invention include: (A) a composition comprising: (i) at least one low molecular weight polyolefin; (ii) a block copolymer obtainable by selectively hydrogenating a block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a mid-block prepared originally with an olefin and subsequently hydrogenated; (iii) polypropylene; and (iv) at least one plastomer, wherein the plastomer is an ethylene based polymer having a density of 0.86 g/cc to about 0.910 g/cc or a propylene based polymer having a heat of fusion (Hf) of 70 J/g or less; or even more preferred such a composition with the proviso that when (i) is a PAO having a molecular weight of between about 400 and 1000 g/mole, either: (a) (iii) is a homopolymer characterized by an MFR>2 g/10 min, preferably >5 g/10 min, still more preferably >10 g/10 min, yet more preferably >20 g/10 min, yet still more preferably >30 g/10 min, wherein the MFR is preferably measured by ASTM D1238 (230°C/2.16 kg); (b) (iii) is a copolymer; or (c) (iii) is a polymer or copolymer made by a metallocene catalyst; or (d) the composition does not contain calcium carbonate; and also other more preferred embodiments (which can be combined in numerous ways as would be readily apparent to one of ordinary skill in the art in possession of the present disclosure) selected from: a composition wherein (ii) is further characterized by end-blocks having Mn greater than about 10,000, preferably greater than about 12,000, still more preferably greater than 15,000, and mid-blocks having Mn greater than about 75,000, preferably greater than about 80,000 (optional characterizations which can otherwise be expressed as Mn/1000 of >10/>75/>10, >12/>75/>12, >15/>75/>15,

>10/>80/>10, >12/>80/>12, >15/>80/>15) (note: Mn is determined by GPC methods set forth herein, and said GPC methods can have an error as high as 10%), and/or wherein (ii) is further characterized by a vinyl aromatic monomer content of greater than 15 wt%, preferably 20 wt% or greater (an thus providing, as an example of the permissible combinations of embodiments that would be clear to one of ordinary skill in the art in possession of the present disclosure, an embodiment characterizable as a proviso that when (ii) comprises at least one SEBS, said SEBS is further characterized by at least one of the following: (a) endblocks having Mn greater than about 10,000 and mid-blocks having Mn greater than about 75,000; and (b) a styrenic content of greater than about 15 wt%, based on the weight of the block copolymer); wherein the at least one low molecular weight polyolefin is selected from oligomers of C3-C18 alphaolefins, C3-C14 alpha olefins, C3-C12 alphaolefins, C6-C14 alphaolefins, C6-C12 alphaolefins, C8-C12 alphaolefins, or wherein the at least one low molecular weight polyolefin is selected from oligomers of C10 alpha olefins; wherein the at least one low molecular weight polyolefin has a number average molecular weight of from greater than about 100 g/mol and less than about 2,000 g/mol, or a number average molecular weight of greater than 1000 g/mol, or a number average molecular weight of 2000 g/mol or greater (with limits on Mn of less then 21,000 g/mol and other limits set forth herein, such as upper limits for PAOs of 10,000, 3,000, and so forth, which can be applied in general for ingredient (i) of the invention); wherein the at least one low molecular weight polyolefin is liquid at 25°C; wherein (ii) is selected from selectively hydrogenated SIS, SBS, starbranched SIS, and star-branched SBS; wherein the polypropylene component is at least one polypropylene selected from atactic polypropylene, isotactic polypropylene, syndiotactic polypropylene, and mixtures thereof; wherein said polypropylene component is at least one polypropylene selected from polypropylene produced using a Zeigler Natta catalyst, a polypropylene produced using a metallocene catalyst, or mixtures thereof; wherein said at least one low molecular weight polyolefin is a non-functional plasticizer (NFP) characterized as a liquid with no distinct melting point above 0°C and a kinematic viscosity at 25°C of 30,000 cSt or less, and further characterized by at least one of the

parameters selected from the following: (a) kinematic viscosity at 100°C (KV100) < 400 cSt; (b) Flash Point > 200°C; (c) Pour Point < -25°C; (d) Specific Gravity of 0.85 or less; a distillation range having a difference between the upper temperature and the lower temperature of 40°C or less; and (e) a final boiling point of from 115°C to 500°C (or wherein said NFP is characterized by at least two of said parameters, or wherein said NFP is characterized by at least three of said parameters, or wherein said NFP is characterized by at least four of said parameters, or wherein said NFP is characterized by all of said parameters, any of the aforementioned still further characterized by the case where said NFP is produced using a metallocene catalyst, wherein said NFP is produced using a reduced metal oxide catalyst, or wherein said NFP is produced using a zeolite catalyst, or a mixture of these materials as the NFP); wherein said at least one low molecular weight polyolefin is selected from Group III hydrocarbon oil basestocks, GTL-derived basestocks, polyisobutenes, wax isomerate lubricant oil basestocks, ethylene/butene copolymers, and mixtures thereof; and particularly preferred would be any of the aforementioned limitations or combinations thereof wherein said composition is characterized by the absence of at least one of vulcanizing agents, phthlate plasticizers, and UV and gamma radiation stabilizers, and/or the composition does not contain calcium carbonate or even case where the composition does not contain any filler or wherein the composition is further characterized as consisting essentially of (i), (ii), and (iii), or even cases where the composition is characterized as consisting of (i), (ii), and (iii), wherein the terms "consisting essentially of" and "consisting of" take there ordinary meaning in the patent literature; wherein said composition is characterized by parameters selected from at least one of the following, measured after aging at 125°C in air for 5 days, wherein the decrease is measured relative to the original sample prior to aging: (a) decrease in 100% Modulus of <15%, preferably <10 %; (b) decrease in Tensile Strength of <55%, preferably <45%; (c) decrease in Elongation at Break of <25%, preferably <20%, still more preferably <15%; and (d) decrease in Toughness of <60%, preferably <50%, still more preferably <45%, and still more preferably such a composition characterized by at least two of said parameters, or characterized by at least three of said parameters, or characterized by all four of

