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| (54) Title: COMPATIBLE THERMOPLASTIC POLYURETHANE-POLYOLEFIN BLEND COMPOSITIONS | | |
| (57) Abstract | | |
| <p>A thermoplastic polyurethane/olefin-graft polymer blend with an optional compatibilizing polymer that demonstrates improved tensile strength, compression set and abrasion resistance properties relative to a blend prepared from the same thermoplastic polyurethane and an ungrafted version of the olefin-graft polymer.</p> | | |

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TITLE**COMPATIBLE THERMOPLASTIC POLYURETHANE-POLYOLEFIN
BLEND COMPOSITIONS**FIELD OF THE INVENTION

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This invention relates generally to crosslinkable polymer blend compositions. This invention particularly relates to such compositions wherein crosslinking occurs at least partially through a silane moiety, preferably a hydrolyzable silane moiety such as an alkoxy silane. Skilled artisans recognize that a preferred starting material to graft such a moiety onto a polymer backbone via a free radical mechanism is a vinyl silane, preferably a vinyl alkoxy silane.

15 This invention also relates particularly to polymer compositions that include thermoplastic polyurethane, a first olefin graft polymer and, optionally, a compatibilizing polymer. The first graft polymer includes at least one silane moiety and, optionally, at least one acid or anhydride moiety. Where the first

20 graft polymer contains both moieties, addition of a compatibilizing polymer provides no substantial improvement in composition tensile or compression set properties.

BACKGROUND OF THE INVENTION

25

A perceived need exists for a polymer blend composition that exhibits desirable thermoplastic polyurethane (TPU) properties such as mechanical (tensile) properties and abrasion resistance and desirable polyolefin properties such as low density, resistance to polar solvents and low moisture sensitivity. Such a composition should have an improved resistance to

30 compression set, relative to its polyolefin component, while retaining sufficient tensile strength at break of the TPU component.

SUMMARY OF THE INVENTION

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A first aspect of the invention is a polymer composition comprising a thermoplastic polyurethane and a first olefin graft polymer, the graft polymer including at least one first graft moiety and at least one second graft moiety, the

5 first graft moiety being a silane moiety that promotes crosslinking of the grafted elastomer in the presence of moisture, the second graft moiety being an unsaturated organic compound that, prior to grafting, contains at least one ethylenic unsaturation and a polar functionality that promotes compatibilization of the olefin and the TPU.

10

A second aspect of the invention is a polymer composition comprising a thermoplastic polyurethane, a first olefin graft polymer, the graft polymer including at least one first graft moiety, the first graft moiety being a silane moiety that promotes crosslinking of the grafted elastomer in the presence of moisture, and a compatibilizing polymer. The compatibilizing polymer, also referred to as a modified polymer, is desirably selected from the group consisting of (a) ionomers and (b) random, block or graft olefin polymer that have, in a main or side chain thereof, an unsaturated organic compound that, prior to incorporation into the copolymer or grafting thereto, contains at least one ethylenic unsaturation and a polar functionality that promotes compatibilization of the olefin and the TPU. The unsaturated organic compound, also known as a functional group, is selected from the group consisting of carboxylic acids, carboxylate esters, carboxylic acid anhydrides, carboxylate salts, amides, epoxies, hydroxys, and acyloxys. The modified polyolefin preferably contains a grafted polar functionality (e.g. an anhydride). Skilled artisans understand that incorporation of the organic compound into a polymer backbone or grafting the organic compound onto the polymer backbone necessarily converts the ethylenic unsaturation to a saturated moiety. An alternated preferable modified polyolefin is an ethylene copolymer that has polymerized therein a polar comonomer (e.g. an acrylic or methacrylic acid functionality) and is at least partially neutralized by a reaction with an ionizable metal compound to yield an ionomer.

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DESCRIPTION OF PREFERRED EMBODIMENTS

Unless otherwise stated herein, all ranges include both end points.

35

5 A “modified polyolefin” typically includes an olefin monomer
such as ethylene, propylene or another alpha-olefin monomer that contains up to
twenty carbon atoms as well as a vinyl functional group containing monomer.
The latter monomer includes, for example, acrylic acid, methacrylic acid, maleic
acid, maleic anhydride, acrylamide, methacrylamide, glycidyl acrylate, glycidyl
10 methacrylate, vinyl acetate, vinyl butyrate, methyl acrylate, ethyl acrylate, butyl
acrylate, 2-hydroxyethyl acrylate, sodium acrylate, and zinc acrylate.

TPUs suitable for use in compositions of the present invention
include those described in U.S. Patent (USP) 4,883,837 (Zabrocki), the relevant
15 teachings of which are incorporated herein by reference for purposes of U.S.
patent practice. See, e.g., column 4, line 12 through column 6, line 5. As noted
therein, any TPU may be used so long as it is thermoplastic in nature. This means
that it is prepared from substantially difunctional ingredients such as an organic
diisocyanate. A representative teaching on the preparation of TPU materials may
20 be found in Polyurethanes: Chemistry and Technology, Part II, Saunders and
Frisch, 1964, pages 767-769, Interscience Publishers, New York, NY and
Polyurethane Handbook, Edited by G. Oertel, 1985, pages 405-417, Hanser
Publications, distributed in the United States by Macmillan Publishing Co., Inc.,
New York, NY. Specific teachings may be found in a number of U.S. Patents
25 including, for example, USP 4,245,081; 4,371,684; 4,379,904; 4,447,590;
4,523,005; 4,621,113 and 4,631,329. The relevant teachings of the foregoing
patents and texts are incorporated herein by reference for purposes of US patent
practice.

30 Preferred TPUs included polymers prepared from a mixture
comprising an organic diisocyanate, at least one polymeric diol and at least one
difunctional extender. The TPU may be prepared by the prepolymer, quasi-
prepolymer, or one-shot methods in accordance with methods described in the
incorporated references cited above.

35 Any of the organic diisocyanates previously used in TPU
preparation can be used herein, including aromatic, aliphatic, and cycloaliphatic
diisocyanates, and mixtures thereof.

5 The TPUs are present in an amount that is sufficient to impart
desirable TPU properties to the compositions without being so high that it
effectively eliminates cost advantages, performance benefits or both that result
from inclusion of a polyolefin. The amount is desirably sufficient to provide a
composition that has compression set and tensile strength values that exceed what
10 one would expect using a monotonic (straight-line) rule of mixture approach for
the TPU and polyolefin. The amount of TPU is preferably from 5 to 95 percent
by weight (wt%), more preferably from 30 to 85 wt%, based on total composition
weight. A TPU content of less than 5 wt% or greater than 95 wt%, while
possible, does not appear to take full advantage of the presence of both polymers.

15

When one blends a TPU with a polyolefin, the resulting blend will
have a morphology that varies between two extremes. At one extreme, a low TPU
level relative to the polyolefin level yields a continuous polyolefin phase with
discrete TPU domains dispersed therein. At the second extreme, a high TPU level
20 relative to the polyolefin yields a continuous TPU phase with discrete polyolefin
domains dispersed therein. At an intermediate point where the levels of TPU and
polyolefin are equal or nearly so, the morphology shows co-continuous phases.
When a compatibilizer or a polymer with a compatibilizing functionality is added
to the blend, the disperse phase particle size changes relative to that of blends
25 lacking the compatibilizer or compatibilizing functionality. The change in the
disperse phase leads, in turn, to variations in blend mechanical properties relative
to mechanical properties of blends that lack the compatibilizer or compatibilizing
functionality.

30

The first olefin graft polymer is suitably prepared by grafting one
or more functional groups onto an ethylene polymer.

“Ethylene polymers” means an ethylene/ α -olefin copolymer or
diene-modified ethylene/ α -olefin copolymer. Illustrative ethylene polymers
35 include ethylene/propylene (EP) copolymers, ethylene/octene (EO) copolymers,
ethylene/butylene (EB) copolymers, ethylene/propylene/diene (EPDM)
interpolymers and ethylene/styrene interpolymers. More specific examples
include ultra low linear density polyethylene (ULDPE) (e.g., Attane™ made by
The Dow Chemical Company), homogeneously branched, linear ethylene/ α -olefin
40 copolymers (e.g. Tafmer™ by Mitsui PetroChemicals Company Limited and

5 Exact™ by Exxon Chemical Company), homogeneously branched, substantially
linear ethylene/ α -olefin polymers (e.g. the Affinity™ polymers available from
The Dow Chemical Company and Engage® polymers available from DuPont
Dow Elastomers L.L.C., and Nordel® IP hydrocarbon rubbers available from
10 DuPont Dow Elastomers L.L.C.). More preferred ethylene/alpha-olefin polymers
include homogeneously branched linear and substantially linear ethylene
copolymers with a density (measured in accordance with ASTM D-792) from
0.85 to 0.92 g/cm³, especially from 0.85 to 0.90 g/cm³ and a melt index or I₂
(measured in accordance with ASTM D-1238 (190°C/2.16 kg) from 0.01 to 500,
preferably from 0.05 to 30 g/10 minutes. The substantially linear ethylene
15 copolymers are especially preferred.

