

**PROPYLENE-BASED POLYMER ADDITIVES FOR
IMPROVED TIRE TREAD PERFORMANCE**

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CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This invention claims priority to and the benefit of USSN 62/655,977, filed April 11, 2018 which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

10 **[0002]** The present invention relates to propylene-ethylene-diene terpolymers useful as modifiers for tire treads.

BACKGROUND OF THE INVENTION

[0003] The tire tread compound is an important compound in a tire that dictates wear, traction, and rolling resistance. It is a technical challenge to deliver excellent traction, low
15 rolling resistance while providing good tread wear. The challenge lies in the trade-off between wet traction and rolling resistance/tread wear. Raising the compound glass transition temperature (T_g) would provide better wet traction but, at the same time, increase the rolling resistance and tread wear. There are needs to develop a tread compound additive that can provide good wet traction without increasing the rolling resistance and tread wear.

20 **[0004]** Functionalized SBR (styrene butadiene rubber) is one method to improve this trade-off by improving filler dispersion. Nanoprene™, sub-micron to micron sized gels from Lanxess with cross-linked butadiene cores and acrylic shells, is another additive used to increase the wet traction without affecting rolling resistance. However, Nanoprene can only deliver limited improvement in wet traction.

25 **[0005]** Related references include U.S. Patent Nos. 8,835,563; 8,501,894; 9,527,993; and 9,273,163.

SUMMARY OF THE INVENTION

[0006] Described herein is an elastomeric composition comprising, per 100 parts by weight of rubber (phr): about 30 to about 50 phr of polybutadiene having a cis-1,4 linkage content of
30 at least 95%; about 40 to about 60 phr of styrene/butadiene copolymer; about 0 to about 20 phr of natural rubber or polyisoprene; about 0 to about 30 phr of a processing oil; about 10 to about 30 phr of a hydrocarbon resin; about 50 to about 75 phr of a filler; a curative agent; an antioxidant; a silane coupling agent; and about 5 to about 30 phr of a propylene-ethylene-diene terpolymer containing from about 2 wt% to about 30 wt% of ethylene and/or C₄-C₂₀ α-olefins

derived units.

- [0007] Also disclosed is a method of balancing the wet traction performance and rolling resistance in a tire tread comprising combining at least a filler, polybutadiene, a styrene/butadiene copolymer, natural rubber or polyisoprene, and a curative agent with one or more propylene-ethylene-diene terpolymers to form a tire tread; and effecting a cure of the components to form a tire tread; wherein the level of the propylene-ethylene-diene terpolymer(s) relative to the other components, and its comonomer content, can be varied to improve the balance of wet traction and rolling resistance of a tire tread.

DETAILED DESCRIPTION OF THE INVENTION

- 10 [0008] This invention is directed to the use of propylene-ethylene-diene terpolymers in tire tread compositions. The propylene-ethylene-diene terpolymers are prepared by polymerizing (i) propylene with (ii) at least one of ethylene and C₄-C₂₀ α -olefins and (iii) one or more dienes such as ethylidene norbornene.

- 15 [0009] The tire tread composition is an important aspect in a tire that dictates wear, traction, and rolling resistance. It is a technical challenge to deliver excellent traction and low rolling resistance while providing good tread wear. The challenge lies in the trade-off between wet traction and rolling resistance/tread wear. Typically, raising the composition's glass transition temperature (T_g) would provide good wet traction but, at the same time, increase the rolling resistance and tread wear. The embodiments described herein, on the other hand, provide a tread compound additive that can deliver superior wet traction without lowering the rolling resistance and tread wear.

[0010] The problem has been approached by developing an additive, a propylene-ethylene-diene terpolymer that increases hysteresis in the wet traction region (0°C) and lowers hysteresis in the rolling resistance region (60°C) without changing the overall compound T_g.

- 25 [0011] The additive compounding step allows one to address the known deficiencies of polyolefin blends with styrene-butadiene rubber/polybutadiene/natural rubber (SBR/PBD/NR) compositions by concentrating the carbon black and antioxidant in the polyolefin domain to improve abrasion resistance, cure state and UV stability. These deficiencies include poorly vulcanized and poorly reinforced polyolefin domains as curatives and fillers migrate away from the polyolefin due to unfavorable solubility parameter differences. The present embodiments described herein overcome one or more of these deficiencies.

Propylene-ethylene-diene terpolymer

- [0012] The "propylene-ethylene-diene terpolymer" as used herein may be any polymer

comprising propylene and other comonomers. The term “polymer” refers to any carbon-containing compound having repeat units from one or more different monomers. The term “terpolymer” as used herein refers to a polymer synthesized from three different monomers. Terpolymers, in some embodiments, may be produced (1) by mixing all three monomers at the same time or (2) by sequential introduction of the different comonomers. The mixing of comonomers may be done in one, two, or possible three different reactors in series and/or in parallel. Preferably the propylene-ethylene-diene terpolymer comprises (i) propylene-derived units, (ii) α -olefin-derived units and (iii) diene-derived units. The propylene-ethylene-diene terpolymer may be prepared by polymerizing (i) propylene with (ii) at least one of ethylene and C₄-C₂₀ α -olefins and (iii) one or more dienes.

[0013] The comonomers may be linear or branched. Preferred linear comonomers include ethylene or C₄ to C₈ α -olefins, more preferably ethylene, 1-butene, 1-hexene, and 1-octene, even more preferably ethylene or 1-butene. Preferred branched comonomers include 4-methyl-1-pentene, 3-methyl-1-pentene, and 3,5,5-trimethyl-1-hexene. In one or more embodiments, the comonomers may include styrene.