said parameters, or characterized by each of said "preferably" parameters (a) - (d), and so on; and also (B) an article comprising the composition according to any one of the preceding limitations or combinations thereof, and particularly thermoformed articles comprising such compositions, and also articles (whether formed using a thermoforming step or not using a thermoforming step) characterized as comprising an insulation material and a material insulated by said insulation material, wherein said insulation material comprises the composition according to any one of the limitations or combination of limitation set forth herein, particularly wherein said material insulated by said insulation material is selected from the group consisting of wire, cable, fiber, and combinations thereof; and also (C) a thermoforming process comprising thermoforming an article from a composition comprising an elastomeric material, the improvement comprising providing a composition according to any one of the limitations set forth in (A) of this paragraph, or combinations of those limitations, especially a thermoforming operation including injection molding and/or extrusion.

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#### Additional Embodiments

[00234] In another embodiment, the invention relates to:

## 1. A composition comprising:

- (i) at least one low molecular weight polyolefin;
- (ii) at least one block copolymer obtainable by selectively hydrogenating a block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a mid-block prepared originally with an olefin and subsequently hydrogenated;
  - (iii) at least one polypropylene; and
- (iv) at least one plastomer, wherein the plastomer is an ethylene based polymer having a density of 0.86 g/cc to about 0.910 g/cc or a propylene based polymer having a heat of fusion (Hf) of 70 J/g or less;
- (v) preferably with the proviso that when (i) is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, either:

- (iii) is a homopolymer characterized by an MFR greater than 2 g/10 min,
  - (iii) is a copolymer; or
  - (iii) is a polymer or copolymer made by a metallocene catalyst; or the composition does not contain calcium carbonate.
- 2. The composition of paragraph 1, wherein when (i) is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, either:
  - (iii) is a homopolymer characterized by an MFR greater than 2 g/10 min,
    - (iii) is a copolymer; or
  - (iii) is a polymer or copolymer made by a metallocene catalyst; or the composition does not contain calcium carbonate.
- 3. The composition of paragraph 1 or 2, wherein (ii) is further characterized by at least one of:
  - (a) end-blocks having Mn greater than about 10,000; and
  - (b) mid-blocks having Mn greater than about 75,000.
- 4. The composition of paragraph 1, 2, or 3 wherein (ii) is further characterized by a vinyl aromatic monomer content of greater than 15 wt%, based on the weight of the block copolymer.
- 5. The composition of any of paragraphs 1 to 4, with the proviso that when (ii) comprises at least one SEBS, said SEBS is further characterized by at least one of the following:
  - (a) end-blocks having Mn greater than about 10,000 and midblocks having Mn greater than about 75,000; and
  - (b) a styrenic content of greater than 15 wt%, based on the weight of the block copolymer.
- 6. The composition of any of paragraphs 1 to 5, wherein the at least one low molecular weight polyolefin is selected from oligomers of C3-C14 alpha olefins.
- 7. The composition of any of paragraphs 1 to 6, wherein the at least one low molecular weight polyolefin has a number average molecular weight of from greater than about 100 g/mol and less than about 2,000 g/mol.

- 8. The composition of any of paragraphs 1 to 7, wherein (ii) is selected from selectively hydrogenated SIS, SBS, star-branched SIS, and star-branched SBS.
- 9. The composition of any of paragraphs 1 to 8, wherein the at least one polypropylene is selected from atactic polypropylene, isotactic polypropylene, syndiotactic polypropylene, and mixtures thereof.
- 10. The composition of any of paragraphs 1 to 9, wherein the at least one polypropylene is selected from polypropylene produced using a Zeigler Natta catalyst, a polypropylene produced using a metallocene catalyst, or mixtures thereof.
- 11. The composition of any of paragraphs 1 to 10, wherein said at least one low molecular weight polyolefin is a non-functional plasticizer (NFP) characterized as a liquid with no distinct melting point above 0°C and a kinematic viscosity at 25°C of 30,000 cSt or less, and further characterized by at least one of the parameters selected from the following: (a) kinematic viscosity at 100°C (KV<sub>100</sub>) < 400 cSt; (b) Flash Point > 200°C; (c) Pour Point < -25°C; (d) Specific Gravity of 0.85 or less; a distillation range having a difference between the upper temperature and the lower temperature of 40°C or less; and (e) a final boiling point of from 115°C to 500°C.
- 12. The composition according to paragraph 11, wherein said NFP is characterized by at least two of said parameters.
- 13. The composition according to paragraph 11, wherein said NFP is characterized by at least three of said parameters.
- 14. The composition according to paragraph 11, wherein said NFP is characterized by at least four of said parameters.
- 15. The composition according to paragraph 11, wherein said NFP is characterized by all of said parameters.
- 16. The composition according to paragraph 11, wherein said NFP is produced using a metallocene catalyst.
- 17. The composition according to paragraph 11, wherein said NFP is produced using a reduced metal oxide catalyst.
- 18. The composition according to paragraph 11, wherein said NFP is produced using a zeolite catalyst.