"Substantially linear" means that a polymer has a backbone
substituted with from 0.01 to 3 long-chain branches per 1000 carbons in the
backbone.

20

"Long-chain branching" or "LCB" means a chain length that
exceeds that of a short chain that results from incorporation of an α -olefin into the
backbone of an EAO polymer or EAO polymer blend. Although carbon-13
nuclear magnetic resonance (C¹³ NMR) spectroscopy cannot distinguish or
25 determine an actual number of carbon atoms in the chain if the length is greater
than six carbon atoms, the presence of LCB can be determined, or at least
estimated, from EAO polymer MWD. It can also be determined from a melt flow
ratio (MFR) or ratio (I₁₀/I₂) of melt index (I₁₀) via ASTM D-1238 (190°C, 10-kg
weight) to I₂.

30

Polymers that contain two monomers fall into a group often
referred to as "copolymers" whereas "interpolymers" typically refers to polymers
that contain three or more monomers. Skilled artisans recognize, however, that
some do not make such a distinction and use either "copolymer" or
35 "interpolymer" as a generic reference to any polymer that contains two or more
monomers. As used herein "interpolymer" refers to a polymer having
polymerized therein at least two monomers. It includes, for example, copolymers,
terpolymers and tetrapolymers. It particularly includes a polymer prepared by
polymerizing ethylene with at least one comonomer, typically an α -olefin of 3 to
40 20 carbon atoms (C₃-C₂₀). Illustrative α -olefins include propylene, 1-butene, 1-

5 hexene, 4-methyl-1-pentene, 1-heptene, 1-octene and styrene. The α -olefin is
desirably has a C_3 - C_{10} α -olefin. Preferred copolymers include EP and EO
copolymers. Illustrative terpolymers include an ethylene/propylene/1-octene
terpolymer as well as terpolymers of ethylene, a C_3 - C_{20} α -olefin and a diene such
10 2-norbornene (ENB). The terpolymers are also known as EPDM terpolymers,
when the α -olefin is propylene, or generically as EAODM terpolymers.

The substantially linear ethylene α -olefin interpolymers (also
known as "SLEPs" or "substantially linear ethylene polymers") are characterized
15 by narrow molecular weight distribution (MWD) and narrow short chain
branching distribution (SCBD) and may be prepared as described in United States
Patent (USP) 5,272,236 and 5,278,272, relevant portions of both being
incorporated herein by reference for purposes of U.S. patent practice. The SLEPs
exhibit outstanding physical properties by virtue of their narrow MWD and
20 narrow SCBD coupled with long chain branching (LCB). The presence of LCB in
these olefinic polymers allows for easier processing (faster mixing, faster
processing rates) and the narrow MWD allows for more efficient free radical
crosslinking. USP 5,272,236 (column 5, line 67 through column 6, line 28)
describes SLEP production via a continuous controlled polymerization process
25 using at least one reactor, but allows for multiple reactors, at a polymerization
temperature and pressure sufficient to produce a SLEP having desired properties.
Polymerization preferably occurs via a solution polymerization process at a
temperature of from 20°C to 250°C, using constrained geometry catalyst
technology.

30
Suitable constrained geometry catalysts are disclosed at column 6,
line 29 through column 13, line 50 of USP 5,272,236. These catalysts may be
described as comprising a metal coordination complex that comprises a metal of
groups 3-10 or the Lanthanide series of the Periodic Table of the Elements and a
35 delocalized pi-bonded moiety (π -bm) substituted with a constrain-inducing
moiety. The complex has a constrained geometry about the metal atom such that
the angle at the metal between the centroid of the delocalized, substituted π -bm
and the center of at least one remaining substituent is less than such angle in a
similar complex containing a similar π -bm lacking in such constrain-inducing
40 substituent. If such complexes comprise more than one delocalized, substituted π -

5 bm, only one such moiety for each metal atom of the complex is a cyclic,
delocalized, substituted π -bm. The catalyst further comprises an activating co-
catalyst such as tris(pentafluorophenyl)borane. Specific catalyst complexes are
discussed in USP 5,272,236 at column 6, line 57 through column 8, line 58 and in
10 USP 5,278,272 at column 7, line 48 through column 9, line 37. The teachings
regarding the catalyst complexes in general and these specific complexes are
incorporated by reference.

Additional constrained geometry catalysts may be found in US Serial
Number 09/11,895, filed 19 February 1998, its corresponding PCT Application number
15 96/16012, filed 3 October 1996, its predecessors US Serial Number 08/592,756, filed 26
January 1996 and US Serial Number 60/005,913, filed 17 October 1995; and in PCT/US
97/07252, filed 30 April 1997. The relevant teachings of these applications are
incorporated herein by reference.

20 A SLEP is characterized by a narrow MWD and, if an
interpolymer, by a narrow comonomer distribution. A SLEP is also characterized
by a low residuals content, specifically in terms of catalyst residue, unreacted
comonomers and low molecular weight oligomers generated during
polymerization. A SLEP is further characterized by a controlled molecular
25 architecture that provides good processibility even though the MWD is narrow
relative to conventional olefin polymers.

A preferred SLEP has a number of distinct characteristics, one of
which is a comonomer content that is between 20 and 80 weight percent (wt%),
30 more preferably between 30 and 70 wt%, ethylene, with the balance comprising
one or more comonomers. SLEP comonomer content can be measured using
infrared (IR) spectroscopy according to ASTM D-2238 Method B or ASTM D-
3900. Comonomer content can also be determined by C^{13} NMR Spectroscopy.
When the SLEP is an ethylene/1-octene copolymer, an ethylene content of from
35 40 to 92 wt%, based on copolymer weight, should equate to a density of 0.850
grams per cubic centimeter (g/cm^3) - 0.920 g/cm^3 . An ethylene content of 40-81
wt% should yield a density of 0.850 g/cm^3 - 0.900 g/cm^3 .

5 Additional distinct SLEP characteristics include melt index or I_2
and melt flow ratio (MFR or I_{10}/I_2). The interpolymers desirably have an I_2
(ASTM D-1238, condition 190°C/2.16 kilograms (kg) (formerly condition E), of
from 0.01 to 500 grams/10 minutes (g/10 min), more preferably from 0.05 to 150
g/10 min. The SLEP also has an I_{10}/I_2 (ASTM D-1238) ≥ 5.63 , preferably from
10 6.5 to 15, more preferably from 7 to 10. For a SLEP, the I_{10}/I_2 ratio serves as an
indication of the degree of LCB such that a larger I_{10}/I_2 ratio equates to a higher
degree of LCB in the polymer.

A further distinct characteristic of a SLEP is MWD (M_w/M_n or
15 "polydispersity index"), as measured by gel permeation chromatography (GPC).
A suitable M_w/M_n satisfies the equation:

$$0 < M_w/M_n \leq (I_{10}/I_2) - 4.63$$

20 The MWD, also known as a "narrow MWD", is desirably > 0 and < 5 , especially
from 1.5 to 3.5, and preferably from 1.7 to 3.

