

PLASTICIZED ALPHA-OLEFIN/VINYLLIDENE AROMATIC MONOMER OR HINDERED
ALIPHATIC OR CYCLOALIPHATIC VINYLLIDENE MONOMER INTERPOLYMERS

The present invention pertains to the modification of compositions containing interpolymers of α -olefin/vinylidene aromatic and/or hindered aliphatic and/or cycloaliphatic vinylidene monomer by the use of plasticizer.

The generic class of materials of α -olefin/hindered vinylidene monomer substantially random interpolymers, including materials such as α -olefin/vinyl aromatic monomer interpolymers, and their preparation, are known in the art, such as described in EP 416 815 A2. These materials offer a wide range of material structures and properties which makes them useful for varied applications, such as asphalt modifiers or as compatibilizers for blends of polyethylene and polystyrene, as described in US 5,460,818.

The structure, thermal transitions and mechanical properties of substantially random interpolymers of ethylene and styrene containing up to 50 mole percent styrene have been described (see Y.W. Cheung, M.J. Guest; Proc. Antec '96 pages 1634-1637). These polymers are found to have glass transitions in the range -20°C to $+35^{\circ}\text{C}$, and show no measurable crystallinity above 25 mole percent styrene incorporation, that is, they are essentially amorphous.

Although of utility in their own right, Industry is constantly seeking to improve the applicability of these interpolymers. To perform well in certain applications, these interpolymers could be desirably improved, for example, in the areas of processing characteristics or enhanced glass transition temperature depression or reduced modulus or reduced hardness or lower viscosity or improved ultimate elongation compared to a like property of the unmodified interpolpolymer. In relation to this invention, it is also considered advantageous to be able to engineer the glass transition process for the interpolymers to a particular temperature range, so that the energy absorbing capabilities of the polymer can be best utilized for example in sound and vibration damping.

This invention discloses the utility of plasticizers to achieve modification of the α -olefin/hindered vinylidene monomer substantially random interpolymers. There is a broad knowledge base on the plasticization of poly(vinyl chloride) (PVC), and it is generally known that many thermoplastics can be plasticized. Reference can be made, for example, to "Plasticizers" in "The Encyclopedia of Polymer

Science and Engineering" (Supplement Volume; Wiley Interscience, 1989) regarding this type of technology. Depending upon the polymer type, typical plasticizer families include phosphoric acid derivatives, phthalic acid derivatives, trimellitate esters, benzoates, adipate esters, epoxy compounds, phosphate esters, glutarates and mineral oils. On the basis of their molecular weight, plasticizers are further classified as "monomeric" or "polymeric". In comparison with monomeric plasticizers, polymeric plasticizers generally tend to show higher permanence, lower compatibility, and lower plasticization efficiency. Plasticizers are also classed as "primary", and having high compatibility with a particular polymer, or "secondary" if they have lower compatibility. Mixtures of the various types of plasticizers can be employed to achieve cost/performance balances.

One well known effect of the addition of small amounts of plasticizer is that many polymers, including polystyrene, polycarbonate, and Nylon 66 exhibit "antiplasticization" in which significant increases in modulus and tensile strength and loss of toughness are observed. This effect is also found for PVC when plasticizers are utilized at relatively low concentrations of up to 10-17 weight percent, depending on the plasticizer nature. Because of antiplasticization effects, compositions including less than about 20 parts per hundred of PVC are seldom encountered.

Based on the available background information, combinations of α -olefin/hindered vinylidene monomer substantially random interpolymers, and especially ethylene/styrene interpolymers, with typical plasticizers associated with PVC modification would not appear to offer an effective route to modify their performance. It is well-known that amorphous thermoplastic polymers, such as atactic polystyrene, will accept large amounts of plasticizers, and although they lower the glass transition temperature they rapidly form gums or liquids, that is, they have no function as solid-state polymers. Addition of small (less than 3 weight percent) of dibutyl phthalate (DBP) has been used in latex formulations used for polish based on thermoplastics including polystyrene. The compatibility of vinyl-type plasticizers with low density polyethylene (LDPE) is usually 0 to 2 weight percent, although some hydrocarbons such as certain mineral oils may be compatible up to 20 weight percent. United States patent number 3,821,149 describing "Plasticized thermoplastic semi-crystalline block copolymers" teaches that random copolymers of ethylene and t-butyl styrene are non-crystalline, and when plasticized with 50 to 100 parts of dibutyl phthalate provides a product of little desirable physical properties. Random and

statistical copolymers are specifically excluded from United States patent number 3,821,149.

A further approach to consider regarding plasticization is the relative compatibility of the plasticizing molecule with the polymer.

5 Reference to Buszard ("Theoretical Aspects of Plasticization" in "PVC Technology; Fourth Edition" ed. W.V. Titow, Applied Science Publishers 1984) outlines theoretical techniques for assessing the compatibility, and hence utility of plasticizers with PVC by the use of the solubility parameter. The matching of solubility parameters of

10 polymer and effective plasticizers is one guide to defining nominal compatibility. Although there are some assumptions and limitations in adopting this approach, in general it is evident that effective plasticizers will have good compatibility or miscibility with the polymer. Reference to "Polymer Handbook" (Third edition, ed. J.

15 Brandrup, E.H. Immergut, Wiley Interscience, 1989) gives the solubility parameter of PVC as around $19.8 \text{ (MPa)}^{0.5}$, and appropriate plasticizers have solubility parameters which fall between the limits of $17.2 \text{ (MPa)}^{0.5}$ and $23.3 \text{ (MPa)}^{0.5}$.

The reported solubility parameters of poly(ethylene) and

20 poly(styrene) are $16.2 \text{ (MPa)}^{0.5}$ and $18.6 \text{ (MPa)}^{0.5}$ respectively. Based on group additivity theories, it is expected that substantially random copolymers of ethylene and styrene will have solubility parameters falling somewhere between these values.

It is not anticipated that interpolymers which are rich in

25 ethylene would be effectively modified by many typical plasticizers used for vinyl modification, because of the differences in solubility parameters between polymer and plasticizer. Additionally, it is not anticipated that interpolymers which are relatively rich in styrene (about 25-60 mole percent), and amorphous in nature, would be

30 effectively modified by many typical plasticizers used for vinyl modification.

Based on the available background information, it would not be anticipated that α -olefin/hindered vinylidene monomer substantially random interpolymers, and especially ethylene/styrene interpolymers,

35 would be effectively modified by many typical plasticizers associated with PVC modification, and particularly in the ranges of plasticizer incorporation described in this invention.

One aspect of the present invention pertains to a composition comprising

40 (A) from 50 to 99 percent by weight of at least one substantially random interpolymer resulting from polymerizing a monomer composition comprising



- (1) from 1 to 65 mole percent of
- (a) at least one vinylidene aromatic monomer, or
 - (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
 - (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
- (2) from 35 to 99 mole percent of at least one C₂₋₂₀ α -olefin,;
- and
- (B) from 1 to 50 percent by weight of at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters (including adipates azelates and sebacates), epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.

Another aspect of the present invention pertains to such modified interpolymers in the form of a film or sheet, or as a component of a multilayered structure resulting from calendering, blowing, casting or (co-)extrusion operations.

Another aspect of the present invention pertains to such modified interpolymers and their utility in the form of foams, fibers or emulsions.

Another aspect of the present invention pertains to the utilization of such modified interpolymers in adhesives, adhesive formulations and adhesive/sealant applications.