- 19. The composition of any of paragraphs 1 to 18, wherein said at least one low molecular weight polyolefin is selected from Group III hydrocarbon oil basestocks, GTL-derived basestocks, polyisobutenes, wax isomerate lubricant oil basestocks, ethylene/butene copolymers, and mixtures thereof.
- 20. The composition of any of paragraphs 1 to 19, wherein said composition does not contain calcium carbonate.
- 21. The composition of any of paragraphs 1 to 20, characterized by the absence of vulcanizing agents, phthalate plasticizers, and UV and gamma radiation stabilizers.
- 22. The composition of any of paragraphs 1 to 21, wherein said composition is characterized by parameters selected from at least one of the following, measured after aging at 125°C in air for 5 days,

decrease in 100% Modulus of less than 15%;

decrease in Tensile Strength of less than 55%;

decrease in Elongation at Break of less than 25%; and

decrease in Toughness of less than 60%,

wherein the decrease is measured relative to the original sample prior to aging.

23. The composition of any of paragraphs 1 to 22, wherein said composition is characterized by parameters selected from at least one of the following, measured after aging at 125°C in air for 5 days,

decrease in 100% Modulus of less than 10%;

decrease in Tensile Strength of less than 45%;

decrease in Elongation at Break of less than 20% or less than 15%; and decrease in Toughness of less than 50% or less than 45%,

wherein the decrease is measured relative to the original sample prior to aging:

- 24. The composition of paragraph 22, characterized by at least two of said parameters.
- 25. The composition of paragraph 22, characterized by at least three of said parameters.
- 26. The composition of paragraph 22, characterized by all four of said parameters.

- 27. The composition of paragraph 22, characterized by each of said parameters (a) (d).
- 28. The composition of any of paragraphs 1 to 27, wherein the at least one low molecular weight polyolefin has a number average molecular weight of greater than about 1,000 g/mol.
- 29. The composition of any of paragraphs 1 to 28, wherein the plastomer has a composition distribution breadth index (CDBI) above 90%, and a density of 0.86 to 0.925 g/cm<sup>3</sup>.
- 30. The composition of any of paragraphs 1 to 29, wherein the plastomer has a density 0.87 g/cm<sup>3</sup> to 0.92 g/cm<sup>3</sup>.
- 31. The composition of any of paragraphs 1 to 30, wherein the plastomer has a composition distribution breadth index (CDBI) above 95%.
- 32. The composition of any of paragraphs 1 to 31, wherein the plastomer has a melt flow rate at 190°C of 0.1 dg/min to 100 dg/min.
- 33. The composition of any of paragraphs 1 to 32, wherein the plastomer has a melt flow rate at 190°C of 0.5 dg/min to 50 dg/min.
- 34. The composition of any of paragraphs 1 to 33, wherein the plastomer has a melt flow rate at 190°C of 0.8 dg/min to 30 dg/min.
- 35. The composition of any of paragraphs 1 to 34, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 5 g/10 min.
- 36. The composition of any of paragraphs 1 to 35, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 10 g/10 min.
- 37. The composition of any of paragraphs 1 to 36, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 20 g/10 min.
- 38. The composition of any of paragraphs 1 to 37, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular

weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 30 g/10 min.

- 39. The composition of any of paragraphs 1 to 38, wherein the at least one plastomer comprises one or more copolymers comprising at least 50 wt% ethylene, and up to 50 wt % of a C3-C20 comonomer.
- 40. The composition of any of paragraphs 1 to 39, wherein the at least one plastomer comprises one or more copolymers comprising at least 50 wt% ethylene, and 1 wt% to 35 wt % of a C3-C20 comonomer.
- 41. The composition of any of paragraphs 1 to 40, wherein the at least one plastomer comprises one or more copolymers comprising at least 50 wt% ethylene, and 1 wt% to 6 wt% of a C3-C20 comonomer.
- 42. The composition of any of paragraphs 1 to 41, wherein the at least one plastomer comprises ethylene and one or more monomers selected from the group consisting of propylene, butene, isobutylene, pentene, isopentene, cyclopentene, hexene, isohexene, cyclohexene, heptene, isoheptene, cycloheptene, octene, isooctene, cyclooctene, nonene, cyclononene, decene, isodecene, dodecene, isodecene, 4-methyl-pentene-1, 3-methyl-pentene-1, and 3,5,5-trimethyl hexene-1.
- 43. The composition of any of paragraphs 1 to 42, wherein the at least one plastomer comprises ethylene and one or more dienes, trienes, styrenic monomers, or mixtures thereof.
- 44. The composition of any of paragraphs 1 to 43, wherein the at least one plastomer comprises ethylene and one or more monomers selected from the group consisting of styrene, alpha-methyl styrene, para-alkyl styrene, butadiene, pentadiene, cyclopentadiene, hexadiene, cyclohexadiene, norbornene, vinyl norbornene, ethylidene norbornene, butadiene, isoprene, heptadiene, octadiene, and nonadiene.
- 45. The composition of any of paragraphs 1 to 44, wherein the at least one plastomer comprises ethylene and propylene, butene, hexene, octene, or mixtures thereof.
- 46. The composition of any of paragraphs 1 to 45, wherein the at least one plastomer comprises metallocene polyethylenes or copolymers thereof produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination

with an activator of alumoxane and/or a non-coordinating anion in solution, slurry, high pressure or gas phase.