[0014] The dienes may be conjugated or non-conjugated. Preferably, the dienes are non-conjugated. Illustrative dienes may include, but are not limited to, 5-ethylidene-2-norbornene (ENB); 1,4-hexadiene; 5-methylene-2-norbornene (MNB); 1,6-octadiene; 5-methyl-1,4-hexadiene; 3,7-dimethyl-1,6-octadiene; 1,3-cyclopentadiene; 1,4-cyclohexadiene; vinyl norbornene (VNB); dicyclopentadiene (DCPD); and combinations thereof. Preferably, the diene is ENB or VNB. Preferably, the propylene-ethylene-diene terpolymer comprises an ENB content of from 0.5 wt% to 5 wt% based on the weight of the terpolymer, or from 1 wt% to 5 wt%, or from 2 wt% to 4 wt%.

[0015] The propylene-ethylene-diene terpolymer may have a propylene amount of from 65 wt% to 95 wt%, or from 70 wt% to 95 wt%, or from 75 wt% to 95 wt%, or from 80 wt% to 95 wt%, or from 83 wt% to 95 wt%, or from 84 wt% to 95 wt%, or from 84 wt% to 94 wt%, or from 75 wt% to 90 wt%, based on the weight of the polymer. The balance of the propylene-ethylene-diene terpolymer comprises at least one of ethylene and C₄-C₂₀ α -olefin and one or more dienes. The α -olefin may be ethylene, butene, hexane, or octene. When two or more α -olefins are present in the polymer, ethylene and at least one of butene, hexane, or octene are preferred.

[0016] Preferably, the propylene-ethylene-diene terpolymer comprises an ethylene content of from 5 wt% to 25 wt% based on the weight of the terpolymer, or from 7.5 wt% to 22.5 wt%.

[0017] Preferably, the propylene-ethylene-diene terpolymer comprises from 2 to 30 wt% of C₂ and/or C₄-C₂₀ α -olefins based the weight of the propylene-ethylene-diene terpolymer. When two or more of ethylene and C₄-C₂₀ α -olefins are present the combined amounts of these olefins in the polymer is preferably at least 2 wt% and falling within the ranges described
5 herein. Other preferred ranges of the amount of ethylene and/or one or more α -olefins include from 2 wt% to 25 wt%.

[0018] Preferably, the propylene-ethylene-diene terpolymer comprises a diene content of from 0.2 wt% to 20 wt% based on the weight of the polymer. In one or more embodiments, the propylene-ethylene-diene terpolymer may comprise 5-ethylidene-2-norbornene in an
10 amount of from 0.2 wt% to 20wt%.

[0019] The propylene-ethylene-diene terpolymer may have a melt flow rate (MFR, 2.16 kg weight at 230°C), equal to or greater than 0.2 g/10min as measured according to the ASTM D-1238-13. Preferably, the MFR (2.16 kg at 230°C) is from 0.2 g/10min to 200 g/10min, or from 0.2 g/10min to 30 g/10min, or from 0.2 g/10min to 10 g/10min.

15 [0020] The propylene-ethylene-diene terpolymer may have a heat of fusion (H_f) determined by the DSC procedure described herein, which is greater than or equal to 0 Joules per gram (J/g) and is equal to or less than 80 J/g.

[0021] The crystallinity of the propylene-ethylene-diene terpolymer may be expressed in terms of percentage of crystallinity (i.e., %crystallinity), as determined according to the DSC
20 procedure described herein. The propylene-ethylene-diene terpolymer may have a %crystallinity of from 0% to 40%.

[0022] The propylene-ethylene-diene terpolymer preferably may have a single broad melting transition. However, the propylene-ethylene-diene terpolymer may show secondary melting peaks adjacent to the principal peak, but for purposes herein, such secondary melting
25 peaks are considered together as a single melting point, with the highest of these peaks (relative to baseline as described herein) being considered as the melting point of the propylene-ethylene-diene terpolymer.

[0023] The propylene-ethylene-diene terpolymer may have a melting point, as measured by the DSC procedure described herein, of equal to or less than 100°C.

30 [0024] The Differential Scanning Calorimetry (DSC) procedure may be used to determine heat of fusion and melting temperature of the propylene-ethylene-diene terpolymer. The method is as follows: approximately 6 mg of material placed in microliter aluminum sample pan. The sample is placed in a Differential Scanning Calorimeter (Perkin Elmer Pyris 1

Thermal Analysis System) and is cooled to -80°C. The sample is heated at 10°C/min to attain a final temperature of 120°C. The sample is cycled twice. The thermal output, recorded as the area under the melting peak of the sample, is a measure of the heat of fusion and may be expressed in Joules per gram of polymer and is automatically calculated by the Perkin Elmer System. The melting point is recorded as the temperature of the greatest heat absorption within the range of melting of the sample relative to a baseline measurement for the increasing heat capacity of the polymer as a function of temperature.

[0025] The propylene-ethylene-diene terpolymer may be a blend of discrete random propylene-ethylene-diene terpolymers as long as the polymer blend has the properties of the propylene-ethylene-diene terpolymer as described herein. The number of propylene-ethylene-diene terpolymers may be three or less, or two or less. In one or more embodiments, the propylene-ethylene-diene terpolymer may include a blend of two propylene-ethylene-diene terpolymers differing in the olefin content, the diene content, or the both. Preparation of such polymer blend may be found in U.S. Publication Nos. 2004/0024146 and 2006/0183861.

[0026] The inventive compositions may include the propylene-ethylene-diene terpolymer in an amount of from 5 phr to 40 phr, or from 5 phr to 25 phr, or from 10 phr to 20 phr.

Elastomers

[0027] The inventive tire tread compositions also comprise an elastomer. Generally the range of the elastomer is from 5 to 75% by weight of the tire tread composition. Suitable elastomers include, for example, diene elastomers.