Another aspect of the present invention pertains to injection, compression, extruded or blow molded parts prepared from such modified interpolymers.

The compositions of the present invention can "comprise", "consist essentially of" or "consist of" any two or more of such polymers or interpolymers or plasticizers enumerated herein.

These compositions provide an improvement in one or more of the properties such as, but not limited to, processing characteristics or enhanced glass transition temperature depression or reduced modulus or reduced hardness or lower viscosity or improved ultimate elongation compared to a like property of the unmodified interpolymer.

The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer.

The term "copolymer" as employed herein means a polymer wherein at least two different monomers are polymerized to form the copolymer.

The term "mer(s)" means the polymerized unit of the polymer derived from the indicated monomer(s).

When references are made herein to a polymer containing monomer(s) or polymer units derive from, it really means that the polymer contains monomer(s) residues resulting from polymerizing the indicated monomer(s) to make the polymer.

The term "substantially random" in the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer or hindered aliphatic or cycloaliphatic vinylidene monomer as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, the substantially random interpolymer comprising an α -olefin and a vinylidene aromatic monomer does not contain more than 15 percent of the total amount of vinylidene aromatic monomer in blocks of vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer was not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-13 NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

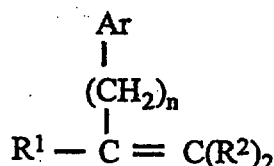
Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The interpolymers suitable for blending to make the blends comprising the present invention include, but are not limited to

interpolymers prepared by polymerizing one or more α -olefins with one or more vinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers.

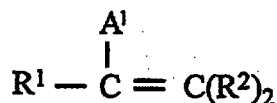
Suitable α -olefins include for example, α -olefins containing
 5 from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1, 4-methyl-1-pentene, hexene-1 and octene-1. These α -olefins do not contain an aromatic moiety.

Suitable vinylidene aromatic monomers which can be employed to
 10 prepare the interpolymers employed in the blends include, for example, those represented by the following formula:



wherein R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms,
 15 preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} -haloalkyl; and n has a value from zero to 4, preferably from
 20 zero to 2, most preferably zero. Exemplary monovinylidene aromatic monomers include styrene, vinyl toluene, α -methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers
 25 include styrene, α -methyl styrene, the lower alkyl- ($\text{C}_1 - \text{C}_4$) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof. A more preferred aromatic
 30 monovinylidene monomer is styrene.

By the term "hindered aliphatic or cycloaliphatic vinylidene compounds", it is meant addition polymerizable vinylidene monomers corresponding to the formula:



35 wherein A^1 is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R^1 is selected from the group of

radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; or alternatively R^1 and A^1 together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic or cycloaliphatic vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl. Most preferred hindered aliphatic or cycloaliphatic vinylidene compounds are the various isomeric vinyl- ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene.

The interpolymers of one or more α -olefins and one or more monovinylidene aromatic monomers and/or one or more hindered aliphatic or cycloaliphatic vinylidene monomers employed in the present invention are substantially random polymers. These interpolymers usually contain from 5 to 65, preferably from 5 to 50, more preferably from 10 to 50 mole percent of at least one vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinylidene monomer and from 35 to 95, preferably from 50 to 95, more preferably from 50 to 90 mole percent of at least one aliphatic α -olefin having from 2 to 20 carbon atoms.

The number average molecular weight (M_n) of the polymers and interpolymers is usually greater than 10,000, preferably from 20,000 to 1,000,000, more preferably from 50,000 to 500,000.

While preparing the substantially random interpolymer, an amount of atactic vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinylidene aromatic monomer at elevated temperatures. The presence of vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinylidene aromatic homopolymer may be separated from the interpolymer, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolymer or the vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than

20 weight percent, preferably less than 15 weight percent based on the total weight of the interpolymers of vinylidene aromatic homopolymer is present.

The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

The substantially random interpolymers can be prepared as described in US Application Number 07/545,403 filed July 3, 1990 (corresponding to EP-A-0,416,815) by James C. Stevens et al. and is allowed US Application Number 08/469,828 filed June 6, 1995 all of which are incorporated herein by reference in their entirety. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3,000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in U.S. Application No. 07/545,403, filed July 3, 1990 corresponding to EP-A-416,815; U.S. Application No. 07/702,475, filed May 20, 1991 corresponding to EP-A-514,828; U.S. Application No. 07/876,268, filed May 1, 1992 corresponding to EP-A-520,732; U.S. Application No. 08/241,523, filed May 12, 1994; as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635 and 5,556,928 all of which patents and applications are incorporated herein by reference in their entirety.

The substantially random α -olefin/vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one α -olefin/vinyl aromatic/vinyl aromatic/ α -olefin tetrad disclosed in U. S. Application No. 08/708,809 filed September 4, 1996 by Francis J. Timmers et al. These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range

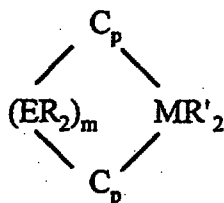


43.75-44.25 ppm and 38.0-38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.75-44.25 ppm are methine carbons and the signals in the region 38.0-38.5 ppm are methylene carbons.

In order to determine the carbon-13 NMR chemical shifts of the interpolymers described, the following procedures and conditions are employed. A five to ten weight percent polymer solution is prepared in a mixture consisting of 50 volume percent 1,1,2,2-tetrachloroethane-d₂ and 50 volume percent 0.10 molar chromium tris(acetylacetonate) in 1,2,4-trichlorobenzene. NMR spectra are acquired at 130°C using an inverse gated decoupling sequence, a 90° pulse width and a pulse delay of five seconds or more. The spectra are referenced to the isolated methylene signal of the polymer assigned at 30.000 ppm.

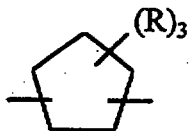
It is believed that these new signals are due to sequences involving two head-to-tail vinyl aromatic monomer preceded and followed by at least one α-olefin insertion, for example, an ethylene/styrene/styrene/ethylene tetrad wherein the styrene monomer insertions of said tetrads occur exclusively in a 1,2 (head to tail) manner. It is understood by one skilled in the art that for such tetrads involving a vinyl aromatic monomer other than styrene and an α-olefin other than ethylene that the ethylene/vinyl aromatic monomer/vinyl aromatic monomer/ethylene tetrad will give rise to similar carbon-13 NMR peaks but with slightly different chemical shifts.

These interpolymers are prepared by conducting the polymerization at temperatures of from -30°C to 250°C in the presence of such catalysts as those represented by the formula



wherein: each C_p is independently, each occurrence, a substituted cyclopentadienyl group π-bound to M; E is C or Si; M is a group IV metal, preferably Zr or Hf, most preferably Zr; each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms; each R' is

independently, each occurrence, H, halo, hydrocarbyl, hydrocarbyloxy, silahydrocarbyl, hydrocarbylsilyl containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms or two R' groups together can be a C₁₋₁₀ hydrocarbyl substituted 1,3-butadiene; m is 1 or 2; and optionally, but preferably in the presence of an activating cocatalyst. Particularly, suitable substituted cyclopentadienyl groups include those illustrated by the formula:



wherein each R is independently, each occurrence, H, hydrocarbyl, silahydrocarbyl, or hydrocarbylsilyl, containing up to 30 preferably from 1 to 20 more preferably from 1 to 10 carbon or silicon atoms or two R groups together form a divalent derivative of such group. Preferably, R independently each occurrence is (including where appropriate all isomers) hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl or silyl or (where appropriate) two such R groups are linked together forming a fused ring system such as indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, or octahydrofluorenyl.