- 47. An article comprising the composition of any of paragraphs 1 to 46.
- 48. A thermoformed article comprising the composition according to any of paragraphs 1 to 46.
- 49. An article comprising an insulation material and a material insulated by said insulation material, wherein said insulation material comprises the composition according to any of paragraphs 1 to 46.
- 50. The article according to paragraph 49, wherein said material insulated by said insulation material is selected from the group consisting of wire, cable, fiber, and combinations thereof.
- 51. A thermoforming process comprising thermoforming an article from a composition comprising an elastomeric material, the improvement comprising providing a composition according to any of paragraphs 1 to 46.
- 52. The thermoforming process according to paragraph 51, said thermoforming process selected from injection molding and extrusion.
- [00235] The foregoing discussion can be further described with reference to the following non-limiting examples.

## **EXAMPLES**

[00236] The elastomeric-like compositions described surprisingly demonstrate improved processability and flexibility after prolonged heat-aging, cooling, or both. The compositions also surprisingly demonstrate improved surface appearance and decreased surface blooming without detriment to mechanical properties. The following examples are intended to illustrate the improved processability, surface appearance, mechanical properties, and surface blooming of the elastomeric-like compositions described.

[00237] For purposes of convenience, various specific test procedures have been identified for determining certain properties. However, when a person of ordinary skill reads this patent and wishes to determine whether a composition or polymer

has a particular property identified in a claim, then any published or well-recognized method or test procedure can be followed to determine that property, although the specifically identified procedure is preferred. Each claim should be construed to cover the results of any of such procedures, even to the extent different procedures may yield different results or measurements. Thus, a person of ordinary skill in the art is to expect experimental variations in measured properties that are reflected in the claims. All numerical values can be considered to be "about" or "approximately" the stated value, in view of the nature of testing in general.

#### Blend Samples

[00238] Six samples were prepared. Samples 1, 3, and 5 contain a block copolymer, polypropylene, polyalphaolefin and plastomer. Samples 2, 4, and 6 are comparative samples and do not include a polyalphaolefin. Each of the samples was prepared according to the formulations shown in Table 1.

Table 1: Formulations in weight percent

Blend	Blend Samples						
Component, wt%	1	2	3	4	5	66	
PP3155	16	16	16	16 ·	16	16	
Exact 4033	14	14	-	-	-	_	
Exact 4056	-	-	14	14	<u>-</u>	<b>-</b>	
Exact 8201	-	-	-	-	14	14	
Kraton G 1650	50	50	50	50	50	50	
SpectraSyn 10	20	-	20	_	20	-	
Sunpar 150	_	20	-	20	-	20	
Irganox 2215	0.08	0.08	0.08	0.08	0.08	0.08	

[00239] PP3155 is a homopolypropylene having a density of 0.90 g/cc and a MFR of 36 g/10 min. PP3155 has no nucleating agent and contains only

stabilizers. The GPC molecular weights of this polypropylene are Mn = 64,000, Mw = 304,000 and Mz = 1,145,000. PP3155 is commercially available from ExxonMobil Chemical.

[00240] Exact 4033 is an ethylene/butene copolymer (plastomer) having an ethylene content of 79 wt% and a butene content of 21 wt%. Exact 4033 has a density of 0.88 g/cc; Tg = -36°C as measured by DMTA; Tc= 44°C, Tm= 60°C; and a heat of fusion (Hf) of 54 J/g. Exact 4033 is commercially available from ExxonMobil Chemical Corporation.

[00241] Exact 4056 is an ethylene/hexene copolymer (plastomer) having an ethylene content of 73 wt% and a hexene content of 27 wt%. Exact 4056 has a density of 0.883 g/cc; Tg = -32°C as measured by DMTA; Tc= 55°C, Tm= 72°C; and a heat of fusion (Hf) of 55 J/g. Exact 4056 is commercially available from ExxonMobil Chemical Corporation.

[00242] Exact 8201 is a ethylene/octene copolymer (plastomer) having an ethylene content of 70 wt% and a octene content of 30 wt%. Exact 8201 has a density of 0.882 g/cc; Tg = -34°C as measured by DMTA; Tc= 53°C, Tm= 67°C; and a heat of fusion (Hf) of 54 J/g. Exact 8201 is commercially available from ExxonMobil Chemical Corporation.

[00243] Kraton G is a selectively hydrogenated block copolymer having terminal polymeric blocks of styrene (28 wt%/ 24.6 vol%) and a mid-block of ethylene-butene (SEBS). This copolymer was obtained from Shell Chemical Company and used as received.

[00244] SpectraSyn 10 is a polyalphaolefin (PAO) having a Mn = 720 g/mol as measured by GC; Mw = 760 g/mol as measured by GC; kinematic viscosity of 10 cSt at 100°C as determined by ASTM D445; and a pour point of -54°C. SpectraSyn 10 is commercially available from ExxonMobil Chemical.

[00245] Sunpar 150 is a mineral oil available from Sunoco, Inc. Sunpar 150 has a Mn = 520 g/mol as measured by ASTM D 2502; kinematic viscosity of 11 cSt at 100°C as determined by ASTM D445; and pour point of -9°C

[00246] Table 2 below reports the characterization data of the blend materials described above.

Table 2: Characterization data of the blend materials.