[0028] “Diene elastomer” is understood to mean, in known manner, an elastomer resulting at least in part (homopolymer or copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not).

[0029] A diene elastomer can be “highly unsaturated,” resulting from conjugated diene monomers, which have a greater than 50% molar content of units.

[0030] According to one aspect, each diene elastomer having a Tg from -75°C to 0°C is selected from the group consisting of styrene-butadiene copolymers, natural polyisoprenes, synthetic polyisoprenes having a cis-1,4 linkage content greater than 95%, styrene/butadiene/isoprene terpolymers and a mixture of these elastomers, and each diene elastomer having a Tg from -110°C to -75°C, preferably from -100°C to -80°C, is selected from the group consisting of polybutadienes having a cis-1,4 linkage content greater than 90% and isoprene/butadiene copolymers comprising butadiene units in an amount equal to or greater than 50%.

- [0031] In another aspect, each diene elastomer having a Tg from -75°C to -40°C is selected from the group consisting of natural polyisoprenes and synthetic polyisoprenes having a cis-1,4 linkage content greater than 95%, and each diene elastomer having a Tg from -110°C to -75°C is a polybutadiene having a cis-1,4 linkage content greater than 90%, or greater than 95%.
- 5 [0032] In one embodiment, the composition comprises a blend of the diene elastomer(s) having a Tg from -75°C to 0°C and each of the diene elastomer(s) having a Tg from -110°C to -75°C.
- [0033] In one aspect, the composition comprises a blend of at least one of the polybutadienes having a cis-1,4 linkage content greater than 90% with at least one of the natural
10 or synthetic polyisoprenes (having a cis-1,4 linkage content greater than 95%).
- [0034] In another aspect, the composition comprises a blend of at least one of the polybutadienes having a cis-1,4 linkage content greater than 90% with at least one of the terpolymers of styrene, isoprene and butadiene.
- [0035] These diene elastomers can be classified into two categories: “essentially
15 unsaturated” or “essentially saturated”. The term “essentially unsaturated” is understood to mean generally a diene elastomer resulting at least in part from conjugated diene monomers having a level of units of diene origin (conjugated dienes) which is greater than 15% (mol %); thus it is that diene elastomers such as butyl rubbers or copolymers of dienes and of alpha-olefins of EPDM type do not come within the preceding definition and can in particular
20 be described as “essentially saturated” diene elastomers (low or very low level of units of diene origin, always less than 15%). In the category of “essentially unsaturated” diene elastomers, the term “highly unsaturated” diene elastomer is understood to mean in particular a diene elastomer having a level of units of diene origin (conjugated dienes) which is greater than 50%.
- [0036] Given these definitions, the term diene elastomer capable of being used herein is
25 understood more particularly to mean: (a) any homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms; (b) any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic compounds having from 8 to 20 carbon atoms; (c) a ternary copolymer obtained by copolymerization of ethylene and of an alpha-olefin having 3 to 6 carbon atoms with a non-
30 conjugated diene monomer having from 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene and propylene with a non-conjugated diene monomer of the abovementioned type, such as, in particular, 1,4-hexadiene, ethylidenenorbornene or dicyclopentadiene; (d) a copolymer of isobutene and of isoprene (butyl rubber) and also the

halogenated versions, in particular chlorinated or brominated versions, of this type of copolymer.

[0037] The following are suitable in particular as conjugated dienes: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C₁-C₅ alkyl)-1,3-butenes, such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene or 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene or 2,4-hexadiene. The following, for example, are suitable as vinylaromatic compounds: styrene, ortho-, meta- or para-methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene or vinylnaphthalene.

[0038] The copolymers can comprise from 99% to 20% by weight of diene units and from 1% to 80% by weight of vinylaromatic units. The elastomers can have any microstructure which depends on the polymerization conditions used, in particular on the presence or absence of a modifying and/or randomizing agent and on the amounts of modifying and/or randomizing agent employed. The elastomers can, for example, be block, random, sequential or microsequential elastomers and can be prepared in dispersion or in solution; they can be coupled and/or star-branched or also functionalized with a coupling and/or star-branching or functionalization agent. Mention may be made, for coupling to carbon black, for example, of functional groups comprising a C--Sn bond or aminated functional groups, such as benzophenone, for example; mention may be made, for coupling to a reinforcing inorganic filler, such as silica, of, for example, silanol or polysiloxane functional groups having a silanol ends, alkoxysilane groups, carboxyl groups, or polyether groups.

[0039] The following are suitable: polybutadienes, in particular those having a content (molar %) of 1,2-units of from 4% to 80% or those having a content (molar %) of cis-1,4-units of greater than 80%, polyisoprenes, butadiene/styrene copolymers and in particular those having a T_g (glass transition temperature, measured according to Standard ASTM D3418-15) of from 0°C to -70°C and more particularly from -10°C to -60°C, a styrene content of from 5% to 60% by weight and more particularly from 20% to 50%, a content (molar %) of 1,2-bonds of the butadiene part of from 4% to 75% and a content (molar %) of trans-1,4-bonds of from 10% to 80%, butadiene/isoprene copolymers, in particular those having an isoprene content of from 5% to 90% by weight and a T_g of -40°C to -80°C, or isoprene/styrene copolymers, in particular those having a styrene content of from 5% to 50% by weight and a T_g of from -25°C to -50°C. In the case of butadiene/styrene/isoprene copolymers, those having a styrene content of from 5% to 50% by weight and more particularly of from 10% to 40%, an isoprene content

of from 15% to 60% by weight and more particularly from 20% to 50%, a butadiene content of from 5% to 50% by weight and more particularly of from 20% to 40%, a content (molar %) of 1,2-units of the butadiene part of from 4% to 85%, a content (molar %) of trans-1,4-units of the butadiene part of from 6% to 80%, a content (molar %) of 1,2- plus 3,4-units of the isoprene part of from 5% to 70% and a content (molar %) of trans-1,4-units of the isoprene part of from 10% to 50%, and more generally any butadiene/styrene/isoprene copolymer having a Tg of from 0°C to -70°C, are suitable in particular.