The SLEP has a homogenous comonomer branching distribution.
That is, the SLEP is a polymer in which the comonomer is randomly distributed
25 within a given interpolymer and wherein substantially all of the interpolymer
molecules have the same ethylene/comonomer ratio within that interpolymer. The
homogeneity of the polymers is typically described by the SCDBI (Short Chain
Branch Distribution Index) or CDBI (Composition Distribution Branch Index)
and is defined as the weight percent of the polymer molecules having a
30 comonomer content within 50 % (25 % on each side) of the median total molar
comonomer content. The CDBI of a polymer is readily calculated from data
obtained from techniques known in the art such as, for example, temperature
rising elution fractionation (abbreviated herein as "TREF") as described, for
example, in Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20,
35 page 441 (1982), in USP 5,008,204 (Stehling), in USP 5,246,783 (Spenadel et al.),
in USP 5,322,728 (Davey et al.), in USP 4,798,081 (Hazlitt et al.), or in USP
5,089,321 (Chum et al.), the disclosures of which are incorporated herein by
reference. USP 5,382,631 provides a summary description of CDBI
determination at column 5, lines 36-55. The SCDBI or CDBI, also known as a
40 narrow comonomer distribution, for the SLEPs used in the present invention is

5 greater than 50 wt%, desirably greater than 60 wt%, preferably greater than 70 wt% and more preferably greater than 90 wt%.

The SLEPs used in this invention essentially lack a measureable “high density” fraction as measured by the TREF technique. In other words, the
10 SLEPs do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls per 1000 carbon atoms. The SLEPs also do not contain any highly short chain branched fraction. In other words, the SLEPs do not contain a polymer fraction with a degree of branching equal to or greater than 30 methyls per 1000 carbon atoms.

15

A homogeneously branched SLEP surprisingly has a MFR that is essentially independent of its MWD. This contrasts markedly with conventional linear homogeneously branched and linear heterogeneously branched ethylene copolymers where the MWD must be increased to increase the MFR.

20

A SLEP may be still further characterized as having a critical shear rate at onset of surface melt fracture (OSMF) of at least 50 % greater than the critical shear rate at the OSMF of a linear olefin polymer that has about the same I_2 and M_w/M_n . “About the same”, as used herein, means within ten percent (10%)
25 of each other.

25

SLEPs that meet the aforementioned criteria are suitably produced via constrained geometry catalysis by The Dow Chemical Company and DuPont Dow Elastomers L.L.C. As noted above with regard to USP 5,272,236 and USP
30 5,278,272, SLEPs may be prepared in two or more reactors. These reactors may be set up in parallel or serially, and each may use the same or different catalyst system as well as the same or different operating conditions. The use of different catalyst systems, different operating conditions or both favors a broad MWD whereas the use of the same catalyst systems and operating conditions favors a
35 relatively narrower MWD. See also WO 93/13143, USP 5,210,142 and WO 97/12934, the relevant teachings of which are incorporated herein by reference.

35

WO 93/13143 discusses a polymerization process whereby two ethylene polymers are combined in certain ratios at page 2, lines 19-31. One
40 ethylene polymer results from use of a first constrained geometry catalyst

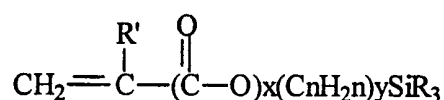
5 composition with a first reactivity and has a melt index of 0.05 to 50 grams/10
 minutes. The other ethylene polymer results from use of a second constrained
 geometry catalyst composition with a different reactivity and also has a melt index
 of 0.05 to 50 grams/10 minutes. The ethylene polymers are suitably
 ethylene/alpha-olefin interpolymers as noted at page 2, lines 32-33.

10

USP 5,210,142 discloses preparation of interpolymer products in a
 multiple zone reactor at column 3, lines 3-24. At least one higher molecular
 weight ethylene interpolymer is produced in one zone of the reactor. The
 remaining fraction of total interpolymer product at a lower molecular weight is
 15 produced in at least one other zone produces .

WO 97/12934 discusses various techniques for preparing polymer
 blends at page 18, line 25 through page 19, line 10. The techniques include
 preparation of physical admixtures by dry blending, melt blending or solution
 20 blending and preparation of in-reactor blends using two or more reactors operated
 in series or parallel, two or more catalysts in a single reactor or a combination of
 multiple catalysts and multiple reactors.

Any silane, or a mixture of such silanes, that will effectively graft
 25 to components of the elastomer compositions of the present invention, especially
 the elastomer phase, can be used as the silane moiety in the practice of this
 invention. Suitable silanes include those of the general formula:



30

in which R' is a hydrogen atom or methyl group; x and y are 0 or 1 with the
 proviso that when x is 1, y is 1; n is an integer from 1 to 12 inclusive, preferably 1
 to 4, and each R independently is a hydrolyzable organic group such as an alkoxy
 group having from 1 to 12 carbon atoms (e.g. methoxy, ethoxy, butoxy), aryloxy
 35 group (e.g. phenoxy), aralkoxy group (e.g. benzyloxy), aliphatic acyloxy group
 having from 1 to 12 carbon atoms (e.g. formyloxy, acetyloxy, propanoyloxy),
 amino or substituted amino groups (alkylamine, arylamino), or a lower alkyl
 group having 1 to 6 carbon atoms inclusive, with the proviso that not more than

5 two of the three R groups is an alkyl (e.g., vinyl dimethyl methoxy silane).
Silanes useful in curing silicones that have ketoximino hydrolyzable groups, such
as vinyl tris(methylethylketoamino) silane, are also suitable. Useful silanes
include unsaturated silanes that comprise an ethylenically unsaturated
hydrocarboxyl group, such as a vinyl, allyl, isopropyl, butyl, cyclohexenyl or
10 gamma-(meth)acryloxy allyl group, and a hydrolyzable group, such as, for
example, a hydrocarbyloxy, hydrocarbonyloxy, or hydrocarbylamino group.
Examples of hydrolyzable groups include methoxy, ethoxy, formyloxy, acetoxy,
propionyloxy, and alkyl or arylamino group. Preferred silanes are the
unsaturated alkoxy silanes that can be grafted onto the polymer. Vinyl trimethoxy
15 silane, vinyl triethoxy silane, gamma-(meth)acryloxy propyl trimethoxy silane and
mixtures of these silanes are the preferred silanes for use in establishing
crosslinks.

The amount of silane used in the practice of this invention can vary
20 widely depending upon the nature of the olefin polymer being grafted by a silane,
the silane, the processing conditions, the grafting efficiency, the amount of silane-
graft polymer, the ultimate application, and similar factors, but typically at least
0.1, preferably at least 0.3, more preferably at least 0.4, part per hundred parts of
elastomer resin (phr) is used. Considerations of convenience and economy are
25 usually the principal limitations on the maximum amount of silane used in the
practice of this invention. Typically the maximum amount of silane does not
exceed 3.5, preferably it does not exceed 2.5, more preferably it does not exceed
2.0, phr. As used in "phr", "resin" means the elastomer plus any other polymer(s)
included with the elastomer during grafting. An amount of less than 0.1 wt% is
30 undesirable because it does not result in enough interaction or crosslinking of the
olefin polymer to yield an improvement in compression set. An amount in excess
of 3.5 wt% is undesirable in blends where the silane-grafted olefin polymer
constitutes the continuous phase because such blends become progressively more
difficult to process as the amount of interaction or crosslinking increases.

35
The silane is grafted to the resin (elastomer plus any other
polymer(s) included with the elastomer during grafting), by any conventional
method, typically in the presence of a free radical initiator e.g. a peroxide or an
azo compound, or by ionizing radiation, etc. Organic initiators, especially
40 peroxide initiators, are preferred. Examples of peroxide initiators include dicumyl

5 peroxide, di-tert-butyl peroxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, t-butyl perbenzoate, benzoyl peroxide, cumene hydroperoxide, t-butyl peroctoate, methyl ethyl ketone peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane, lauryl peroxide, and tert-butyl peracetate. A suitable azo
10 compound is azobisisobutyl nitrite. The amount of initiator can vary, but it is typically present in an amount of at least 0.04, preferably at least 0.06, phr. Typically the amount of initiator does not exceed 0.15, preferably it does not exceed 0.10 phr. The ratio of silane to initiator can also vary widely, but a typical silane:initiator ratio is between 10:1 and 30:1, preferably between 18:1 and 24:1.

15 While any conventional method can be used to graft the silane to the resin (elastomer plus any other polymer(s) included with the elastomer during grafting), one preferred method involves blending the resin and silane with the initiator in the first stage of a reactor extruder, such as a single screw or a twin screw extruder, preferably one with a length to diameter (L:D) ratio of 25:1 or
20 greater. The grafting conditions can vary, but the melt temperatures are typically between 160°C and 280°C, preferably between 190°C and 250°C, depending upon the residence time and the half-life of the initiator. If desired, a second functionality, such as that provided via an ethylenically unsaturated acid or acid anhydride, may be grafted onto the resin either simultaneously with the silane or
25 subsequent to silane grafting.