Blend Component	$T_{ m g}$	T <sub>c</sub>	$\mathbf{T}_{\mathbf{m}}$	Pour Point
	°C	°C	°C	°C
Kraton G 1650	-60		34	
PP 3155			169	
Exact 4033	-36	44	63	
Exact 4056	-32	55	77	
Exact 8201	-34	53	72	
SpectraSyn 10			,	-54
Sunpar 150				-9

[00247] A Waters GPC using THF as carrier or permeation solvent equipped with UV and DRI detectors was used to determine Mn. The composition of the block copolymers (expressed as wt% end block) was obtained by 1H NMR using a Varian XL 400 with deuterated chloroform as the solvent. Thermal characterization of the block copolymers was performed using a Perkin Elmer Pyris I DSC with sub-ambient capability at a heating rate of 10°C/min. Molecular weights of the polypropylene was measured by a Waters 150C GPC (column set: 3 Polymer Labs PLgel Mixed-B LS or equivalent) using 1,2,4-trichlorobenzene as the permeation solvent (polymer concentration ~ 3-4 mg/ml).

[00248] Each sample blend was mixed thoroughly and homogeneously in a Brabender mixer. First, the mixer was heated to 190°C. Exact plastomer and PP

3155 were added, followed by Irganox 2215. SEBS was then added and the temperature was raised to 240°C. The temperature was then lowered to 210°C and SpectraSyn 10 or Sunpar 150 was added slowly until the fluid or oil was all incorporated in the blend.

# Stress-Strain Measurements

Blends recovered from the Brabender were compression-molded into sheets of thickness about 2 mm between Teflon-coated aluminum foil by using a heated hydraulic press at a temperature of  $180^{\circ}$ C, a molding time of 25 min, and a press force of 10,000 lb. Micro-dumbbell specimens (the base is  $\sim 1$  cm  $\times 1$  cm and the center, narrow strip is  $\sim 0.6$  cm  $\times 0.2$  cm) were cut from these sheets and stress-strain measurements under tension were performed in an Instron tester. Measurements using triplicate samples (conditioned under ambient conditions for 24 hr prior to tests) were performed at room temperature and at a separation speed of 2"/min = 850  $\mu$ m/s. The stress was calculated based on the undeformed cross-sectional area of the test specimen. Strain measurements were based on clamp separation. The tensile toughness was measured as the total area under the stress-strain curve.

# Dynamic Mechanical Measurements

strain mechanical response (relaxation behavior) of samples in the solid-state as a function of temperature over a temperature range that included the viscoelastic region prior to melting. The output is the storage modulus E' and loss modulus E". The storage modulus measures the elastic response or the ability of the material to store energy, and the loss modulus measures the viscous response or the ability of the material to dissipate energy. The ratio of E"/E' (loss tangent) gives a measure of the damping ability of the material. Energy dissipation mechanisms (i.e., relaxation modes) show up as peaks in loss tangent and are associated with a drop in E' as a function of temperature. The uncertainty associated with reported values of E' is expected to be on the order of ±10% due to

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experimental variability. DMTA was used to measure the glass transition temperatures, Tg1's and Tg2's, of the TPE compositions, assigned based on the loss tangent maximum. The instrument used was the Rheometrics Solid Analyzer RSA II in tension mode (0.5% strain, 1 Hz frequency, 2°C/min heating rate, and a temperature range of ca. -100 to 150°C). Molded samples had dimensions of about 23 mm  $\times$  6.42 mm  $\times$  0.7 mm and were conditioned under ambient conditions for 24 hr before the DMTA runs.

# Hardness and Vicat Measurements

[00251] A portable hardness Type A durometer (Shore® Instrument & Mfg. Co., Inc., Freeport, NY) was used to measure hardness. The instantaneous value was reported. The high-temperature softening behavior was tested using a CEAST HDT 300 VICAT. A needle of 1-mm2 area was applied with a force of 200 g to the specimen surface submerged in the heat transfer fluid, Dow 220, while the temperature was raised at a heating rate of 120°C/hr. The temperature at which the needle penetrated 1-mm into the sample was reported as the Vicat softening point.

# **DSC Measurements**

[00252] The crystallization temperature Tc and melting temperature Tm of all polymeric materials except the Kraton G polymer were measured using an TA Instruments MDSC 2920. Typically, 6-10 mg of polymeric material was sealed in an aluminum pan and loaded into the instrument at room temperature. All runs were carried out in a nitrogen environment. Melting data (first heat) were acquired by heating the sample to at least 30°C above its melting temperature at a heating rate of 10°C/min. This provides information on the melting behavior under asblended conditions, which can be influenced by thermal history. The sample was then held for 10 min at this temperature to destroy its thermal history. Crystallization data was acquired by cooling the sample from the melt to at least 50°C below the crystallization temperature at a cooling rate of 10°C/min. The sample was then held at 25°C for 10 min and finally heated at 10°C/min to acquire additional melting data (second heat). This provides information about the

melting behavior after a controlled thermal history. The endothermic melting transition (first and second heat) and exothermic crystallization transition were analyzed for the occurrence of peak temperature. The Tm's reported are the peak melting temperatures from the second heat.