Particularly preferred catalysts include, for example, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium dichloride, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium 1,4-diphenyl-1,3-butadiene, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C₁₋₄ alkyl, racemic-(dimethylsilanediyl(2-methyl-4-phenylindenyl))zirconium di-C₁₋₄ alkoxide, or any combination thereof.

Further preparative methods for the interpolymer component (A) of the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl₃) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am.Chem.Soc., Div.Polym.Chem.) Volume 35, pages 686, 687 [1994]) have reported copolymerization using a MgCl₂/TiCl₄/NdCl₃/Al(iBu)₃ catalyst to give random copolymers of styrene and propylene. Lu et al (Journal of Applied Polymer Science, Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of ethylene and styrene using a TiCl₄/NdCl₃/MgCl₂/Al(Et)₃ catalyst. The manufacture of α -olefin/vinyl aromatic



monomer interpolymers such as propylene/styrene and butene/styrene are described in United States patent number 5,244,996, issued to Mitsui Petrochemical Industries Ltd. All the above methods disclosed for preparing the interpolpolymer component are incorporated herein by
5 reference.

Suitable modifiers which can be employed herein as the plasticizer component (B) include at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters (including adipates azelates and
10 sebacates), epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.

Particularly suitable phthalate esters include, for example, dialkyl C₄-C₁₈ phthalate esters such as diethyl, dibutyl phthalate,
15 diisobutyl phthalate, butyl 2-ethylhexyl phthalate, dioctyl phthalate, diisooctyl phthalate, dinonyl phthalate, diisononyl phthalate, didecyl phthalate, diisodecyl phthalate, diundecyl phthalate, mixed aliphatic esters such as heptyl nonyl phthalate, di(n-hexyl, n-octyl, n-decyl) phthalate (P610), di(n-octyl, n-decyl) phthalate (P810), and aromatic
20 phthalate esters such as diphenyl phthalate ester, or mixed aliphatic-aromatic esters such as benzyl butyl phthalate or any combination thereof.

Particularly suitable trimellitate esters include, for example, tri(2-ethylhexyl) trimellitate, tri(heptyl, nonyl) trimellitate, tri
25 isooctyl trimellitate, tri isodecyl trimellitate, tri (octyl, decyl) trimellitate.

Particularly suitable benzoates include, for example, diethylene glycol dibenzoate and dipropylene glycol dibenzoate.

Particularly suitable epoxy compounds include, for example,
30 epoxidised vegetable oils such as epoxidized soyabean oil and epoxidized linseed oil.

Particularly suitable phosphate esters include, for example, triaryl, trialkyl, mixed alkyl aryl phosphates such as tributyl
phosphate, trioctyl phosphate, tri(2-ethylhexyl) phosphate,
35 tributoxyethyl phosphate, triphenyl phosphate, tricresyl phosphate, isopropylphenyl diphenyl phosphate, t-butylphenyl diphenyl phosphate,
- 2-ethylhexyl diphenyl phosphate and isodecyl diphenyl phosphate.

Particularly suitable oils include, for example, mineral oils, natural oils, naphthenic oils, paraffinic oils and aromatic oils.

40 Most preferred oils are those having an aromatic content of from 12 to 28.5 percent by weight; a flash point of from 315°C to 420°C and an ASTM

D445 viscosity at 40°C of 9 to 85 centistokes (9×10^{-6} to 85×10^{-6} m²/sec).

The compositions of the present invention suitably comprise from 50 to 99, preferably from 55 to 95, more preferably from 60 to 90, percent by weight based on the combined weight of components (A) and (B) of the interpolymer(s) of α -olefin/vinylidene aromatic monomer and/or hindered aliphatic and/or cycloaliphatic vinylidene monomer as component (A); and from 1 to 50, preferably from 5 to 45, more preferably from 10 to 40, percent by weight based on the combined weight of components (A) and (B) of plasticizer(s) as component (B).

The compositions of the present invention may be prepared by any suitable means known in the art such as, but not limited to, dry blending in a pelletized form in the desired proportions followed by melt blending in a screw extruder, an internal batch mixer for example, a Banbury mixer, a calender or a roll mill, or the like.

Alternatively, the processing oil or plasticizer may be added to a solution of the interpolymer, followed by devolatilization of the solvent by any suitable means such as in a steam-stripper, flash devolatilizer, wiped-film evaporator, or devolatilizing extruder. For example, the plasticizer or oil may be added to the solution of interpolymer solvent after it exits the interpolymer polymerization reactor. This may be accomplished by mixing the two liquid streams for example with an in-line static mixer.

Additives such as antioxidants (for example, hindered phenols such as, for example, IRGANOX™ 1010), phosphites (for example, IRGAFOS® 168)), U. V. stabilizers, cling additives (for example, PIB), antiblock additives, slip agents, colorants, pigments, fillers, and the like can also be included in the interpolymers employed in the blends of the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants. Minor amounts, up to 50 percent by weight, of other polymers including polystyrene, syndiotactic polystyrene, styrenic copolymers such as styrene/acrylonitrile, polyolefin homo and copolymers, polyethylene, polypropylene, poly(vinyl chloride), polycarbonate, polyethylene terephthalate, urethane polymers and polyphenylene oxide, can also be included in the interpolymers employed in the blends of the present invention, to the extent that they do not interfere with the enhanced properties discovered by Applicants.

The additives are employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or



polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers. Such amounts of antioxidants is usually in the range of from 0.01 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 2 percent by weight based upon the weight of the polymer or polymer blend.

Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment. Such additives can suitably be employed in the range of from 0.05 to 50, preferably from 0.1 to 35 more preferably from 0.2 to 20 percent by weight based upon the weight of the polymer or polymer blend. However, in the instance of fillers, they could be employed in amounts up to 90 percent by weight based on the weight of the polymer or polymer blend.

The compositions of the present invention can be utilized to produce, but not limited to, a wide range of fabricated articles such as, for example, calendered sheet, blown films and injection molded parts. The compositions can also be used in the manufacture of fibers, foams and latices. The compositions of the present invention can also be utilized in adhesive and sealant formulations.

The following examples are illustrative of the invention, but are not to be construed as to limiting the scope of the invention in any manner.

Preparation of Interpolymers (A), (B), (C), and (D)

Polymer is prepared in a 400 gallon agitated semi-continuous batch reactor. The reaction mixture consisted of approximately 250 gallons a solvent comprising a mixture of cyclohexane (85 wt percent) & isopentane (15 wt percent), and styrene. Prior to addition, solvent, styrene and ethylene are purified to remove water and oxygen. The inhibitor in the styrene is also removed. Inerts are removed by purging the vessel with ethylene. The vessel is then pressure controlled to a set point with ethylene. Hydrogen is added to control molecular weight. Temperature in the vessel is controlled to set-point by varying the jacket water temperature on the vessel. Prior to polymerization, the vessel is heated to the desired run temperature and the catalyst components : Titanium: (N-1,1-dimethylethyl)-dimethyl(1-(1,2,3,4,5-eta)-2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silanaminato)) (2-)N)-dimethyl, CAS# 135072-62-7, Tris(penta-fluorophenyl)boron, CAS# 001109-15-5, Modified methylaluminoxane Type 3A, CAS# 146905-79-5, are flow controlled, on a mole ratio basis of 1/3/5 respectively, combined and added to the vessel. After starting,

the polymerization is allowed to proceed with ethylene supplied to the reactor as required to maintain vessel pressure. In some cases, hydrogen is added to the headspace of the reactor to maintain a mole ratio with respect to the ethylene concentration. At the end of the run, the catalyst flow is stopped, ethylene is removed from the reactor, 1000 ppm of Irganox™ 1010 anti-oxidant is then added to the solution and the polymer is isolated from the solution. The resulting polymers are isolated from solution by either stripping with steam in a vessel or by use of a devolatilizing extruder. In the case of the steam stripped material, additional processing is required in extruder like equipment to reduce residual moisture and any unreacted styrene. Table 1 provides a summary of the process conditions used to produce the polymers, together with characterization data.