[0040] The diene elastomer chosen from the group of the highly unsaturated diene elastomers consisting of polybutadienes (abbreviated to “BR”), synthetic polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more preferably chosen from the group consisting of butadiene/styrene copolymers (SBR), isoprene/butadiene copolymers (BIR), isoprene/styrene copolymers (SIR) and isoprene/butadiene/styrene copolymers (SBIR).

[0041] According to a specific embodiment, the diene elastomer is predominantly (i.e., for more than 50 wt%) an SBR, whether an SBR prepared in emulsion (“ESBR”) or an SBR prepared in solution (“SSBR”), or an SBR/BR, SBR/NR (or SBR/IR), BR/NR (or BR/IR) or also SBR/BR/NR (or SBR/BR/IR) blend (mixture). In the case of an SBR (ESBR or SSBR) elastomer, use is made in particular of an SBR having a moderate styrene content, for example of from 20% to 35% by weight, or a high styrene content, for example from 35 to 45%, a content of vinyl bonds of the butadiene part of from 15% to 70%, a content (molar %) of trans-1,4-bonds of from 15% to 75% and a Tg of from -10°C to -55°C; such an SBR can advantageously be used as a mixture with a BR preferably having more than 90% (molar %) of cis-1,4-bonds.

[0042] The term “isoprene elastomer” is understood to mean, in a known way, an isoprene homopolymer or copolymer, in other words a diene elastomer chosen from the group consisting of natural rubber (NR), synthetic polyisoprenes (IR), the various copolymers of isoprene and the mixtures of these elastomers. Mention will in particular be made, among isoprene copolymers, of isobutene/isoprene copolymers (butyl rubber IM), isoprene/styrene copolymers (SIR), isoprene/butadiene copolymers (BIR) or isoprene/butadiene/styrene copolymers (SBIR). This isoprene elastomer is preferably natural rubber or a synthetic cis-1,4-polyisoprene; use is preferably made, among these synthetic polyisoprenes, of the polyisoprenes having a level (molar %) of cis-1,4-bonds of greater than 90%, more preferably still of greater than 98%.

[0043] According to still another aspect, the rubber composition comprises a blend of a (one or more) "high Tg" diene elastomer exhibiting a Tg of from -70°C to 0°C and of a (one or more) "low Tg" diene elastomer exhibiting a Tg of from -110°C to -80°C, more preferably from -100°C to -90°C. The high Tg elastomer is preferably chosen from the group consisting of S-SBRs, E-SBRs, natural rubber, synthetic polyisoprenes (exhibiting a level (molar %) of cis-1,4-structures preferably of greater than 95%), BIRs, SIRs, SBIRs and the mixtures of these elastomers. The low Tg elastomer preferably comprises butadiene units according to a level (molar %) at least equal to 70%; it preferably consists of a polybutadiene (BR) exhibiting a level (molar %) of cis-1,4-structures of greater than 90%.

10 [0044] According to another embodiment of the invention, the rubber composition comprises, for example, from 40 to 70 phr (parts by weight per hundred parts of total elastomer) of a high Tg elastomer as a blend with 30 to 50 phr, of a low Tg elastomer; according to another example, it comprises, for the whole of the 100 phr, one or more SBR(s) prepared in solution.

[0045] According to another embodiment of the invention, the diene elastomer of the composition according to the invention comprises a blend of a BR (as low Tg elastomer) exhibiting a level (molar %) of cis-1,4-structures of greater than 90% with one or more S-SBRs or E-SBRs (as high Tg elastomer(s)).

[0046] The compositions described herein can comprise a single diene elastomer or a mixture of several diene elastomers, it being possible for the diene elastomer or elastomers to be used in combination with any type of synthetic elastomer other than a diene elastomer, indeed even with polymers other than elastomers, for example thermoplastic polymers.

[0047] Useful tire tread compositions can also comprise 15 to 70 wt% of a styrenic copolymer; 0 or 70 wt% of a polybutadiene polymer; 0 to 70 wt% of natural rubber or synthetic polyisoprene; 15 to 70 wt% of a functionalized styrenic copolymer; 0 or 70 wt% of a functionalized polybutadiene polymer; 0 or 70 wt% of natural rubber or functionalized synthetic polyisoprene; 0 or 40 wt% of processing oil; 20 wt% to 60 wt% of filler, especially silica-based filler as described herein; a curative agent; and 5 wt% to 20 wt% of a propylene-ethylene-diene terpolymer described herein, and 0 or 5 wt% to 40 wt% of a hydrocarbon resin, the weight percentages based on the total composition.

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Inorganic Filler

[0048] The term “filler” as used herein refers to any material that is used to reinforce or modify physical properties, impart certain processing properties, or reduce cost of an elastomeric composition.

- 5 [0049] Examples of preferred filler include, but are not limited to, calcium carbonate, clay, mica, silica, silicates, talc, titanium dioxide, alumina, zinc oxide, starch, wood flour, carbon black, or mixtures thereof. The fillers may be any size and range, for example in the tire industry, from 0.0001 μm to 100 μm .

- 10 [0050] As used herein, the term “silica” is meant to refer to any type or particle size silica or another silicic acid derivative, or silicic acid, processed by solution, pyrogenic, or the like methods, including untreated, precipitated silica, crystalline silica, colloidal silica, aluminum or calcium silicates, fumed silica, and the like. Precipitated silica can be conventional silica, semi-highly dispersible silica, or highly dispersible silica. A preferred filler is commercially available by Rhodia Company under the trade name ZEOSIL™ Z1165.