[00253] Thermal characterization of the block copolymers was performed using a Perkin-Elmer Pyris I DSC with sub-ambient capability at a heating rate of 10°C/min. Temperature was varied between -100 to 200°C. A thermal scan of the EBC was performed using a modulated DSC (DSC 2910, TA Instruments). The encapsulated sample was first heated at 10°C/min to 200°C and was held at this temperature for 2 min. It was then cooled at 10°C/min to -100°C and was held at this temperature for 5 min. The thermogram was recorded at a heating rate of 10°C/min (modulated at ± 0.5°C/min) up to the final temperature of 200°C.

# Thermogravimetric Analysis (TGA)

[00254] The permanence of the fluid in the polymer was studied by TGA. A Perkin-Elmer TGA 7 was used to measure the weight loss from a sample purged by nitrogen with a flow rate of 20 ml/min. Test specimens of 10-mil thickness and 5-mg weight were prepared by compression molding between Teflon-coated aluminum foil by using a heated hydraulic press at a temperature of 180°C, a molding time of 25 min, and a press force of 10,000 lb. In the TGA, temperature was ramped from ambient to 150°C at 150°C/min then held at 150°C for 2 hr. The weight loss over this time period was recorded.

[00255] The test results are shown in Table 3.

[00256] Table 3: Mechanical Properties

	1	2	3	4	5	6
Hardness	69A	63A	70A	71A	72A	72A
100% Modulus, MPa	2.68	2.37	2.54	2.54	2.57	2.64
Tensile Strength, MPa	3.44	3.22	5.79	4.97	5.51	4.71
Elongation at Break, %	400	300	580	530	520	470
Toughness, MPa	12	11	32	28	28	24
DMTA:					¢	
Tg1, °C	-50	-48	-52	-48	-51	-48
$\tan\delta \mathbin{@} T_{g1}$	0.36	0.39	0.36	0.36	0.36	0.34
T <sub>g2</sub> , °C	101	96	102	95	101	97
$tan \; \delta \; @ \; T_{g2}$	0.37	0.37	0.28	0.42	0.33	0.35
DSC:						
T <sub>c1</sub> , °C	30	30	35	35	36	35
T <sub>c2</sub> , °C	89	86	87	81	87	81
T <sub>m1</sub> , °C	59	62	69	69	66	68
T <sub>m2</sub> , °C	155	158	156	159	156	159
Heat Resistance:						
Vicat, 200 g, °C	102	89	95	77	92	78

[00257] Figure 1 shows the stress-strain curves of samples 1-6. As shown in Table 3 and Figure 1, the PAO-based compositions for polymeric formulations containing a given Exact plastomer (samples 1, 3 and 5) showed better stress-strain properties (tensile strength, elongation at break, and tensile toughness), a lower  $T_{g1}$ , a higher  $T_{g2}$ , and a higher Vicat temperature than the corresponding Oil-based compositions (samples 2, 4, and 6). The PAO-based compositions also had a wider application temperature window than the Oil-based compositions as measured by a difference in  $T_{g2} - T_{g1}$ .

[00258] Figure 2 shows the relationship between the Vicat softening temperature and the  $T_{g2}$  of the blends 1-6. It is interesting to note that, at similar blend  $T_{g2}$  and for the same liquid, blends based on EB have higher Vicat's than blends based on EH or EO. Not wishing to be bound by theory, it is believed that blend phase morphology varies because compatibility of the various components in the blends will be slightly different.

[00259] Figure 3 show the weight losses in TGA at 150°C for 2 hr of samples 1-6 and Table 4 summarizes the difference in  $T_{\rm g2}-T_{\rm g1}$ .

[00260] Table 4: Difference in  $T_{g2} - T_{g1}$ .

Sample	$T_{\rm g2}-T_{\rm g1}$
1	151 °C
2	144 °C
3	154 °C
4	143 °C
5	152 °C
6	145 °C

[00261] Table 5 shows the weight losses from TGA at 150°C for 2 hr. Although all the weight losses are quite low, those in the PAO-containing blends (samples 1, 3 and 5) are considerably lower (i.e. 35% to 160% lower) than those in the Oil-containing blends (samples 2, 4 and 6).

[00262] Table 5: Weight loss from TGA (2 hours at 150°C in nitrogen), %

Wt. Loss (2 hr at 150°C in N <sub>2</sub> )
0.14 %
0.23 %
0.09 %
0.23 %
0.20 %
0.27 %

[00263] All patents and patent applications, test procedures (such as ASTM methods, ISO methods, and the like), and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent with this

invention and for all jurisdictions in which such incorporation is permitted. When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated. Parameters given in the claims are measured according to the methods set forth herein for the relevant parameter or in the absence of a stated method can be determined by one of ordinary skill in the art using known method.

[00264] Trade names used herein are indicated by a <sup>TM</sup> symbol or ® symbol, indicating that the names can be protected by certain trademark rights, e.g., they can be registered trademarks in various jurisdictions.

[00265] 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.

[00266] Various terms have been defined above. 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.