Table 1

ESI	Solvent loaded		Styrene loaded		Pressure		Temp.	Total H ₂ Added	Run Time	Polym. in Solution
	lbs	kg	lbs	kg	Psig	kPa	°C	Gms	Hrs	Wt. %
A	252	114	1320	599	42	290	60	0	2.8	11.5
B	252	114	1320	599	40	276	60	23	6.5	18.0
C	842	382	662	300	105	724	60	8.8	3.7	8.6
D	1196	542	225	102	70	483	60	7.5	6.1	7.2

Table 1 cont.

Sample Number	Melt Index	Total Wt % Styrene in Polymer*	Talc Level Wt %	Isolation Method
A	0.18	81.7	<2.5	Stm.Str.
B	1.83	81.6	<2.0	Stm.Str.
C	0.01	48.3	<1.0	Stm.Str.
D	0.03	29.8	0	Extruder

- * Styrene content measured by FTIR technique

Preparation of Interpolymers (E) - (T)Reactor Description

A 6 gallon (22.7 L), oil jacketed, Autoclave continuously stirred tank reactor (CSTR) was employed as the reactor. A magnetically coupled agitator with Lightning A-320 impellers provides the mixing. The reactor ran liquid full at 475 psig (3,275 kPa). Process flow was in the bottom and out the top. A heat transfer oil was circulated through the jacket of the reactor to remove some of the heat of reaction. After the exit from the reactor was a Micromotion flow meter that measured flow and solution density. All lines on the exit of the reactor were traced with 50 psi (344.7 kPa) steam and insulated.

Procedure

Toluene solvent was supplied at 30 psig (207 kPa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. At the discharge of the solvent pump a side stream was taken to provide flush flows for the catalyst injection line (1 lb/hr (0.45 kg/hr)) and the reactor agitator (0.75 lb/hr (0.34 kg/hr)). These flows were measured by differential pressure flow meters and controlled by manual adjustment of micro-flow needle valves. Uninhibited styrene monomer was supplied to the mini-plant at 30 psig (207 kPa). The feed to the reactor was measured by a Micro-Motion mass flow meter. A variable speed diaphragm pump controlled the feed rate. The styrene stream was mixed with the remaining solvent stream. Ethylene was supplied to the mini-plant at 600 psig (4,137 kPa). The ethylene stream was measured by a Micro-Motion mass flow meter just prior to the Research valve controlling flow. A Brooks flow meter/controller was used to deliver hydrogen into the ethylene stream at the outlet of the ethylene control valve. The ethylene/hydrogen mixture combines with the solvent/styrene stream at ambient temperature. The temperature of the solvent/monomer as it enters the reactor was dropped to ~5 °C by an exchanger with -5°C glycol on the jacket. This stream entered the bottom of the reactor. The three component catalyst system and its solvent flush also enter the reactor at the bottom but through a different port than the monomer stream. Preparation of the catalyst components took place in an inert atmosphere glove box. The diluted components were put in nitrogen padded cylinders and charged to the catalyst run tanks in the process area. From these run tanks the catalyst was pressured up with piston pumps and the flow was measured with Micro-Motion mass flow meters. These streams combine with each

other and the catalyst flush solvent just prior to entry through a single injection line into the reactor.

Polymerization was stopped with the addition of catalyst kill (water mixed with solvent) into the reactor product line after the
5 Micromotion flow meter measuring the solution density. Other polymer additives can be added with the catalyst kill. The catalyst kill/additive tank was a 50 gallon stirred and recycled tank. The tank had toluene solvent added. Catalyst kill and additives were added through a flange on the top of the tank to the mixing toluene
10 solvent. The tank was sealed and purge with nitrogen to remove any oxygen. Concentrations of catalyst kill and additive were determined by polymer production rate and the desired concentration in the polymer. The recycled and stirred tank allowed for the use of oils and both soluble and insoluble solid additives. A side stream was
15 taken off of the tank recycle loop to feed a Pulsafeeder pump that pumped the catalyst kill/additive solution into the reactor product line. A static mixer in the line provided dispersion of the catalyst kill and additives in the reactor effluent stream. This stream next entered post reactor heaters that provide additional energy for the
20 solvent removal flash. This flash occurred as the effluent exited the post reactor heater and the pressure was dropped from 475 psig (3,275 kPa) down to ~250mm of pressure absolute at the reactor pressure control valve. This flashed polymer entered a hot oil jacketed devolatilizer. Approximately 85 percent of the volatiles were removed
25 from the polymer in the devolatilizer. The volatiles exit the top of the devolatilizer. The stream was condensed and with a glycol jacketed exchanger, entered the suction of a vacuum pump and was discharged to a glycol jacket solvent and styrene/ethylene separation vessel. Solvent and styrene were removed from the bottom of the
30 vessel and ethylene from the top. The ethylene stream was measured with a Micro-Motion mass flow meter and analyzed for composition. The measurement of vented ethylene plus a calculation of the dissolved gasses in the solvent/styrene stream were used to calculate the ethylene conversion. The polymer separated in the devolatilizer was
35 pumped out with a gear pump to a ZSK-30 devolatilizing vacuum extruder. The dry polymer exits the extruder as a single strand. This strand was cooled as it was pulled through a water bath. The excess water was blown from the strand with air and the strand was chopped into pellets with a strand chopper.

Catalysts Employed

Interpolymer	Catalyst Type	CoCatalyst		MMAO ^a Al/Ti Ratio
		Type	Boron/Ti Ratio	
ESI-E	A ^b	A ^c	1.12:1	9.8:1
ESI-F	A ^b	A ^c	1.24:1	10:1
ESI-G	A ^b	A ^c	1.25:1	10:1
ESI-H	A ^b	A ^c	1.24:1	10:1
ESI-I	A ^b	A ^c	1.25:1	10:1
ESI-J	A ^b	B ^d	3.5:1	3.5:1
ESI-K	A ^b	B ^d	3.5:1	3.5:1
ESI-L	A ^b	B ^d	3.5:1	3.5:1
ESI-M	A ^b	B ^d	3.5:1	3.5:1
ESI-N	A ^b	B ^d	3.49:1	3.5:1
ESI-O	A ^b	B ^d	3.5:1	3:1
ESI-P	A ^b	B ^d	3.5:1	3:1
ESI-Q	A ^b	B ^d	3.51:1	3:1
ESI-R	A ^b	B ^d	3.5:1	3:1
ESI-S	A ^b	B ^d	3.5:1	3:1
ESI-T	A ^b	B ^d	3.5:1	3:1

a a modified methylaluminoxane commercially available from Akzo Nobel as MMAO-3A.

b dimethyl[N-(1,1-dimethylethyl)-1,1-dimethyl-1-((1,2,3,4,5-eta.)-1,5,6,7-tetrahydro-3-phenyl-s-indacen-1-yl)silanaminato(2-)-N]-titanium.

c bis-hydrogenated tallowalkyl methylammonium tetrakis(pentafluorophenyl)borate.

d tris(pentafluorophenyl)borane.