- 15 [0051] Use may be made of any type of reinforcing filler known for its capabilities of reinforcing a rubber composition which can be used for the manufacture of tires, for example an organic filler, such as carbon black, a reinforcing inorganic filler, such as silica, or a blend of these two types of filler, in particular a blend of carbon black and silica.

- 20 [0052] All carbon blacks, in particular blacks of the HAF, ISAF or SAF type, conventionally used in tires (“tire-grade” blacks) are suitable as carbon blacks. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series (ASTM grades), such as, for example, the N115, N134, N234, N326, N330, N339, N347 or N375 blacks, or also, depending on the applications targeted, the blacks of higher series (for example, N660, N683 or N772). The carbon blacks might, for example, be already
25 incorporated in the isoprene elastomer in the form of a masterbatch (see, for example, International Applications WO 97/36724 and WO 99/16600).

- [0053] The term “reinforcing inorganic filler” should be understood, in the present patent application, by definition, as meaning any inorganic or mineral filler, whatever its color and its origin (natural or synthetic), also known as “white filler”, “clear filler” or even “non-black
30 filler”, in contrast to carbon black, capable of reinforcing by itself alone, without means other than an intermediate coupling agent, a rubber composition intended for the manufacture of tires, in other words capable of replacing, in its reinforcing role, a conventional tire-grade

carbon black; such a filler is generally characterized, in a known way, by the presence of hydroxyl (—OH) groups at its surface.

[0054] The physical state under which the reinforcing inorganic filler is provided is not important, whether it is in the form of a powder, of microbeads, of granules, of beads or any other appropriate densified form. Of course, the term reinforcing inorganic filler is also understood to mean mixtures of different reinforcing inorganic fillers, in particular of highly dispersible siliceous and/or aluminous fillers as described below.

[0055] Mineral fillers of the siliceous type, in particular silica (SiO₂), or of the aluminous type, in particular alumina (Al₂O₃), are suitable in particular as reinforcing inorganic fillers. The silica used can be any reinforcing silica known to a person skilled in the art, in particular any precipitated or pyrogenic silica exhibiting a BET surface and a CTAB specific surface both of less than 450 m²/g, preferably from 30 to 400 m²/g. Mention will be made, as highly dispersible (“HDS”) precipitated silicas, for example, of the ULTRASIL™ 7000 and ULTRASIL™ 7005 silicas from Degussa, the ZEOSIL™ 1165 MP, C5 MP and 1115 MP silicas from Rhodia, the HI-SIL™ EZ150G silica from PPG, the Zeopol 8715, 8745 and 8755 silicas from Huber or silicas with a high specific surface.

[0056] Mention may also be made, as other examples of inorganic filler being capable of being used, of reinforcing aluminum (oxide), hydroxides, titanium oxides or silicon carbides (see, for example, International Applications WO 02/053634 and US 2004/0030017).

[0057] When the compositions of the invention are intended for tire treads with a low rolling resistance, the reinforcing inorganic filler used, in particular if it is silica, preferably has a BET surface of from 45 to 400 m²/g, more preferably of from 60 to 300 m²/g.

[0058] Preferably, the level of total reinforcing filler (carbon black and/or reinforcing inorganic filler) is from 20 to 200 phr, more preferably from 30 to 150 phr, the optimum being in a known way different depending on the specific applications targeted: the level of the reinforcement expected with regard to a bicycle tire, for example, is, of course, less than that required with regard to a tire capable of running at high speed in a sustained manner, for example, a motor cycle tire, a tire for a passenger vehicle or a tire for a commercial vehicle, such as a heavy duty vehicle.

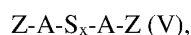
30 Coupling Agent

[0059] As used herein, the term “coupling agent” is meant to refer to any agent capable of facilitating stable chemical and/or physical interaction between two otherwise non-interacting species, e.g., between a filler and a diene elastomer. Coupling agents cause silica to have a

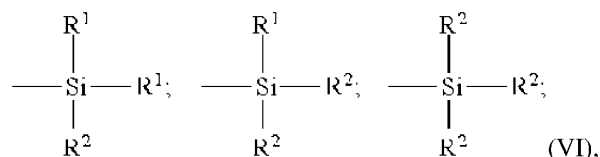
reinforcing effect on the rubber. Such coupling agents may be pre-mixed, or pre-reacted, with the silica particles or added to the rubber mix during the rubber/silica processing, or mixing, stage. If the coupling agent and silica are added separately to the rubber mix during the rubber/silica mixing, or processing stage, it is considered that the coupling agent then combines
 5 in situ with the silica.

[0060] The coupling agent may be a sulfur-based coupling agent, an organic peroxide-based coupling agent, an inorganic coupling agent, a polyamine coupling agent, a resin coupling agent, a sulfur compound-based coupling agent, oxime-nitrosamine-based coupling agent, and sulfur. Among these, preferred for a rubber composition for tires is the sulfur-based
 10 coupling agent.

[0061] In an embodiment, the coupling agent is at least bifunctional. Non-limiting examples of bifunctional coupling agents include organosilanes or polyorganosiloxanes. Other examples of suitable coupling agents include silane polysulfides, referred to as “symmetrical” or “unsymmetrical” depending on their specific structure. Silane polysulphides can be
 15 described by the formula (V):



in which x is an integer from 2 to 8 (preferably from 2 to 5); the A symbols, which are identical or different, represent a divalent hydrocarbon radical (preferably a C₁-C₁₈ alkylene group or a C₆-C₁₂ arylene group, more particularly a C₁-C₁₀, in particular C₁-C₄, alkylene, especially
 20 propylene); the Z symbols, which are identical or different, correspond to one of the three formulae (VI):



in which the R¹ radicals, which are substituted or unsubstituted and identical to or different from one another, represent a C₁-C₁₈ alkyl, C₅-C₁₈ cycloalkyl or C₆-C₁₈ aryl group (preferably
 25 C₁-C₆ alkyl, cyclohexyl or phenyl groups, in particular C₁-C₄ alkyl groups, more particularly methyl and/or ethyl); the R² radicals, which are substituted or unsubstituted and identical to or different from one another, represent a C₁-C₁₈ alkoxy or C₅-C₁₈ cycloalkoxy group (preferably a group selected from C₁-C₈ alkoxy and C₅-C₈ cycloalkoxy, more preferably still a group selected from C₁-C₄ alkoxy, in particular methoxy and ethoxy).