Any unsaturated organic compound that contains at least one ethylenic unsaturation (at least one double bond), and will graft to a SLEP can be used to modify a SLEP. Illustrative unsaturated compounds include vinyl ethers,
30 vinyl-substituted heterocyclic compounds, vinyl oxazolines, vinyl amines, vinyl epoxies, unsaturated epoxy compounds, unsaturated carboxylic acids, and anhydrides, ethers, amines, amides, succinimides or esters of such acids. Representative compounds include maleic, fumaric, acrylic, methacrylic, itaconic, crotonic, α -methyl crotonic, and cinnamic acid and their anhydride, ester or ether derivatives, vinyl-substituted alkylphenols and glycidyl methacrylates. Suitable
35 unsaturated amines include those of aliphatic and heterocyclic organic nitrogen compounds that contain at least one double bond and at least one amine group (at least one primary, secondary or tertiary amine). Representative examples include vinyl pyridine and vinyl pyrrolidone. Maleic anhydride is the preferred
40 unsaturated organic compound.

5

A crosslinking catalyst, while not needed to effect crosslinking of a silane-grafted elastomer, may be added to accelerate crosslinking. Surprisingly, the catalyst does not improve physical properties of the resulting compound. In fact, when used to excess, the catalyst actually leads to a reduction in tensile and
10 compression set properties. The reduction is determined relative to a polymer composition that is identical in every respect save for the absence of a crosslinking catalyst. The catalyst, when present, is suitably used in an amount within a range of from 0.01 to 0.1 percent by weight (wt%), based on composition weight.

15

The crosslinking catalyst is suitably selected from the group consisting of organic bases, carboxylic acids and organometallic compounds including organic titanates and complexes or carboxylates of lead, cobalt, iron, nickel, zinc and tin. Illustrative catalysts include dibutyl tin dilaurate, dioctyl tin
20 maleate, dibutyl tin diacetate, dibutyl tin dioctoate, stannous acetate, stannous octoate, lead naphthenate, zinc caprylate and cobalt naphthenate. Tin carboxylate, especially dibutyl tin dilaurate and dioctyl tin maleate, and titanium compounds, especially titanium 2-ethylhexoxide, are particularly effective for this invention. The catalyst is preferably dibutyl tin dilaurate.

25

Certain compositions of the present invention include a compatibilizing polymer (also known as a "compatibilizer"). As noted in WO96/01291 at page 12, line 26 through page 13, line 8, the relevant teachings of which are incorporated herein by reference, blends between immiscible polymers
30 have poor mechanical properties because the interactions between their components are too low. A solution involves adding another component that functions as an interfacially active material. The latter material must be designed so that each segment or functionality group is compatible in one of the major phases and incompatible in the other. An efficient compatibilizer has the same
35 affinity for each of the major phases and the capability to form a stable blend.

A variety of publications describe known compatibilizers. One such publication is a review of compatibilizing materials by C. Koning et al., Prog. Polym. Sci. Vol. 23 pgs 707-757 (1998).

40

5 For purposes of the present invention, suitable compatibilizers fall into two categories. One category includes graft polymers that are preferably prepared by grafting an unsaturated compound onto a base polymer such as a SLEP. A second category includes non-grafted polymers or interpolymers that have a polar monomer polymerized therein. The non-grafted polymers, described
10 below in greater detail, include metal salts of ethylene/carboxylic acid interpolymers.

The graft polymer compatibilizers suitably include any unsaturated organic compound that contains at least one ethylenic unsaturation (at least one
15 double bond), and will graft to a SLEP can be used to modify a SLEP. Illustrative unsaturated compounds include vinyl ethers, vinyl-substituted heterocyclic compounds, vinyl oxazolines, vinyl amines, vinyl epoxies, unsaturated epoxy compounds, unsaturated carboxylic acids, and anhydrides, ethers, amines, amides, succinimides or esters of such acids. Representative compounds include maleic,
20 fumaric, acrylic, methacrylic, itaconic, crotonic, α -methyl crotonic, and cinnamic acid and their anhydride, ester or ether derivatives, vinyl-substituted alkylphenols and glycidyl methacrylates. Suitable unsaturated amines include those of aliphatic and heterocyclic organic nitrogen compounds that contain at least one double bond and at least one amine group (at least one primary, secondary or
25 tertiary amine). Representative examples include vinyl pyridine and vinyl pyrrolidone. Maleic anhydride (MAH) is the preferred unsaturated organic compound.

Commercially available examples of graft polyolefins that may be
30 used as a compatibilizer include products available from E. I. du Pont de Nemours and Company under the tradename Fusabond®. Illustrative examples include Fusabond® MG 423D (an 8 melt index, 0.85 wt% MAH grafted ethylene/acrylate polymer), Fusabond® MC 197D (a 3 melt index, 0.8 wt% MAH grafted ethylene/vinyl acetate polymer), Fusabond® MF 274D (a 0.3 wt% MAH grafted
35 EPDM), Fusabond® MF-418D (a 27 melt index (280°C/2.18 kilogram (kg))), 0.3 wt% MAH grafted ethylene propylene rubber and Fusabond® MN 494D (a 1 melt index , 0.8 wt% MAH grafted ethylene-octene copolymer of 0.863g/cm³ density).

The unsaturated organic compound content of a grafted SLEP is \geq
40 0.01 wt%, and preferably \geq 0.05 wt%, based on the combined weight of the

5 polymer and the organic compound. The maximum unsaturated organic compound content can vary, but is typically ≤ 10 wt %, preferably ≤ 5 wt% and more preferably ≤ 2 wt%.

10 An unsaturated organic compound can be grafted to a SLEP by any known technique, such as those taught in USP 3,236,917 and USP 5,194,509, the relevant teachings of which are incorporated into and made a part of this application by reference. In USP 3,236,917, a polymer, such as an EP copolymer, is introduced into a two-roll mixer and mixed at a temperature of 60° Centigrade (°C). The unsaturated organic compound, such as maleic anhydride, is then
15 added along with a free radical initiator, such as benzoyl peroxide, and the components are mixed at a temperature sufficient to initiate grafting (e.g. 100°C) and maintained at that temperature for a time sufficient to attain a desired degree of grafting.

20 USP 5,194,509 discloses a procedure like that of USP 3,236,917, but with a higher reaction temperature (210°C to 300°C, preferably 210°C to 280°C) and either omitting or limiting free radical initiator usage. USP 5,194,509 specifically teaches that peroxide-free grafting of unsaturated carboxylic acids, anhydrides and their derivatives can be carried out in a conventional twin-screw
25 extruder, like a ZDSK 53 from Werner & Pfleiderer, or some other conventional apparatus such as a Brabender reactor. The ethylene polymer and, if required, the monomer to be grafted are melted at 140°C or higher, mixed thoroughly and then reacted at elevated temperatures (from 210°C to 300°C, preferably from 210°C to 280°C, more preferably from 210°C to 260°C). It is not important whether the
30 monomer to be grafted is introduced into the reactor before or after the ethylene polymer is melted. The monomers to be grafted are used in a concentration of 0.01-5, preferably from 0.05-2.5wt%, based on ethylene polymer weight. Although amounts in excess of five wt% can be used if desired, such an amount provides no particular advantage that offsets increased graft polymer costs.

35 An alternative and preferred method of grafting is taught in USP 4,950,541, the relevant teachings of which are incorporated herein by reference. The alternative method employs a twin-screw devolatilizing extruder as a mixing apparatus. The SLEP and unsaturated organic compound are mixed and reacted
40 within the extruder at temperatures at which the reactants are molten and in the

5 presence of a free radical initiator. The unsaturated organic compound is preferably injected into a zone that is maintained under pressure within the extruder.

10 A second, alternative and preferred method of grafting is solution grafting as taught in USP 4,810,754, the relevant teachings of which are incorporated herein by reference. The method involves mixing an initiator, a monomer to be grafted and a polymer, such as an EP polymer, in a solvent, such as mineral oil, and then reacting at a temperature sufficient to initiate the grafting reaction. One such temperature is 190°C.