Reactor Data

Inter-polymer	Reactor Temp. °C	Solvent Flow		Ethylene Flow		Hydrogen Flow SCCM	Styrene Flow		Vent Conversion Percent
		lb/hr	kg/hr	lb/hr	kg/hr		lb/hr	kg/hr	
ESI-E	104.1	33	15	4.21	1.90	23	5.9	2.68	94.45
ESI-F	102.4	32.3	14.7	4.2	1.91	23	6.4	2.90	94.15
ESI-G	113.6	32.4	14.7	3.15	1.43	8	4.3	1.95	94.04
ESI-H	102.7	31.3	14.2	3.16	1.43	6	5.4	2.45	95.37
ESI-I	103.0	31.2	14.2	3.17	1.44	6	5.4	2.45	95.48
ESI-J	97.5	45	20.4	4.36	1.98	40	5	2.27	96.27
ESI-K	99.0	45	20.4	4.34	1.97	23	5	2.27	96.5
ESI-L	99.1	45	20.4	4.34	1.97	23	5	2.27	96.45
ESI-M	104.2	45	20.4	4.87	2.21	14	3.7	1.68	96.76
ESI-N	106.9	36	16.3	3.95	1.79	9.6	2.9	1.32	96.13
ESI-O	103.7	36	16.3	3.95	1.79	22	2.6	1.18	96.18
ESI-P	103.4	36	16.3	3.96	1.80	24.6	2.9	1.32	96.43
ESI-Q	102.0	36	16.3	3.96	1.80	35.4	2.9	1.32	96.15
ESI-R	100.9	36	16.3	3.94	1.79	40	2.9	1.32	95.93
ESI-S	101.4	36	16.3	3.95	1.79	36	2.9	1.32	95.48
ESI-T	101.9	36	16.3	3.95	1.79	33.9	2.9	1.32	95.25

Test parts and characterization data for the interpolymers and the blends are generated according to the following procedures:

Part preparation and testing procedures:

The plasticizers employed were: P610, a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester having a molecular weight (MW) of 400 available from the C. P. Hall Co.; G57 is a "polymeric" (MW ~ 5,700) glutarate available from the C. P. Hall Co. and Sunpar 2280, a paraffinic oil available from Sun Company, Inc. and having a molecular weight of 690 and a specific gravity at 60°F of 0.8911.

Compression Molding:

Samples were melted at 190°C for 3 min. and compression molded at 190°C under 20,000 lb (9,072 kg) of pressure for another 2 min. Subsequently, the molten materials were quenched in a press equilibrated at room temperature.

Density:

Density was determined by ASTM D-792.

Melt Index:

Melt index was determined by ASTM D1238 (190°C/2160 g).

Differential Scanning Calorimetry (DSC):

A Dupont DSC-2210 was used to measure the thermal transition temperatures and heat of transition for the samples. In order to eliminate previous thermal history, samples were first heated to 160 °C. Heating and cooling curves were recorded at 10 °C/min. Melting (T_m from second heat) and crystallization (T_c) temperatures were recorded from the peak temperatures of the endotherm and exotherm, respectively.

Dynamic Mechanical Spectroscopy (DMS)

Dynamic mechanical data were generated using a Rheometrics RSA-II solid state analyzer, and melt pressed (~ 20 mil (0.0508 cm) thick) film test specimens. The DMS measurements were conducted at a step rate of 5 °C/min and a fixed frequency of 10 rad/sec. The glass transition temperature (T_g) of the samples was determined from the $\tan \delta$ peak maximum.

Shear Rheology:

Oscillatory shear rheology measurements were performed with a Rheometrics RMS-800 rheometer. Melt rheological properties were monitored at an isothermal set temperature of 190°C in a frequency sweep mode, using parallel plate test geometry.

Thermomechanical Analysis (TMA):

Thermomechanical analysis was determined using a Perkin Elmer TMA-7 instrument with a one millimeter diameter probe. A three millimeter thick sample five millimeters in diameter was penetrated with a force of one newton (102.4 g) as the temperature is increased at a rate of 5 °C/minute. The temperature at 1 mm penetration is recorded.

Processing Index

The "rheological processing index (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R. N. Shroff and L V. Cancio in *Polymer Engineering Science*, Vol. 17, no. 11, p. 770 (1977), and in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on page 77, both publications of which are incorporated by reference herein in their entirety. All GER experiments are performed at a temperature of 190° C., at nitrogen pressures between 5,250 to 500 psig (36,197 kPa to 3,447 kPa) using a 0.0296 inch (0.0752 cm) diameter, 20:1 I/D.die. An apparent shear stress vs. apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in *Journal of Rheology* 30(2), 337-357, 1986, above a certain critical flow rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

For the polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at a temperature of 190° C., at nitrogen pressure of 2,500 psig (17,237 kPa) using a 0.0296 inch (0.752 cm) diameter, 20:1 L/D die, or corresponding apparent shear stress of 2.15×10^6 dyne/cm².

Mechanical Testing:

Tensile properties of the compression molded samples were measured using an Instron 1145 tensile machine equipped with an extensiometer. ASTM-D638 samples were tested at a strain rate of 5 min⁻¹. Micro-tensile samples were tested at a speed of 5 in/min (12.7 cm/min) at -10 °C. Average of four tensile measurements is given. The standard deviation for the ultimate properties is typically 10 percent of the reported average value.

Tensile Stress Relaxation:

Uniaxial tensile stress relaxation was evaluated using an Instron 1145 tensile machine. Compression molded film (~ 20 mil (0.0508 cm) thick) with a 1 inch (2.54 cm) gauge length was deformed to a strain level of 50 percent at a strain rate of 20 min⁻¹. The force required to maintain 50 percent elongation was monitored for 10 min. The magnitude of the stress relaxation is defined as $((f_i - f_f)/f_i)$ where f_i is the initial force and f_f is the final force.

Flexural Modulus (2% Secant)

Flexural modulus was determined by ASTM D-790.

Hardness

Shore A hardness was determined by ASTM D-2240.

EXAMPLES 1 TO 6 AND COMPARATIVE EXPERIMENT A

Six blend compositions, examples 1, 2, 3, 4, 5 and 6, are prepared from interpolymer (A) above and either a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) 400) or mineral oil (Sunpar 2280, a paraffinic oil available from Sun Company. Inc. and having a molecular weight of 690 and a specific gravity at 60°F of 0.8911) or polymeric glutarate (G57 available from the C.P.Hall Company) in weight ratios given in Table 2 with a Haake mixer equipped with a Rheomix 3000 bowl. 180 grams of the dry blended component materials were fed into the mixer equilibrated at 150°C. Feeding and temperature equilibration took 3-5 minutes. The molten material was mixed at 150°C and 40 rpm for 10 minutes.

The characterization data for the examples and the component interpolymer are given in Table 2. It was possible to modify the interpolymers, and produce materials with structural integrity and good mechanical properties.