[0062] Non-limiting examples of silane polysulphides include bis((C₁-C₄)alkoxy(C₁-C₄)alkyl)silyl(C₁-C₄)alkyl polysulphides (in particular disulphides, trisulphides or
 30 - 12 -

tetrasulphides), such as, for example, bis(3-trimethoxysilylpropyl) or bis(3-triethoxysilylpropyl)polysulphides. Further examples include bis(3-triethoxysilylpropyl)tetrasulphide, abbreviated to TESPT, of formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, or bis(triethoxysilylpropyl)disulphide, abbreviated to TESP, of formula $[(C_2H_5O)_3Si(CH_2)_3S]_2$. Other examples include bis(mono(C₁-C₄)alkoxydi(C₁-C₄)alkylsilylpropyl)polysulphides (in particular disulphides, trisulphides or tetrasulphides), more particularly bis(monoethoxydimethylsilylpropyl)tetrasulphide.

[0063] The coupling agent can also be bifunctional POSs (polyorganosiloxanes), or hydroxysilane polysulphides, or silanes or POSs bearing azodicarbonyl functional groups. The coupling agent can also include other silane sulphides, for example, silanes having at least one thiol (—SH) functional group (referred to as mercaptosilanes) and/or at least one masked thiol functional group.

[0064] The coupling agent can also include combinations of one or more coupling agents such as those described herein, or otherwise known in the art. A preferred coupling agent comprises alkoxysilane or polysulphurized alkoxysilane. A particularly preferred polysulphurized alkoxysilane is bis(triethoxysilylpropyl) tetrasulphide, which is commercially available by Degussa under the trade name X50STM.

Plasticizer

[0065] As used herein, the term “plasticizer” (also referred to as a processing oil), refers to a petroleum derived processing oil and synthetic plasticizer. Such oils are primarily used to improve the processability of the composition. Suitable plasticizers include, but are not limited to, aliphatic acid esters or hydrocarbon plasticizer oils such as paraffinic oils, aromatic oils, naphthenic petroleum oils, and polybutene oils. A particularly preferred plasticizer is naphthenic oil, which is commercially available by Nynas under the trade name NYTEXTM 4700.

[0066] MES and TDAE oils are well known to a person skilled in the art; for example, reference is made to publication KGK (Kautschuk Gummi Kunststoffe), 52nd year, No. 12/99, pp. 799-805, entitled “Safe Process Oils for Tires with Low Environmental Impact”.

[0067] Mention may be made, as examples of MES oils (whether they are of the “extracted” or “hydrotreated” type) or of TDAE oils, for example, of the products sold under the names FLEXONTM 683 by ExxonMobil, VIVATECTM 200 or VIVATECTM 500 by H&R European, PLAXOLENETM MS by Total, or CATENEXTM SNR by Shell.

[0068] Other suitable plasticizers for use in the present invention include “triesters” or “fatty acids”. Triester and fatty acid generally refer to a mixture of triesters or a mixture of fatty acids, respectively. The fatty acid preferably consists of more than 50%, more preferably to more than 80% by weight of an unsaturated C18 fatty acid, that is to say one selected from
5 among the group consisting of oleic acid, linoleic acid, linolenic acid and mixtures thereof. More preferably, be it synthetic or natural in origin, the fatty acid used is constituted to more than 50% by weight, more preferably still to more than 80% by weight, of oleic acid.

[0069] In other words, very particularly a glycerol trioleate, derived from oleic acid and glycerol, is used. Among the preferred glycerol trioleates, mention will be made in particular,
10 as examples of natural compounds, of the vegetable oils sunflower oil or rapeseed oil having a high content of oleic acid (more than 50%, more preferably more than 80% by weight).

[0070] The glycerol trimester is used in a preferred amount of between 5 and 80 phr, more preferably of between 10 and 50 phr, in particular within a range from 15 to 30 phr, in particular when the tread of the invention is intended for a passenger-type vehicle. In the light of the
15 present description, the person skilled in the art will be able to adjust this amount of ester as a function of the specific conditions of embodiment of the invention, in particular the amount of inorganic filler used.

[0071] The resins (it should be remembered that the term “resin” is reserved by definition for a solid compound) formed of C₅ fraction/vinylaromatic copolymer, in particular of C₅
20 fraction/styrene or C₅ fraction/C₉ fraction copolymer, are well known; they have been essentially used to date for application as tackifying agents for adhesives and paints but also as processing aids in tire rubber compositions.

[0072] The C₅ fraction/vinylaromatic copolymer is, by definition and in a known way, a copolymer of a vinylaromatic monomer and of a C₅ fraction.

25 [0073] Styrene, alpha-methylstyrene, ortho-, meta- or para-methylstyrene, vinyltoluene, para-(tert-butyl)styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene, vinylnaphthalene and any vinylaromatic monomer resulting from a C₉ fraction (or more generally from a C₈ to C₁₀ fraction), for example, are suitable as vinylaromatic monomers. Preferably, the vinylaromatic compound is styrene or a vinylaromatic monomer resulting from
30 a C₉ fraction (or more generally from a C₈ to C₁₀ fraction).