15 Although graft polymers provide satisfactory results, ethylene interpolymers that have a polar monomer polymerized therein also work to an extent. The polar monomer may, for example, be an alpha-, beta-ethylenically unsaturated carboxylic acid such as methacrylic acid or acrylic acid. Metal salts
20 of such interpolymers, more commonly known as "ionomers", yield particularly satisfactory results. Ionomers are commercially available from E. I. du Pont de Nemours and Company under the tradename Surlyn®. Illustrative examples of suitable ionomers include Surlyn® 9020 (a 0.9 melt index (ASTM D-1238) zinc ionomer with a melting point of 88°C, a low acid content and a high neutralization
25 rate) and Surlyn® 9970 (a zinc ionomer with a 14 melt index (ASTM D-1238), a melting point of 93°C, a high acid content and a low neutralization rate. Other high acid, low neutralization rate ionomers include Surlyn® 8940 and Surlyn® 9950. Other low acid, high neutralization rate ionomers include Surlyn® 9520, Surlyn® 9650, Surlyn® 8527 and Surlyn® 8528.

30 USP 3,264,272 and USP 5,866,658, the relevant teachings of which are incorporated herein by reference, describe ionomers. USP 3,264,272 describes ionomers as partially neutralized alpha-olefin/alpha-, beta-ethylenically unsaturated carboxylic acid copolymers that have an acid content of 0.2 to 25
35 mole percent, based on the polymer, with at least 10 percent of the carboxylic acid being neutralized by a metal ion. See column 2, lines 7-56. Neutralization refers to a reaction between the copolymer and an ionizable metal compound. The metal in such compounds is described at column 5, lines 27-73. Illustrative metals include zinc, alkali metals such as sodium and lithium, alkaline earth metals such
40 as calcium and magnesium, and trivalent metals such as aluminum. As noted at

5 column 6, lines 11-24, the degree of neutralization for optimum properties varies with the acid concentration and copolymer molecular weight and may reach a level of as much as 90 percent.

10 Skilled artisans understand the inverse relationship between acid content and neutralization rate. In other words, a low neutralization rate means that few of the acid groups are neutralized to form a salt and corresponds to a high acid content. Conversely, a high neutralization rate means that most of the acid groups are converted to salts, thereby leaving a low acid content. In other words, it is simply a means of expressing amounts of acid and salt relative to each other.

15 For purposes of the present invention, a "high" neutralization is a neutralization level in excess of 50 percent, desirably in excess of 60 percent and preferably in excess of 70 percent. The high neutralization rate is desirably less than 95 percent and preferably less than 90 percent. Conversely, a low neutralization rate is less than 50 percent, desirably less than 35 percent and preferably less than 30 percent.

20 The low neutralization rate is greater than 5 percent and preferably greater than 10 percent.

USP 5,866,658 notes that the acid employed has an effect upon what may be considered a "high" acid content. For methacrylic acid, this is

25 preferably 15-25 wt% based on total copolymer weight. For acrylic acid, a typical "high" acid content is 14 wt% as a result of molecular weight differences between methacrylic acid and acrylic acid.

Polymer compositions of the present invention may be fabricated

30 into parts, sheets or other form using any one of a number of conventional procedures. These procedures include, for example, injection molding, blow molding and extrusion, with injection molding being preferred. The compositions can also be formed, spun or drawn into films, fibers, multi-layer laminates or extruded sheets, or can be compounded with one or more organic or inorganic

35 substances, on any machine suitable for such purposes. Fabrication may be conducted either before or after moisture curing, but is preferably conducted before moisture curing for ease of processing.

A variety of additives may be advantageously used in the

40 compositions of this invention for other purposes such as the following, any one

5 or more of which may be used: antimicrobial agents such as organometallics,
isothiazolones, organosulfurs and mercaptans; antioxidants such as phenolics (e.g.
Irganox™ 1076 antioxidant, available from Ciba-Geigy Corp.), secondary
amines, phosphites and thioesters; antistatic agents such as quaternary ammonium
10 and reinforcing agents such as glass, metal carbonates such as calcium carbonate,
metal sulfates such as calcium sulfate, talc, clays, silicas, carbon blacks, graphite
fibers and mixtures thereof; hydrolytic stabilizers; lubricants such as fatty acids,
fatty alcohols, esters, fatty amides, metallic stearates, paraffinic and
microcrystalline waxes, silicones and orthophosphoric acid esters; mold release
15 agents such as fine-particle or powdered solids, soaps, waxes, silicones,
polyglycols and complex esters such as trimethylolpropane tristearate or
pentaerythritol tetrastearate; pigments, dyes and colorants; plasticizers such as
esters of dibasic acids (or their anhydrides) with monohydric alcohols such as o-
phthalates, adipates and benzoates; oil extenders such as epoxidised soybean oil,
20 mineral oils; heat stabilizers such as organotin mercaptides, an octyl ester of
thioglycolic acid and a barium or cadmium carboxylate; ultraviolet light
stabilizers used as a hindered amine, an o-hydroxy-phenylbenzotriazole, a 2-
hydroxy,4-alkoxybenzophenone, a salicylate, a cyanoacrylate, a nickel chelate and a
benzylidene malonate and oxalanilide. Such additives, if used, typically do not
25 exceed 45 wt% of the total composition, and are advantageously in an amount of
from 0.001 to 20 wt%, preferably from 0.01 to 15 wt% and more preferably from
0.1 to 10 wt%, based on total composition weight.

Articles of manufacture that may be fabricated from the polymer
compositions of the present invention include, without limitation, those selected
30 from the group consisting of gaskets, seals, automotive weather-stripping, casters,
trolley wheels, animal tags, hoses, coated fabrics, laminated sheets, and extruded
profiles. Skilled artisans will readily appreciate other articles of manufacture that
may be fabricated from the compositions of the present invention.

35 The following examples illustrate but do not, either explicitly or by
implication, limit the present invention. Unless otherwise stated, all parts and
percentages are by weight, on a total weight basis. Arabic numbers identify
examples that illustrate the invention while letters of the alphabet designate
comparative examples.

5

Examples 1-6 and Comparative Examples A-J**Preparation of Silane Grafted Polyolefin**

10 In broad, general terms preparation involves extruding a polyolefin in the presence of a radical source such as dicumyl peroxide (DCP) or another peroxide and a vinyl hydrolyzable silane such as vinyl trimethoxy silane (VTMOS). By following a specific time and temperature profile, one obtains a polyolefin grafted with a hydrolyzable silane functionality.

15 Using a sealed mixing vessel operating at room temperature (nominally 25°C), prepare a first extrudable composition by mixing, for 30 minutes, 984 grams (g) of ethylene/1-octene (EO) copolymer (Engage® 8842, melt index (I₂) (determined at 190°C) using a 2.16 kilogram (kg) weight in accordance with ASTM D-1238) of 1.0 grams per 10 minutes (g/10 min), density
20 of 0.855 grams per cubic centimeter (g/cm³) and Shore A hardness of 50, DuPont Dow Elastomers L.L.C.), 15 g of VTMOS and one g of DCP. Vary this procedure by adding four g of maleic anhydride (MAH) to prepare a second extrudable composition consisting of a polyolefin grafted with both VTMOS and MAH. This procedure and its variation allow the polymer to efficiently absorb the
25 VTMOS or VTMOS/MAH mixture.

Convert an extrudable composition, either the first or the second, into a graft polymer using a single screw extruder that operates at 20 revolutions per minute (rpm) and has a L:D ratio of 28:1 and a compression ratio of 3:1. The
30 extruder operates at conditions sufficient to promote full peroxide decomposition (at least seven peroxide half-lives). The conditions include temperature settings, for zones 1-4 of, 160°C, 180°C, 200°C and 220°C. The extruder die is set at 220°C. Collect the resulting graft polymer for further work. The first and second extrudable compositions, when converted to graft polymers, are respectively
35 referred to as "PO-2" and "PO-6".

5 Preparation of TPU-PO Polymer Blends

In a Brabender internal mixer set at a temperature above the melting point of the TPU, add 27.5 g of polyolefin and, when used, five g of a selected compatibilizer to form a first mixture. Blend the first mixture for two minutes and then add 17.5 g of a TPU. After adding the TPU, blend the contents
10 of the mixer at a high shear rate of 75 rpm and at a set temperature of 190 °C for five minutes to form a polymer blend. Press the polymer blend into the shape of a plate for further testing. The plate measures 16 millimeters (mm) by 16 mm and has a thickness of 2 mm. When all three components are present, the respective contents are 35 wt% TPU, 55 wt% polyolefin and 10 wt% compatibilizer, all
15 percentages being based on blend weight. When only two components are present due to the omission of a compatibilizer, the respective contents are 40 wt% TPU and 60 wt% polyolefin, both percentages being based on blend weight.