Analysis of examples 4 and 5 of modification with the P610 phthalate ester shows the good plasticization achieved. There is no significant broadening of the Tan δ of the loss peak associated with the interpolymer glass transition process. These modified interpolymers show good low temperature performance, and significant retention of stress relaxation behavior. The level of hardness can be controlled by appropriate selection of plasticizer. The combination of mechanical properties, relaxation behavior, hardness and processability is particularly desirable, for example in many film applications.

Table 2

	Example or Comparative Experiment						
	A*	1	2	3	4	5	6
Wt ratio Interpolymer (A)**/Mineral oil	100/0	95/5	90/10	80/20			
Wt ratio Interpolymer (A)/P610 plasticizer					90/10	80/20	
Wt ratio Interpolymer (A)/G57 glutarate							90/10
Tg(DMS), °C	30	22	22	21	7	4.5	24
Tanδ peak width at half height deg.C	16					15	
Mechanical Properties (@ 23°C)							
Tensile Mod, MPa	617.6	6.4	6.8	6.3	2.4	0.94	7.4
% Strain @ Break	257	313	290	310	370	546	273
Total energy @ Break, N.m	122.4					21.6	
Mechanical Properties (@ -10°C)							
Tensile Mod, MPa							
% Strain @ Break	18.6					281	
Total energy @ Break, N.m	9.9					145.6	
% Stress Relaxation (@ 23°C)	92.9					68.7	
Hardness: Shore A (@ 23°C)	96	95	92	92	66	49	96
Melt Rheology (190°C)							
10 ⁵ η(0.1 rad/sec), Poise	6.53					0.17	
η(100/0.1)	0.048					0.11	
Tan δ (0.1 rad/sec)	4.42					10.2	

* Not an example of the present invention.

** Interpolymer (A) is an ethylene/styrene interpolymer containing 69.4 weight percent (37.9 mole percent) styrene (measured by NMR technique), having an I₂ melt flow index of 0.18 and containing 8.4 weight percent atactic polystyrene. The polymer showed no measurable crystallinity by DSC techniques.

As a further comparative experiment, a blend of polystyrene (PS; Styron™ 685D, a polystyrene having a Melt Flow Index (200 °C/5.0 kg) of 1.5 g/10 min and a specific gravity of 1.04, commercially available

from The Dow Chemical Company) and P610 plasticizer was produced in a PS/P610 weight ratio of 80/20. This produced a material which had a Tg of 37°C compared to 106°C for the unmodified PS. No properties could be measured due to the form of this composition, confirming past
5 experience that phthalate esters do not function as effective plasticizers in PS.

EXAMPLES 7 & 8 and COMPARATIVE EXPERIMENT B

Two blend compositions, examples 7 and 8, are prepared from interpolymer (B) above and a mixed linear dialkyl (hexyl, octyl, decyl)
10 phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) 400) in weight ratios given in Table 3 with a Haake mixer equipped with a Rheomix 3000 bowl. 180 grams of the dry blended component materials were fed into the mixer equilibrated at 150 °C. Feeding and temperature equilibration took 3-5 minutes. The molten material was
15 mixed at 150°C and 40 rpm for 10 minutes.

The characterization data for the examples and the component Interpolymer are given in Table 3. It was possible to modify the interpolymers, and produce materials with structural integrity and good mechanical properties.

20 Analysis of examples 7 and 8 of modification with the P610 phthalate ester shows the good plasticization achieved. There is no significant broadening of the Tan δ of the loss peak associated with the interpolymer glass transition process. These modified interpolymers show good low temperature performance, and surprising
25 retention of stress relaxation behavior. The combination of mechanical properties, relaxation behavior, hardness and processability is particularly desirable, for example in many film applications.

Table 3

	Example or Comparative Experiment		
	B*	7	8
Wt ratio Interpolymer (B)**/P610 plasticizer		80/20	70/30
Tg(DMS), °C	29.8	7.5	-10.8
Tanδ peak width at half height deg.C	15	18	17
Mechanical Properties (@ 23°C)			
Tensile Mod, Mpa	617.6	1.7	0.6
% Strain @ Break	248	587	320
Total energy @ Break, N.m	101.4	8.7	1.4
Mechanical Properties (@ -10°C)			
Tensile Mod, Mpa			
% Strain @ Break	5.7	249	403
Total energy @ Break, N.m	9.9	100	32.1
% Stress Relaxation (@ 23°C)	93.5	78.5	90.7
Hardness: Shore A (@ 23°C)	98	37	21
Melt Rheology (190°C)			
10 ⁵ η(0.1 rad/sec), Poise	1.01	0.19	0.082
η(100/0.1)	0.14	0.29	0.36
Tan δ (0.1 rad/sec)	9.98	21.0	25.3

* Not an example of the present invention.

** Interpolymer (B) is an ethylene/styrene interpolymer containing 69.9 weight percent (38.4 mole percent) styrene (measured by NMR technique), having an I₂ melt flow index of 1.83 and containing 8.2 weight percent atactic polystyrene. The polymer shows no measurable crystallinity by DSC techniques.

EXAMPLE 9 and COMPARATIVE EXPERIMENT C

Example 9 is prepared from interpolymer (C) above and a mixed linear dialkyl (hexyl, octyl, decyl) phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) 400) in weight ratios given in Table 4 with a Haake mixer equipped with a Rheomix 3000 bowl. 180 gram of the dry blended component materials were fed into the mixer equilibrated at 150 °C. Feeding and temperature equilibration takes 3-5 minutes. The molten material is mixed at 150°C and 40 rpm for 10 minutes.

The characterization data for the example and the component Interpolymer are given in Table 4. The modified interpolymers has structural integrity and good mechanical properties. The solid materials shows increased crystallinity compared to the unmodified interpolymer. There is some broadening of the Tan δ of the loss peak associated with the interpolymer glass transition process, which could find utility in some energy absorbing applications. The modified interpolymers show good low temperature performance, and retention of stress relaxation behavior. The combination of mechanical properties, relaxation behavior, hardness and processability is again desirable, for example in many film applications.

Table 4

	Example or Comparative Experiment	
	C*	9
Wt ratio Interpolymer (C) **/P610 plasticizer		80/20
DSC data		
Percent crystallinity	4.7	10.5
T _m °C	45.7	44.8
T _g (DMS), °C	-2.2	-21.7
Tan δ peak width at half height deg.C	15	22
Mechanical Properties (@ 23°C)		
Tensile Mod, Mpa	6.8	4.1
% Strain @ Break	475	557
Total energy @ Break, N.m	105.6	65.2
Mechanical Properties (@ -10°C)		
Tensile Mod, Mpa	81.9	8.8
% Strain @ Break	258	480
Total energy @ Break, N.m	79.2	160.7
% Stress Relaxation (@ 23°C)	26.2	29.6
Hardness: Shore A (@ 23°C)	75	52
Melt Rheology (190°C)		
10 ³ η (0.1 rad/sec), Poise	31	0.094
η (100/0.1)	-	-
Tan δ (0.1 rad/sec)	4.2	2.1

* Not an example of the present invention.

** Interpolymer (C) is an ethylene/styrene interpolymer containing 47.3 weight percent (19.5 mole percent) styrene, having an I₂ melt flow index of 0.01 and containing 3.7 weight percent atactic polystyrene.