[00267] 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**

We claim:

- 1. A composition comprising:
  - (i) at least one low molecular weight polyolefin;
- (ii) at least one block copolymer obtainable by selectively hydrogenating a block copolymer having terminal polymeric blocks of a vinyl aromatic monomer and a mid-block prepared originally with an olefin and subsequently hydrogenated;
  - (iii) at least one polypropylene; and
- (iv) at least one plastomer, wherein the plastomer is an ethylene based polymer having a density of 0.86 g/cc to about 0.910 g/cc or a propylene based polymer having a heat of fusion (Hf) of 70 J/g or less;
- (v) preferably with the proviso that when (i) is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, either:
  - (iii) is a homopolymer characterized by an MFR greater than 2 g/10 min,
    - (iii) is a copolymer; or
    - (iii) is a polymer or copolymer made by a metallocene catalyst; or the composition does not contain calcium carbonate.
- 2. The composition of claim 1, wherein when (i) is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, either:
  - (iii) is a homopolymer characterized by an MFR greater than 2 g/10 min,
    - (iii) is a copolymer; or
  - (iii) is a polymer or copolymer made by a metallocene catalyst; or the composition does not contain calcium carbonate.
- 3. The composition of claim 1 or 2, wherein (ii) is further characterized by at least one of:

- (a) end-blocks having Mn greater than about 10,000; and
- (b) mid-blocks having Mn greater than about 75,000.
- 4. The composition of claim 1, 2, or 3 wherein (ii) is further characterized by a vinyl aromatic monomer content of greater than 15 wt%, based on the weight of the block copolymer.
- 5. The composition of any of claims 1 to 4, with the proviso that when (ii) comprises at least one SEBS, said SEBS is further characterized by at least one of the following:
  - (a) end-blocks having Mn greater than about 10,000 and midblocks having Mn greater than about 75,000; and
  - (b) a styrenic content of greater than 15 wt%, based on the weight of the block copolymer.
- 6. The composition of any of claims 1 to 5, wherein the at least one low molecular weight polyolefin is selected from oligomers of C3-C14 alpha olefins.
- 7. The composition of any of claims 1 to 6, wherein the at least one low molecular weight polyolefin has a number average molecular weight of from greater than about 100 g/mol and less than about 2,000 g/mol.
- 8. The composition of any of claims 1 to 7, wherein (ii) is selected from selectively hydrogenated SIS, SBS, star-branched SIS, and star-branched SBS.
- 9. The composition of any of claims 1 to 8, wherein the at least one polypropylene is selected from atactic polypropylene, isotactic polypropylene, syndiotactic polypropylene, and mixtures thereof.
- 10. The composition of any of claims 1 to 9, wherein the at least one polypropylene is selected from polypropylene produced using a Zeigler Natta

catalyst, a polypropylene produced using a metallocene catalyst, or mixtures thereof.

- 11. The composition of any of claims 1 to 10, wherein said at least one low molecular weight polyolefin is a non-functional plasticizer (NFP) characterized as a liquid with no distinct melting point above 0°C and a kinematic viscosity at 25°C of 30,000 cSt or less, and further characterized by at least one of the parameters selected from the following: (a) kinematic viscosity at 100°C (KV<sub>100</sub>) < 400 cSt; (b) Flash Point > 200°C; (c) Pour Point < -25°C; (d) Specific Gravity of 0.85 or less; a distillation range having a difference between the upper temperature and the lower temperature of 40°C or less; and (e) a final boiling point of from 115°C to 500°C.
- 12. The composition according to claim 11, wherein said NFP is characterized by at least two of said parameters.
- 13. The composition according to claim 11, wherein said NFP is characterized by at least three of said parameters.
- 14. The composition according to claim 11, wherein said NFP is characterized by at least four of said parameters.
- 15. The composition according to claim 11, wherein said NFP is characterized by all of said parameters.
- 16. The composition according to claim 11, wherein said NFP is produced using a metallocene catalyst.
- 17. The composition according to claim 11, wherein said NFP is produced using a reduced metal oxide catalyst.

- 18. The composition according to claim 11, wherein said NFP is produced using a zeolite catalyst.
- 19. The composition of any of claims 1 to 18, wherein said at least one low molecular weight polyolefin is selected from Group III hydrocarbon oil basestocks, GTL-derived basestocks, polyisobutenes, wax isomerate lubricant oil basestocks, ethylene/butene copolymers, and mixtures thereof.
- 20. The composition of any of claims 1 to 19, wherein said composition does not contain calcium carbonate.
- 21. The composition of any of claims 1 to 20, characterized by the absence of vulcanizing agents, phthlate plasticizers, and UV and gamma radiation stabilizers.
- 22. The composition of any of claims 1 to 21, wherein said composition is characterized by parameters selected from at least one of the following, measured after aging at 125°C in air for 5 days,

decrease in 100% Modulus of less than 15%;

decrease in Tensile Strength of less than 55%;

decrease in Elongation at Break of less than 25%; and

decrease in Toughness of less than 60%,

wherein the decrease is measured relative to the original sample prior to aging.

23. The composition of any of claims 1 to 22, wherein said composition is characterized by parameters selected from at least one of the following, measured after aging at 125°C in air for 5 days,

decrease in 100% Modulus of less than 10%;

decrease in Tensile Strength of less than 45%;

decrease in Elongation at Break of less than 20% or less than 15%; and

decrease in Toughness of less than 50% or less than 45%,

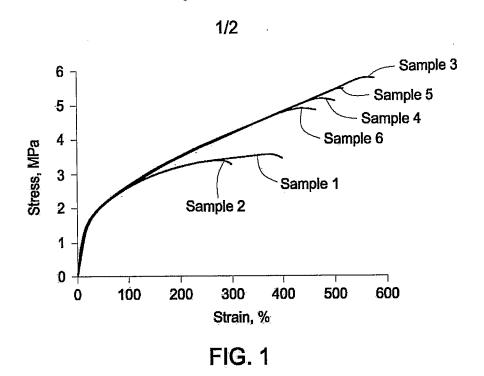
wherein the decrease is measured relative to the original sample prior to aging:

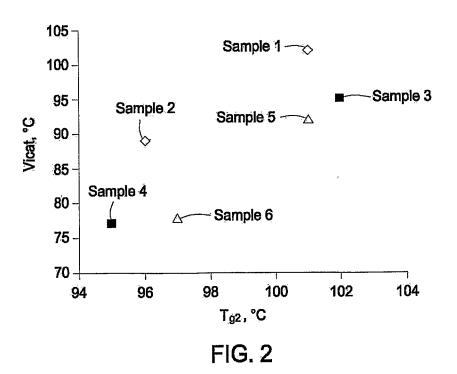
- 24. The composition of claim 22, characterized by at least two of said parameters.
- 25. The composition of claim 22, characterized by at least three of said parameters.
- 26. The composition of claim 22, characterized by all four of said parameters.
- 27. The composition of claim 22, characterized by each of said parameters (a)- (d).
- 28. The composition of any of claims 1 to 27, wherein the at least one low molecular weight polyolefin has a number average molecular weight of greater than about 1,000 g/mol.
- 29. The composition of any of claims 1 to 28, wherein the plastomer has a composition distribution breadth index (CDBI) above 90%, and a density of 0.86 to 0.925 g/cm<sup>3</sup>.
- 30. The composition of any of claims 1 to 29, wherein the plastomer has a density  $0.87 \text{ g/cm}^3$  to  $0.92 \text{ g/cm}^3$ .
- 31. The composition of any of claims 1 to 30, wherein the plastomer has a composition distribution breadth index (CDBI) above 95%.
- 32. The composition of any of claims 1 to 31, wherein the plastomer has a melt flow rate at 190°C of 0.1 dg/min to 100 dg/min.
- 33. The composition of any of claims 1 to 32, wherein the plastomer has a melt flow rate at 190°C of 0.5 dg/min to 50 dg/min.
- 34. The composition of any of claims 1 to 33, wherein the plastomer has a melt flow rate at 190°C of 0.8 dg/min to 30 dg/min.

- 35. The composition of any of claims 1 to 34, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 5 g/10 min.
- 36. The composition of any of claims 1 to 35, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 10 g/10 min.
- 37. The composition of any of claims 1 to 36, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 20 g/10 min.
- 38. The composition of any of claims 1 to 37, wherein the at least one low molecular weight polyolefin is a polyalphaolefin (PAO) having a molecular weight of between about 400 and 1000 g/mole, and the at least one polypropylene is a homopolymer characterized by an MFR greater than 30 g/10 min.
- 39. The composition of any of claims 1 to 38, wherein the at least one plastomer comprises one or more copolymers comprising at least 50 wt% ethylene, and up to 50 wt % of a C3-C20 comonomer.
- 40. The composition of any of claims 1 to 39, wherein the at least one plastomer comprises one or more copolymers comprising at least 50 wt% ethylene, and 1 wt% to 35 wt % of a C3-C20 comonomer.
- 41. The composition of any of claims 1 to 40, wherein the at least one plastomer comprises one or more copolymers comprising at least 50 wt% ethylene, and 1 wt% to 6 wt% of a C3-C20 comonomer.

- 42. The composition of any of claims 1 to 41, wherein the at least one plastomer comprises ethylene and one or more monomers selected from the group consisting of propylene, butene, isobutylene, pentene, isopentene, cyclopentene, hexene, isohexene, cyclohexene, heptene, isoheptene, cycloheptene, octene, isooctene, cyclooctene, nonene, cyclononene, decene, isodecene, dodecene, isodecene, 4-methyl-pentene-1, 3-methyl-pentene-1, and 3,5,5-trimethyl hexene-1.
- 43. The composition of any of claims 1 to 42, wherein the at least one plastomer comprises ethylene and one or more dienes, trienes, styrenic monomers, or mixtures thereof.
- 44. The composition of any of claims 1 to 43, wherein the at least one plastomer comprises ethylene and one or more monomers selected from the group consisting of styrene, alpha-methyl styrene, para-alkyl styrene, butadiene, pentadiene, cyclopentadiene, hexadiene, cyclohexadiene, norbornene, vinyl norbornene, ethylidene norbornene, butadiene, isoprene, heptadiene, octadiene, and nonadiene.
- 45. The composition of any of claims 1 to 44, wherein the at least one plastomer comprises ethylene and propylene, butene, hexene, octene, or mixtures thereof.
- 46. The composition of any of claims 1 to 45, wherein the at least one plastomer comprises metallocene polyethylenes or copolymers thereof produced using mono- or bis-cyclopentadienyl transition metal catalysts in combination with an activator of alumoxane and/or a non-coordinating anion in solution, slurry, high pressure or gas phase.
- 47. An article comprising the composition of any of claims 1 to 46.
- 48. A thermoformed article comprising the composition according to any of claims 1 to 46.

- 49. An article comprising an insulation material and a material insulated by said insulation material, wherein said insulation material comprises the composition according to any of claims 1 to 46.
- 50. The article according to claim 49, wherein said material insulated by said insulation material is selected from the group consisting of wire, cable, fiber, and combinations thereof.
- 51. A thermoforming process comprising thermoforming an article from a composition comprising an elastomeric material, the improvement comprising providing a composition according to any of claims 1 to 46.
- 52. The thermoforming process according to claim 51, said thermoforming process selected from injection molding and extrusion.





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