[0074] In a known way, the term C₅ fraction (or, for example, C₉ fraction respectively) is understood to mean any fraction resulting from a process resulting from petrochemistry or from the refining of petroleums, any distillation fraction predominantly comprising compounds

having 5 (or respectively 9, in the case of a C₉ fraction) carbon atoms; the C₅ fractions, for example, may comprise, by way of illustration and without limitation, the following compounds, the relative proportions of which may vary according to the process by which they are obtained, for example according to the origin of the naphtha and the steam cracking process:

5 1,3-butadiene, 1-butene, 2-butenes, 1,2-butadiene, 3-methyl-1-butene, 1,4-pentadiene, 1-pentene, 2-methyl-1-butene, 2-pentenenes, isoprene, cyclopentadiene, which can be present in the form of its dicyclopentadiene dimer, piperylenes, cyclopentene, 1-methylcyclopentene, 1-hexene, methylcyclopentadiene or cyclohexene. These fractions may be obtained by any chemical process known in the petroleum industry and petrochemistry. Mention may be made,

10 as non-limiting examples, of processes for the steam cracking of naphtha or processes for the fluid catalytic cracking of gasolines, it being possible for these processes to be combined with any possible chemical treatment for the conversion of these fractions known to a person skilled in the art, such as hydrogenation and dehydrogenation.

[0075] The plasticizing hydrocarbon resins useful in an embodiment of the invention

15 include those that are homopolymers or copolymers of cyclopentadiene (CPD) or dicyclopentadiene (DCPD), homopolymers or copolymers of terpene, homopolymers or copolymers of C₅ cut and mixtures thereof.

[0076] Such copolymer plasticizing hydrocarbon resins as discussed generally above may include, for example, resins made up of copolymers of (D)CPD/vinyl-aromatic, of

20 (D)CPD/terpene, of (D)CPD/C₅ cut, of terpene/vinyl-aromatic, of C₅ cut/vinyl-aromatic and of combinations thereof.

[0077] Terpene monomers useful for the terpene homopolymer and copolymer resins include alpha-pinene, beta-pinene and limonene. Particular embodiments include polymers of the limonene monomers that include three isomers: the L-limonene (laevorotatory enantiomer),

25 the D-limonene (dextrorotatory enantiomer), or even the dipentene, a racemic mixture of the dextrorotatory and laevorotatory enantiomers.

[0078] Examples of vinyl aromatic monomers include styrene, alpha-methylstyrene, ortho, meta-, para-methylstyrene, vinyl-toluene, para-tertiobutylstyrene, methoxystyrenes, chloro-styrenes, vinyl-mesitylene, divinylbenzene, vinylnaphthalene, any vinyl-aromatic monomer

30 coming from the C₉ cut (or, more generally, from a C₈ to C₁₀ cut). Particular embodiments that include a vinyl-aromatic copolymer include the vinyl-aromatic in the minority monomer, expressed in molar fraction, in the copolymer.

[0079] Particular embodiments of the present invention include as the plasticizing hydrocarbon resin the (D)CPD homopolymer resins, the (D)CPD/styrene copolymer resins, the polylimonene resins, the limonene/styrene copolymer resins, the limonene/D(CPD) copolymer resins, C₅ cut/styrene copolymer resins, C₅ cut/C₉ cut copolymer resins, and mixtures thereof.

5 Antioxidant

[0080] As used herein, the term “antioxidant” refers to a chemical that combats oxidative degradation. Suitable antioxidants include diphenyl-p-phenylenediamine and those disclosed in *The Vanderbilt Rubber Handbook* (1978), Pages 344 to 346. A particularly preferred antioxidant is para-phenylenediamines, which is commercially available by Eastman under the
10 trade name SANTOFLEX™ 6PPD (N-(1,3-Dimethylbutyl)-N'-phenyl-1,4-phenylenediamine).

Crosslinking Agents, Curatives, Cure Packages, and Curing Processes

[0081] The elastomeric compositions and the articles made from those compositions are generally manufactured with the aid of at least one cure package, at least one curative, at least
15 one crosslinking agent, and/or undergo a process to cure the elastomeric composition. As used herein, at least one curative package refers to any material or method capable of imparting cured properties to a rubber as is commonly understood in the industry. A preferred agent is sulfur.

Processing

20 [0082] These compounds were mixed in suitable mixers, using at least two successive passes well known to the person skilled in the art. The non-productive passes (mixing without crosslinking system) which have mixing at high temperatures between 110°C and 190°C. The non-productive passes are followed by a productive pass where the crosslinking system is added. The temperature for this mixing is typically below 110°C.

25 [0083] The tire tread composition has many desirable properties when the propylene-ethylene-diene terpolymer is present in the compositions. Also, the maximum Energy Loss (Tangent Delta, wherein the slope is zero) of the immiscible polyolefin domain of the cured composition is preferably a temperature within the range from -30 to 10°C. Finally, domains comprising the compatibilizer in the polymer matrix of the other components have sizes that
30 are preferred to be less than 20 microns, more preferably less than 10 microns, and most preferably less than 5 microns; or within a range of from 0.1 or 0.2 or 0.5 or 1.0 microns to 5 or 10 or 20 microns.

[0084] The various descriptive elements and numerical ranges disclosed herein for the propylene-ethylene-diene terpolymers, the reactants used to make the propylene-ethylene-diene terpolymers, and their use in tire tread compositions can be combined with other descriptive elements and numerical ranges to describe the invention(s); further, for a given element, any upper numerical limit can be combined with any lower numerical limit described herein. The features of the invention are described in the following non-limiting examples.