EXAMPLES 10 & 11 AND COMPARATIVE EXPERIMENT D

Two blend compositions, examples 10 and 11, are prepared from interpolymer (D) above and either a mixed linear dialkyl (hexyl, octyl, 5 decyl) phthalate ester (P610, available from the C.P.Hall Company, and having a molecular weight (MW) 400) or mineral oil (Sunpar 2280, a paraffinic oil available from Sun Company. Inc. and having a molecular weight of 690 and a specific gravity at 60°F of 0.8911) in weight ratios given in Table 5 with a Haake mixer equipped with a Rheomix 3000 bowl. 180 10 gram of the dry blended component materials were fed into the mixer equilibrated at 150 °C. Feeding and temperature equilibration takes 3-5 minutes. The molten material is mixed at 150°C and 40 rpm for 10 minutes.

The characterization data for the examples and the component. Interpolymer are given in Table 5. The modified interpolymers have 15 structural integrity and good mechanical properties.

The oil is a more effective modifier for lowering Tg in this Interpolymer compared to Interpolymer (A).

The solid materials show small changes in level of crystallinity compared to the unmodified interpolymer. Both modifiers produce 20 broadening of the Tan δ of the loss peak associated with the interpolymer glass transition process, which could find utility in some energy absorbing applications.

The modified interpolymers show good low temperature performance, and retention of stress relaxation behavior. In 25 addition, the viscosity of the modified interpolymers is significantly reduced, which translates into improved processability in some fabrication processes.

Table '5

	Example or Comparative Experiment		
	D*	10	11
Wt ratio Interpolymer (D**)/Mineral oil		80/20	
Wt ratio Interpolymer (D)/P610 plasticizer			80/20
Percent crystallinity (DSC data)	14.7	20.7	17.8
T _m °C (DSC data)	71.3	69.7	70.4
T _g (DMS), °C	-8	-14.5	-25.4
Tanδ peak width at half height deg.C	23	34	39
Mechanical Properties (@ 23°C)			
Tensile Mod, MPa	19.7	2.1	12.6
% Strain @ Break	378	396	493
Total energy @ Break, N.m	150	82.7	65.2
Mechanical Properties (@ -10°C)			
Tensile Mod, MPa	66.6	2.0	27.2
% Strain @ Break	303	403	484
Total energy @ Break, N.m	91.0	32.1	148
% Stress Relaxation (@ 23°C)	26.2	26.1	26.3
Hardness: Shore A (@ 23°C)	96	92	49
Melt Rheology (190°C)			
10 ³ η(0.1 rad/sec), Poise	16.6	0.43	0.43
η(100/0.1)	0.16	0.19	0.20
Tan δ (0.1 rad/sec)	2.37	2.7	2.6

* Not an example of the present invention.

** Interpolymer (D) is an ethylene/styrene interpolymer containing 29.3 weight percent (10 mole percent) styrene, having an I₂ melt flow index of 0.03 and containing 1 weight percent atactic polystyrene.

EXAMPLE 12

A. Blend Preparation

The blends were prepared in a Haaake mixer equipped with a Rheomix 3000 bowl. The bowl when fully loaded contains 220 grams of polymer and oil. The polymer portion of this mix was fed into the mixer and equilibrated at 190°C. Feeding and temperature equilibration took about 3 to 5 minutes. The molten polymer material was mixed at 190°C at a mixer speed of 20 rpm for 5 minutes. The Oil (Deer Park Naphthenic Oil 3131 having an aromatic content of 28.1 wt. percent; a flash point of 315°C and an ASTM D445 viscosity of 9.18

centistokes ($9.18 \times 10^{-6} \text{ m}^2/\text{sec}$) at 40°C available from Shell Lubricants at Deep Park, Texas) was then added and mixed with the polymer at 90 rpm for 5 minutes at 190°C .

B. Molding of polymer + oil blend

The polymer and oil blend prepared in A above was compression molded into 0.125 in. x 5 in. x 5 in. (0.317 cm x 12.7 cm x 12.7 cm) test plaques for physical testing by subjecting the polymer and oil blend in the mold to a temperature of 190°C and a pressure of 5,000 psi (34,474 kPa) for 5 minutes followed by a pressure of 20,000 psi (137,895 kPa) at 190°C for 3 minutes. The plaques were then removed from the mold and allowed to cool to 32°C at 5,000 psi (34,474 kPa). The composition and properties of the interpolymers used to blend with the oil is provided in table 6 and the properties of the blend of the interpolpolymer and oil is provided in table 7.

Table 6

Base Resin	ESI Resin			Copolymer Styrene		Atactic Styrene	Melt Index	Density	Hardness Shore A	Flexural Modulus (2% Secant)	
	Type	lbs	kg	wt. %	mol %	Wt. %	g/10 mm	g/cc		psi	kPa $\times 10^3$
1	G	2.2	1.0	20.54	6.5	0.7	0.13	0.9353	88.5	7631	52.6
	N	4.5	2.0								
2	O	5.1	2.3	21.02	6.7	0.2	1.97	0.9366	90.4	7729	53.3
	P	4.9	2.2								
3	Q	3.4	1.5	19.82	6.2	0.1	7.48	0.9378	90.9	8753	60.3
	R	3.9	1.8								
4	M	5.9	2.7	26.25	8.7	0.2	0.33	0.9368	82.9	4469	30.8
5	E	4.2	1.9	25.91	8.6	1.5	1.94	0.9411	88.3	5449	37.6
	F	4.1	1.9								
6	S	5.0	2.3	20.04	6.3	0.1	10.97	0.9381	90.0	8837	60.9
	T	4.4	2.0								
7	H	5.2	2.4	31.06	10.8	1.8	0.09	0.9393	79.1	3208	22.1
	I	2.7	1.2								
8	K	6.2	2.8	31.06	10.8	0.2	2.80	0.9390	68.2	3081	21.2
	L	5.3	2.4								
9	J	5.8	2.6	30.02	10.3	0.5	11.18	0.9402	79.7	3719	25.6

Table 7

Blend	ESI Base Resin	Oil wt %	Flexural Modulus (2% secant)		TMA °C	Processing Index		Hardness Shore A
			psi	kPa $\times 10^{-3}$		kpoise @ 10 k sec ⁻¹	kPas @ 10 k sec ⁻¹	
A	1	15.0	6005	41.4	89	7.7	0.77	86.0
B	1	20	5526	38.1	87	5.8	0.58	82.9
C	2	15.0	5119	35.3	87	2.47	0.247	85.5
D	2	20	4244	29.3	85	1.60	0.160	82.6
E	2	25	4233	29.2	83	0.99	0.099	80.5
F	3	15.0	7055	48.6	89	0.96	0.096	86.1
G	3	20	5684	39.2	87	0.60	0.060	82.5
H	3	25	4821	33.2	84	0.39	0.039	81.0
I	4	22.5	3253	22.4	76	2.32	0.232	74.8
J	4	30.0	2805	19.3	73	1.00	0.100	70.7
K	4	37.5	1681	11.6	69	0.35	0.035	63.4
L	5	22.5	3218	22.2	80	0.83	0.083	76.2
M	5	30.0	2607	18.0	76	0.36	0.036	71.2
N	5	37.5	1896	13.1	70	0.12	0.012	62.7
O	6	22.5	4489	30.9	85	0.37	0.037	81.7
P	7	30.0	1360	9.4	63	1.35	0.135	60.8
Q	7	40.0	903	6.2	57	0.30	0.030	51.5
R	7	50.0	1009	7.0	51	0.04	0.004	39.1
S	8	30.0	1379	9.5	60	0.34	0.034	61.0
T	8	40.0	10.97	7.6	58	0.09	0.009	52.2
U	8	50.0	669	4.6	53	0.01	0.001	38.4
V	9	30.0	1495	10.3	62	0.10	0.010	59.4
W	9	40.0	867	6.0	57	0.03	0.003	49.9
X	9	50.0	613	4.2	53	CND*	CND*	35.4

* CND = could not be determined.