The compatibilizer is either a zinc ionomer (based upon an
20 ethylene/methacrylic acid/alkyl acrylate polymer) with a 0.9 melt index, a melting point of 88°C, an acid content of 10 wt% based on ionomer weight and a neutralization rate of 73 percent (nominally a low acid content, high neutralization ionomer) (“Comp-1”) or a MAH-grafted EO polyolefin elastomer (Engage®
8200, I₂ of 5, density of 0.870 g/cm³ and a MAH graft content of 1 wt%, based on
25 graft polymer weight) (“Comp-2”). Engage is a trademark of Dupont Dow Elastomers L.L.C.

The TPU is Pellethane® 2103-80AE, a soft 82 Shore A polyether system based upon 4,4-diphenyl methane diisocyanate, 1,4-butane diol and poly
30 oxy tetramethylene glycol (“TPU-1”), Pellethane® 2102, a soft 84 Shore A polyester system based upon 4,4-diphenyl methane diisocyanate, 1,4-butane diol and polycaprolactone (“TPU-2”), an experimental TPU based upon upon
hexamethyl isocyanate, 1,4-butane diol and a di-hydroxy aliphatic polycarbonate (“TPU-3”), Pellethane® 2103-55D, a hard 55 Shore D polyether system based
35 upon 4,4-diphenyl methane diisocyanate, 1,4-butane diol and poly oxy tetramethylene glycol (“TPU-4”), or Pellethane® 2355-55DE, a hard 52 Shore D polyester system based upon 4,4-diphenyl methane diisocyanate, 1,4-butane diol and polybutyl adipate (“TPU-5”). Pellethane is a trademark of The Dow

5 Chemical Company and TPUs 1, 2, 4 and 5 are available therefrom. TPU-3 is believed to be available from Bayer AG.

10 The polyolefin is one of Engage® 8842 (an EO SLEP with an I₂ of 1.0 g/10 min and a density of 0.855 g/cm³, designated as "PO-1"); PO-2 (prepared as describe above); Nordel® IP 4770 (an ethylene/propylene/5-ethylidene-2-norbornene interpolymer with a Mooney viscosity (ML₁₊₄ at 125°C of 70 and an ethylene content of 70 wt%, based on interpolymer weight, designated as PO-3"); silane grafted (with 0.7 wt% VT MOS) Nordel IP 4770 (PO-4"). Engage and Nordel are registered trademarks of Dupont Dow Elastomers L.L.C.

15

Table I below summarizes results of three physical property tests. One test, Tensile Strength (TS) is measured in units of megapascals (MPa) according to International Standards Organization (ISO) Test 37 T2 (ISO 37 T2) at a test speed of 500 millimeters per minute (mm/min). In a second test, 20 Elongation at Break (% Elong) is measured according to ISO 37 T2. In the third test, Compression Set Percentage (% Comp Set) (22 hours at 70°C) is measured according to ISO 815. ISO 815 requires compressing a laminate formed from three 13 mm diameter, two mm thick discs by 25 %, heating the laminate in an oven at 70°C for 22 hours, removing the heated laminate from the oven, releasing 25 compression, allowing the laminate to recover at room temperature (nominally 25°C) for 30 min and then measuring laminate thickness. Spacers of known dimensions maintain the compression at 25% during testing. Compression set is expressed as a percentage of the initial compression by the formula $\frac{h_0 - h_1}{h_0 - h_s} \times 100$, where h₀ = initial laminate thickness, h₁ = laminate thickness after recovery, 30 and h_s = spacer height..

TABLE I

| Example ID | TPU | PO | COMP | TS (MPa) | % Elong | % Comp Set |
|------------|-------|------|--------|-------------|---------|---------------|
| A | TPU-3 | PO-1 | None | 2.6 | 1430 | 100 |
| B | TPU-3 | PO-1 | Comp-2 | 5.5 | 747 | 99 |
| C | TPU-3 | PO-2 | None | 4.2 | 352 | 80 |
| 1 | TPU-3 | PO-2 | Comp-2 | 8.3 | 407 | 39 |

| | | | | | | |
|---|-------|------|--------|------|------|-----|
| D | TPU-3 | PO-1 | Comp-1 | 3.6 | 1261 | 100 |
| 2 | TPU-3 | PO-2 | Comp-1 | 10.0 | 289 | 44 |
| E | TPU-1 | PO-1 | None | 2.1 | 1190 | 100 |
| F | TPU-1 | PO-1 | Comp-2 | 5.9 | 762 | 95 |
| 3 | TPU-1 | PO-2 | Comp-2 | 7.5 | 423 | 45 |
| 4 | TPU-1 | PO-2 | Comp-1 | 3.2 | 162 | 50 |
| G | TPU-3 | PO-3 | None | 1.5 | 1249 | 100 |
| H | TPU-3 | PO-3 | Comp-2 | 5.3 | 764 | 94 |
| 5 | TPU-3 | PO-4 | Comp-2 | 11.4 | 517 | 51 |
| I | TPU-2 | PO-1 | None | 1.6 | 536 | 100 |
| J | TPU-2 | PO-1 | Comp-2 | 4.1 | 588 | 100 |
| 6 | TPU-2 | PO-2 | Comp-2 | 7.1 | 284 | 47 |

5

The data in Table I illustrate several points. First, binary blends of a TPU and a polyolefin yield poor tensile strength and compression set values as evidenced by Comparative Examples A, E, G and I. Comparative Examples A, E, G and I have both tensile strength and compression set values that are below those predicted by a simple rule of mixtures. The term "rule of mixtures" means, for example, that a 50/50 (wt/wt) blend of PO-1 (tensile strength 2.5MPa) and TPU-3 (tensile strength 23MPa) would have a tensile strength of 12.75 MPa. Second, use of a compatibilizer may improve TPU-polyolefin interactions as suggested by an increase in blend tensile strength and a reduction in compression set relative to the same blend in the absence of a compatibilizer. See, e.g. Example 1 versus (Vs) Comparative Example C. The substitution of a silane-grafted polyolefin elastomer for a non-grafted polyolefin elastomer does lead to an improvement both in tensile strength and in compression set. See, e.g., Comparative Example J Vs Example 6, Comparative Example B Vs Example 1, Comparative Example D Vs Example 2, Comparative Example F Vs Examples 3 and 4, and Comparative Example H Vs Example 5. Similar results are expected with other compatibilizers and silane-grafted polyolefins that represent the present invention, all of which are disclosed herein.

25

Examples 7-8

5 Replicate the procedure of Examples 1-6 save for omitting a
 compatibilizer and using a different polyolefin that contains both silane and MAH
 graft moieties. Prepare the polyolefin for Example 7 (designated "PO-5) by
 replicating the procedure for converting the first extrudable composition into a
 graft polymer using a MAH-grafted ethylene/octene copolymer (Fusabond® MN
 10 494D, melt index of 1, MAH graft moiety content of 0.8 wt% and a density of
 0.863 g/cm³, available from E. I. du Pont de Nemours and Company) as a base
 polymer. Use PO-6 for Example 8. As with other samples where only the TPU
 and the PO are present, the relative amounts are, respectively, 40 and 60 wt%.

15 Table II summarizes physical property test results for Examples 7
 and 8. For purposes of contrast, Table II also extracts test results for Example 1
 and Comparative Examples A and C from Table I.

TABLE II

20

| Example ID | TPU | PO | Comp | TS (MPa) | % Elong | % Comp. Set |
|------------|-------|------|--------|----------|---------|-------------|
| A | TPU-3 | PO-1 | None | 2.6 | 1430 | 100 |
| C | TPU-3 | PO-2 | None | 4.2 | 352 | 80 |
| 1 | TPU-3 | PO-2 | Comp-2 | 8.3 | 407 | 39 |
| 7 | TPU-3 | PO-5 | None | 9.7 | 446 | 70 |
| 8 | TPU-3 | PO-6 | None | 6.8 | 463 | 64 |

The data in Table II demonstrate that polyolefins with both a first
 and a second graft moiety provide satisfactory results similar to those obtained
 through use of a compatibilizer. Similar results are expected with other
 25 polyolefins and first and second graft moieties, all of which are disclosed herein.