CLAIMS

1. A composition comprising
- (A) from 50 to 99 percent by weight of at least one substantially random interpolymer comprising
- (1) from 5 to 65 mole percent of polymer units derived from
- (a) at least one vinylidene aromatic monomer, or
- (b) at least one hindered aliphatic or cycloaliphatic vinylidene monomer, or
- (c) a combination of at least one aromatic vinylidene monomer and at least one hindered aliphatic or cycloaliphatic vinylidene monomer, and
- (2) from 35 to 95 mole percent of polymer units derived from at least one C₂₋₂₀ α -olefin;; and
- (B) from 1 to 50 percent by weight of at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters, epoxy compounds, phosphate esters, glutarates, polymeric plasticizers (polyesters of glycols and aliphatic dicarboxylic acids) and oils.
2. A composition of claim 1 wherein component (A) comprises from 5 to 50 mole percent of polymer units derived from at least one aromatic vinylidene monomer and from 50 to 95 mole percent of polymer units derived from at least one C₂₋₁₀ α -olefin.
3. A composition of claim 1 wherein component (A) comprises from 5 to 50 mole percent of polymer units derived from styrene and from 50 to 95 mole percent of polymer units derived from ethylene, or a combination of ethylene with at least one C₃₋₁₀ α -olefin.
4. A composition of claim 1 comprising
- (A) from 60 to 95 percent by weight of at least one substantially random interpolymer comprising
- (1) from 5 to 50 mole percent of polymer units derived from at least one vinylidene aromatic monomer, and,
- (2) from 50 to 95 mole percent of polymer units derived from ethylene, or a combination of ethylene with at least one C₃₋₁₀ α -olefin.
- (B) from 5 to 40 percent by weight of at least one plasticizer selected from the group consisting of phthalate esters, trimellitate esters, benzoates, aliphatic diesters, epoxy compounds, phosphate





12 esters, glutarates, polymeric plasticizers (polyesters of glycols and
13 aliphatic dicarboxylic acids) and oils.

1 5. A composition of claim 1 comprising

2 (A) from 60 to 95 percent by weight of at least one substantially
3 random interpolymer comprising

4 (1) from 5 to 50 mole percent of polymer units derived from
5 styrene, and,

6 (2) from 50 to 95 mole percent of polymer units derived from
7 ethylene, or a combination of ethylene with at least one C₃₋₁₀
8 α -olefin.

9 (B) from 5 to 40 percent by weight of at least one plasticizer
10 selected from the group consisting of phthalate esters, trimellitate
11 esters, benzoates, aliphatic diesters, epoxy compounds, phosphate
12 esters, glutarates, polymeric plasticizers (polyesters of glycols and
13 aliphatic dicarboxylic acids) and oils.

1 6. A composition of claim 1 comprising

2 (A) from 60 to 95 percent by weight of at least one substantially
3 random interpolymer comprising

4 (1) from 5 to 50 mole percent of polymer units derived from
5 styrene, and,

6 (2) from 50 to 95 mole percent of polymer units derived from
7 ethylene, or a combination of ethylene with at least one C₃₋₁₀
8 α -olefin.

9 (B) from 5 to 40 percent by weight of at least one plasticizer
10 selected from the group consisting of phthalate esters, including
11 dialkyl, mixed linear dialkyl, aryl and mixed alkyl aryl esters.

1 7. A composition of claim 1 comprising

2 (A) from 60 to 95 percent by weight of at least one substantially
3 random interpolymer comprising

4 (1) from 5 to 50 mole percent of polymer units derived from
5 styrene, and

6 (2) from 50 to 95 mole percent of polymer units derived from
7 ethylene, or a combination of ethylene with at least one C₃₋
8 α -olefin.

9 (B) from 5 to 40 percent by weight of at least one oil selected from
10 mineral oils, natural oils, naphthenic oils, paraffinic oils and
11 aromatic oils.

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1 8. A composition of claim 1 comprising
2 (A) from 40 to 85 percent by weight of at least one substantially
3 random interpolymer comprising
4 (1) from 6.3 to 15.2 mole percent of polymer units derived from
5 styrene, and
6 (2) from 84.8 to 93.7 mole percent of polymer units derived from
7 ethylene, or a combination of ethylene with at least one C₃₋₁₀
8 α -olefin;
9 (B) from 15 to 60 percent by weight of at least one naphthenic oil or
10 a blend of at least one naphthenic oil and at least one paraffinic
11 oil;
12 and wherein
13 (i) component (A) has a melt index of from 0.1 to 10; and
14 (ii) said composition has a flexural modulus (2 percent secant) of from
15 600 psi (4,137 kPa) to 7,100 psi (48,953 kPa), a process index of
16 from 0.1 to 2.0, and a TMA of from 60°C to 100°C.

1 9. A composition of claim 8 comprising
2 (A) from 55 to 85 percent by weight of at least one substantially
3 random interpolymer comprising
4 (1) from 6.3 to 10.3 mole percent of polymer units derived from
5 styrene, and
6 (2) from 89.7 to 93.7 mole percent of polymer units derived from
7 ethylene, or a combination of ethylene with at least one C₃₋₁₀
8 α -olefin;
9 (B) from 15 to 45 percent by weight of at least one naphthenic oil and
10 aromatic oils;
11 and wherein
12 (i) component (A) has a melt index of from 0.1 to 2; and
13 (ii) said composition has a flexural modulus (2 percent secant) of
14 from 600 psi (4,137 kPa) to 4000 psi (27,579 kPa), a process index
15 of from 0.1 to 1.0, and a TMA of from 65°C to 100°C.

1 10. A composition of claim 8 comprising
2 (A) from 60 to 65 percent by weight of at least one substantially
3 random interpolymer comprising
4 (1) from 7.8 to 10.3 mole percent of polymer units derived from
5 styrene, and
6 (2) from 89.7 to 92.2 mole percent of polymer units derived from
7 ethylene;
8 (B) from 35 to 40 percent by weight of at least one naphthenic oil;

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- 9 and wherein
10 (i) component (A) has a melt index of from 0.5 to 0.9; and
11 (ii) said composition has a flexural modulus (2 percent secant) of
12 from 600 psi (4,137 kPa) to 2,000 psi (13,790 kPa), a process
13 index of from 0.1 to 0.3, and a TMA of from 70°C to 100°C.

1 11. A composition of any of claims 1-10 containing 1 to
2 50 weight percent of one or more additional polymers selected from
3 polystyrene, syndiotactic polystyrene, styrenic copolymers such as
4 styrene/acrylonitrile copolymer, polyolefin homo and copolymers,
5 polyethylene, polypropylene, poly(vinyl chloride), polycarbonate,
6 polyethylene terephthalate, urethane polymers and polyphenylene oxide.

1 12. A composition of any of claims 1-11 in the form of
2 foams, fibers or emulsions.

1 13. A composition of any of claims 1-11 in the form of an
2 adhesive or sealant compositions.

1 14. A composition of any of claims 1-11 in the form of
2 injection, compression, extruded or blow molded parts.

1 15. A composition of any of claims 1-11 in the form of a
2 film or sheet, or as a component of a multilayered structure resulting
3 from calendering, blowing, casting or (co-)extrusion operations.



* C L M S *