Example 9 and Comparative Examples K and L

The procedure outlined in Examples 1-6 and Comparative
 30 Examples A-J is replicated save for changing component amounts. The TPU is
 now the major component. Where there are two components, the amount of TPU
 is 68% and the amount of polyolefin is 32%. Where there are three components,
 the amounts are 63% TPU, 27% polyolefin or grafted polyolefin and 10%
 compatibilizer. Table III summarizes example composition and test data.

5

TABLE III

| Example ID | TPU | PO | COMP | TS (MPa) | % Elong | % Comp Set |
|------------|-------|------|--------|----------|---------|------------|
| K | TPU-3 | PO-1 | None | 6.3 | 502 | 55 |
| L | TPU-3 | PO-1 | Comp-2 | 12 | 568 | 45 |
| 9 | TPU-3 | PO-2 | Comp-2 | 15.2 | 528 | 39 |

The data presented in Table III conform to the data from Table I and demonstrate that satisfactory results follow even when the relative amounts of TPU and polyolefin change significantly.

When the compositions of Examples 1 and 9 are at least partially cured by immersion for five days in a 60°C water-bath, the resulting compositions retain the ability to be reprocessed as shown in Table IV below. Table IV presents viscosity data (in Pascal seconds (Pa.s)) obtained using a Rosand Capillary Rheometer equipped with a 1 mm die and operating at a temperature of 190°C at the shear rates in reciprocal seconds (s^{-1}) shown in the first column of Table IV. The viscosity data are for the waterbath treatment times (at 60°C) shown in Table IV. Example 9, following curing has a TS of 19 MPa, a % Elongation of 610 and a % Compression Set of 35. As such, the beneficial effects of the invention remain following water treatment and attendant silane curing.

5

TABLE IV

| Shear Rate (s ⁻¹) | Viscosity (Pa.s) after 1 day | Viscosity (Pa.s) after 7 days | Viscosity (Pa.s) after 15 days |
|-------------------------------|---------------------------------|----------------------------------|-----------------------------------|
| 50 | 2254 | 2951 | 2657 |
| 100 | 1429 | 1706 | 1710 |
| 200 | 871 | 1022 | 1052 |
| 500 | 501 | 591 | 608 |
| 700 | 401 | 482 | 496 |
| 1000 | 317 | 391 | 384 |
| 2000 | 193 | 218 | 226 |
| 5000 | 95 | 106 | 106 |
| 10000 | 53 | 58 | 56 |
| 15000 | 38 | 42 | 36 |

Examples 10-14 and Comparative Examples M and N

10 The procedure outlined in Examples 1-6 and Comparative Examples A-J is replicated save for varying the TPU and the polyolefin. Table V summarizes example composition and test data.

TABLE V

15

| Example ID | TPU | PO | COMP | TS (MPa) | % Elong |
|------------|-------|------|--------|-------------|---------|
| 10 | TPU-3 | PO-4 | Comp-2 | 11.4 | 517 |
| M | TPU-3 | PO-3 | None | 1.5 | 1249 |
| N | TPU-3 | PO-3 | Comp-2 | 5.3 | 764 |
| 11 | TPU-1 | PO-4 | Comp-2 | 8.5 | 330 |
| 12 | TPU-2 | PO-4 | Comp-2 | 10.0 | 421 |
| 13 | TPU-4 | PO-4 | Comp-2 | 8.0 | 150 |
| 14 | TPU-5 | PO-4 | Comp-2 | 7.0 | 150 |

5 The data in Table V demonstrate the suitability of the invention for TPUs of varying chemical structure. It also illustrates that ethylene/alpha-olefin/diene terpolymers such as EPDM may also function as the polyolefin component.

10

Example 15

Prepare blend compositions using the ratios shown in Tables VI and VII and subject them to tensile and compression set testing as described above in reference to Examples 1-6. The tensile strength (in Megapascals (MPa))
15 test results are shown in Table VI and percent compression set test results are shown in Table VII.

TABLE VI - TENSILE STRENGTH (IN MPa)

| TPU (wt%) | Blend A* (TPU-3 & PO-1) | Blend B* (TPU-3, PO-1 & Comp-2) | Blend C (TPU-3 & PO-2 & Comp-2) | Rule of Mixtures (for Blend A)** |
|-----------------|-------------------------|---------------------------------|---------------------------------|----------------------------------|
| 84 | 15.1 | 17.6 | 19 | 17.3 |
| 69 ¹ | 11.1 | 12.3 | 19.1 | 14.6 |
| 54 ² | 4.2 | 10.2 | 17.4 | 11.9 |
| 39 ³ | 3 | 7 | 13 | 9.3 |
| 24 | 2 | 6 | 6.7 | 6.7 |

20 ¹ - for Blends B and C the wt% is 68.5; ² - for Blends B and C the wt% is 55; and ³ - for Blends B and C the wt% is 39.5. * Based on 2.5 for 100% PO-1 and 20 for 100% TPU-3.

25 The data in Table VI demonstrate that blends representative of the present invention (Blend C) yield tensile strength results that exceed those of blends that lack both a silane graft moiety and a compatibilizer (Blend A) and blends that have a compatibilizer but no silane graft moiety (Blend B). Blend C test results also exceed projected rule of mixture test results in all instances save for the 24 wt% TPU containing blend where Blend C test results equal that
30 projected by the rule of mixtures.

5

TABLE VII - % COMPRESSION SET

| TPU (wt%) | Blend A* (TPU-3 & PO-1) | Blend B* (TPU-3, PO-1 & Comp-2) | Blend C (TPU-3 & PO-2 & Comp-2) |
|-----------------|-------------------------|---------------------------------|---------------------------------|
| 84 | 39 | 43 | 44 |
| 69 ¹ | 45 | 45 | 40 |
| 54 ² | 75 | 57 | 41 |
| 39 ³ | 98 | 79 | 35 |
| 24 | 100 | 96 | 38 |

¹ - for Blends B and C the wt% is 68.5; ² - for Blends B and C the wt% is 55; and ³ - for Blends B and C the wt% is 39.5. * Comparative blends (not examples of the invention).

10

The data in Table VII demonstrate that blends of the present invention (Blend C) yield compression set percentages that represent, save for the 84% TPU content blends, significant improvements over compression set percentages for blends that lack both a silane graft moiety and a compatibilizer (Blend A) and blends that lack a silane graft moiety (Blend B). Even at the 84% TPU content, the compression set percentage is satisfactory, particularly when coupled with the improved tensile strength value shown in Table VI.

15

Similar results are obtained with other TPUs, polyolefins and compatibilizers or compatibilizing functionalities, all of which are disclosed herein.

20

Example 16

25

Using the procedure of Examples 1-6, prepare a series of blends using 50 wt% TPU-3 and 50 wt% of a combination of PO-2 and, where used, Comp-2. The level of Comp-2 is varied as shown in Table VIII. Table VIII also shows Mixer Torque in Newton meters (Nm), tensile strength (TS) in MPa and percent compression set (Comp Set) (22 hours at 70°C).

30

5

TABLE VIII

| Compatibilizer Level (wt%) | Mixer Torque (Nm) | TS (MPa) | Comp Set (%) |
|----------------------------|-------------------|----------|--------------|
| 0 | 2.5 | 4 | 80 |
| 1 | 2.8 | 4.1 | 79 |
| 5 | 6.2 | 7.9 | 52 |
| 10 | 8.4 | 8.3 | 39 |
| 15 | 10.1 | 9.1 | 37 |

The data in Table VIII demonstrate the effect of increasing compatibilizer levels upon the specified physical property parameters. The effect is more dramatic over the range of 1-5 wt% than it is at levels above 5 wt%. The order of addition used to prepare the blends of the present invention does not appear to be critical. An increase in mixing intensity, in terms of mixer rpm, typically results in increased dispersion of the discontinuous phase. As long as one uses enough mixing time to prepare a generally uniform mixture or blend, no noticeable improvement follows from further increases in mixing time. Similar results are expected with other polyolefins, TPUs and compatibilizers or compatibilizing functionalities, all of which are disclosed herein.

In addition to the foregoing observations, certain blends that represent the present invention have a very low (less than or equal to 10%) haze value when formed into films having a thickness of 100 micrometers (μm). This is particularly true for TPU-3. Other TPUs yield a much higher haze value (in excess of 90%). A haze value of 10% or less means that the film is essentially transparent whereas a haze value of 90% or greater means that the film is virtually opaque or paper white. Certain of the blends have a density of less than one gram per cubic centimeter (g/cm^3) and tend to float on water whereas a pure TPU has a density in excess of one g/cm^3 and sinks when placed in water.

Examples 17-18 and Comparative Examples O-R

30

Prepare polymer blends as in Examples 1-6 and Comparative Examples A-J using the composition proportions shown in Table IX below and

5 subject test samples to German Standards Institute: the Deutsches Institut für Normung (DIN) Abrasion testing (DIN 53516) to measure volume loss in cubic millimeters (mm³). Table IX contains abrasion test results.

TABLE IX

10

| Example ID | TPU-3 (wt%) | Polyolefin Type/wt% | | Comp Type/wt% | | DIN Abrasion Volume Loss (mm ³) |
|------------|-------------|---------------------|-----|---------------|----|---|
| O | 0 | PO-1 | 100 | None | 0 | >1000 |
| P | 35 | PO-1 | 55 | None | 0 | 650 |
| Q | 35 | PO-1 | 55 | Comp-2 | 10 | 398 |
| R | 40 | PO-3 | 60 | None | 0 | 507 |
| 17 | 35 | PO-2 | 55 | Comp-2 | 10 | 134 |
| 18 | 35 | PO-4 | 55 | Comp-2 | 10 | 114 |

15 The data in Table IX demonstrate that the ternary blends of the present invention (Examples 17 and 18) provide better abrasion resistance (DIN Abrasion) than a polyolefin alone (Comparative Example O), a combination of a TPU and a polyolefin that lacks a silane graft moiety (Comparative Examples P and R) or a combination of a TPU, a polyolefin that lacks a silane graft moiety and a compatibilizer (Comparative Example Q). Similar results are expected with other blends of the present invention.

5 **WHAT IS CLAIMED IS:**

10 1. A polymer composition comprising a thermoplastic polyurethane and a first olefin graft polymer, the graft polymer including at least one first graft moiety and at least one second graft moiety, the first graft moiety being a silane moiety that promotes crosslinking of the grafted elastomer in the presence of moisture, the second graft moiety being an unsaturated organic compound that, prior to grafting, contains at least one ethylenic unsaturation and a polar functionality that promotes compatibilization of the olefin and the thermoplastic urethane.

15

20 2. A polymer composition comprising a thermoplastic polyurethane, a first olefin graft polymer, the graft polymer including at least one first graft moiety, the first graft moiety being a silane moiety that promotes crosslinking of the grafted elastomer in the presence of moisture, and a compatibilizing polymer.

20

25 3. The composition of Claim 2, wherein the compatibilizing polymer is a modified polyolefin selected from the group consisting of (a) ionomers and (b) random, block and graft olefin polymers that have, in a main or side chain thereof, a moiety that is an unsaturated organic compound that, prior to incorporation into the polymer or grafting to the polymer, contains at least one ethylenic unsaturation and a polar functionality that promotes compatibilization of the olefin and the thermoplastic urethane.

30 4. The composition of Claim 3, wherein the compatibilizing polymer is an ionomer, the ionomer being a metal salt of an ethylene/acrylic acid copolymer or a metal salt of an ethylene/methacrylic acid copolymer.

35 5. The composition of Claim 4, wherein the metal is selected from the group consisting of zinc, alkali metals, alkaline earth metals and aluminum.

35

6. The composition of Claim 5, wherein the metal is zinc.

5

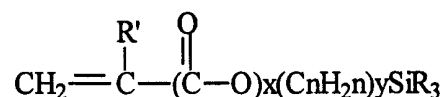
7. The composition of Claim 3, wherein the compatibilizing polymer is a second olefin graft polymer, the second graft polymer including at least one second graft moiety, the second graft moiety being the unsaturated organic compound that, prior to grafting, contains at least one ethylenic unsaturation and a polar functionality that promotes compatibilization of the olefin and the thermoplastic urethane.

8. The composition of Claim 1 or Claim 7, wherein the unsaturated organic compound is selected from the group consisting of vinyl ethers, vinyl-substituted heterocyclic compounds, vinyl oxazolines, vinyl amines, vinyl epoxies, unsaturated epoxy compounds, unsaturated carboxylic acids, and anhydrides, ethers, amines, amides, succinimides or esters of such carboxylic acids.

9. The composition of Claim 8, wherein the unsaturated organic compound is an unsaturated carboxylic acid or anhydride selected from the group consisting of maleic acid, fumaric acid, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, α -methyl crotonic acid, cinnamic acid, maleic anhydride, fumaric anhydride, acrylic anhydride, methacrylic anhydride, itaconic anhydride, crotonic anhydride, α -methyl crotonic anhydride and cinnamic anhydride.

10. The composition of Claim 9, wherein the unsaturated organic compound is maleic anhydride.

11. The composition of Claim 1 or Claim 2, wherein silane moiety is represented by the general formula:



5 in which R' is a hydrogen atom or methyl group; x and y are 0 or 1 with the
proviso that when x is 1, y is 1; n is an integer from 1 to 12 inclusive, and each R
independently is a hydrolyzable organic group selected from the group consisting
of an alkoxy group having from 1 to 12 carbon atoms, an aralkoxy group having
from 1 to 12 carbon atoms, or a lower alkyl group having 1 to 6 carbon atoms
10 inclusive, with the proviso that no more than two of the three R groups is an alkyl.

12. The composition of Claim 11, wherein the silane moiety is at least
one monomer selected from the group consisting of vinyl trimethoxy silane, vinyl
triethoxy silane, and gamma-(meth) acryloxy propyl trimethoxy silane.

15

13. The composition of Claim 1 or Claim 2, wherein the thermoplastic
polyurethane is present in an amount within a range of from 30 to 85 percent by
weight, based on total composition weight.

20 14. The composition of Claim 1 or Claim 2, wherein the first olefin
graft polymer comprises a base polymer and the first graft moiety, the base
polymer being a substantially linear ethylene polymer characterized as having:

- a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$;
- b) a molecular weight distribution, M_w/M_n , defined by the equation
25 $M_w/M_n \leq (I_{10}/I_2) - 4.63$; and
- c) a critical shear rate at onset of surface melt fracture of at least 50
percent greater than the critical shear rate at onset of surface melt fracture of a
linear olefin polymer having a similar I_2 and M_w/M_n .

30 15. The composition of Claim 14, wherein the substantially linear
ethylene polymer is further characterized as being an interpolymer of ethylene
with a C₃-C₂₀ α-olefin and, optionally, at least one diene monomer.

35 16. The composition of Claim 7, wherein the second olefin graft
polymer comprises a base polymer and the second graft moiety, the base polymer
being a substantially linear ethylene polymer characterized as having:

- 5 a) a melt flow ratio, $I_{10}/I_2 \geq 5.63$;
 b) a molecular weight distribution, M_w/M_n , defined by the equation
 $M_w/M_n \leq (I_{10}/I_2) - 4.63$; and
 c) a critical shear rate at onset of surface melt fracture of at least 50
10 percent greater than the critical shear rate at onset of surface melt fracture of a
 linear olefin polymer having a similar I_2 and M_w/M_n .

17. The composition of Claim 16, wherein the base polymer for the
 second olefin graft polymer is a substantially linear ethylene polymer further
 characterized as being an interpolymer of ethylene with a C_3 - C_{20} α -olefin and,
15 optionally, at least one diene monomer.

18. The composition of Claim 15 or Claim 17, wherein the diene
 monomer is selected from dicyclopentadiene, 1,4-hexadiene, piperylene, and 5-
 ethylidene-2-norbornene, 1,7-octadiene and vinyl norbornene.

20

19. The composition of Claim 2, wherein the compatibilizing polymer
 is present in an amount within a range of from 1 to 35 weight percent, based on
 composition weight.

20. The composition of Claim 1 or Claim 2, wherein the first olefin
 graft polymer is at least partially crosslinked through the first graft moiety.

25

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/09882

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L75/04 C08L51/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08J C08F

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

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

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
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| A | US 5 785 916 A (HUARNG ROGER JYH-CHIARNG R) 28 July 1998 (1998-07-28) column 3, line 18 - line 25; claims 1,2,13 --- | 1-3, 13, 19 |
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 00/09882

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