EXAMPLES

[0085] Two propylene-ethylene-diene terpolymer (PEDM) additives (Table 1) were used in tire tread formulations of the following examples.

Preparation of amorphous propylene-based copolymers (PEDMs 1 and 2)

[0086] Catalyst system: Catalyst precursor was bis((4-triethylsilyl)phenyl)methylene(cyclopentadienyl)(2,7-di-tert-butyl-fluoren-9-yl) hafnium dimethyl. However, other metallocene precursors with good diene incorporation and MW capabilities could also be used.

[0087] The activator was dimethylanilinium tetrakis(pentafluorophenyl)borate, but dimethylanilinium-tetrakis(heptafluoronaphthyl)borate and other non-coordinating anion type activators or MAO could also be used.

[0088] Copolymer compositions as described above were synthesized as follows. The copolymer compositions were synthesized in a single continuous stirred tank reactor. A mixture containing unreacted monomers and solvent was fed to the reactor as fuel for a polymerization reaction. The polymerization was performed in solution using isohexane as solvent. During the polymerization process, hydrogen addition and temperature control were used to achieve the desired melt flow rate. The catalyst, activated externally to the reactor, was added as needed in amounts effective to maintain the target polymerization temperature. In the reactor, the copolymer material was produced in the presence of ethylene, propylene, ethylidene norbornene, and a catalyst comprising the reaction product of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate and [cyclopentadienyl(2,7-di-tert-butylfluorenyl)di-p-triethylsilanephénylmethane] hafnium dimethyl.

[0089] The copolymer solution emerging from the reactor was quenched and then devolatilized using conventionally known devolatilization methods, such as flashing or liquid phase separation, first by removing the bulk of the isohexane to provide a concentrated solution, and then by stripping the remainder of the solvent in anhydrous conditions using a devolatilizer so as to end up with a molten polymer composition containing less than 0.5 wt%

of solvent and other volatiles. The molten polymer composition was advanced by a screw to a pelletizer from which the polymer composition pellets are submerged in water and cooled until solid. The composition of the resulting PEDM terpolymer was determined by ^1H and ^{13}C -NMR spectroscopy.

5 ^1H -NMR test method for Propylene Ethylene Diene polymer (PEDM)

[0090] For ^1H NMR, sample preparation (polymer dissolution) was performed at 140°C where 20 milligrams of polymer was dissolved in an appropriate amount of solvent to give a final polymer solution volume of 1 ml.

[0091] The ^1H solution NMR was performed on a 5mm probe at a field of at least 500 MHz in an ODCB (ortho-dichlorobenzene) and benzene- d_6 (C_6D_6) mixture (9:1) at 120°C with a flip angle of 30° , 15s delay, and 512 transients. Chemical shifts were referenced to the ODCB peak at 7.22 ppm. Signals were integrated and the 2-ethylidene-5-norbornene (ENB) weight percent was reported.

[0092] Calculation of ENB and double bonds was performed as shown below:

15 I_{major} = Integral of major ENB species from 5.2-5.4 ppm
 I_{minor} = Integral of minor ENB species from 4.6-5.12 ppm
 I_{aliph} = (Integral of $-\text{CH}_2-$ from 0-3 ppm)
 total = (ENB+EP)
 total wt = (ENB*120+EP*14)

20 **Table A: Proton NMR peak assignment for PEDM**

Peak Assignments	Intensity of species	MOLE %	WEIGHT %
Olef: 5.3 and 5.1 ppm ENB	$\text{ENB} = I_{\text{major}} + I_{\text{minor}}$	$\text{ENB} * 100 / \text{total}$	$\text{ENB} * 120 * 100 / \text{total wt}$
Aliphatic: 3 – 0 ppm	$\text{EP} = (I_{\text{aliph}} - 11 * \text{ENB}) / 2$	$\text{EP} * 100 / \text{total}$	$\text{EP} * 14 * 100 / \text{total wt}$

^{13}C -NMR test method for Propylene Ethylene Diene polymer (PEDM)

[0093] The ^{13}C solution NMR was performed on a 10mm cryoprobe of at least 600MHz in an ODCB (ortho-dichlorobenzene) and benzene- d_6 (C_6D_6) mixture (9:1) at 120°C with a flip angle of 90° and inverse gated decoupling. Sample preparation (polymer dissolution) was performed at 140°C where 0.20 grams of polymer was dissolved in an appropriate amount of solvent to give a final polymer solution volume of 3 ml. Chemical shifts were referenced to the ODCB solvent central peak at 130ppm. ^{13}C NMR determines the ethylene and propylene composition, not accounting for the ENB present.

[0094] Assignments for ethylene-propylene-diene terpolymers are based on Geert van der Velden, *Macromolecules*, 1983, 16, 85-89, and Kolbert et. al. *Journal of Applied Polymer Science*, 1999, 71, 523-530.

Table 1: PEDM formulations

<u>PEDM Formulation</u>	<u>C₃</u> (wt%)	<u>C₂</u> (wt%)	<u>ENB</u> (wt%)	<u>MFR</u> (g/10 min)
PEDM 1	7.68	19.42	2.90	7.66
PEDM 2	87.04	10.30	2.66	7.13

5

Sample preparation of Compounds

[0095] Additive mixing: PEDM 1 and PEDM 2 were compounded with other components to produce PEDM 1 Compound and PEDM 2 Compound. Compound compositions for the PEDM 1 and PEDM 2 Compounds are listed in Tables 2 and 3, respectively. All components are listed in phr, or part per hundred, of polymer unit. These compounds were mixed in suitable mixers, using at least two successive passes well known to the person skilled in the art. The mixing temperatures range between 110°C and 210°C. The duration of the mixing for each of the individual mixing steps is between 1 and 30 minutes depending on desired property.

10

Table 2: PEDM 1 Compound formulation

<u>Component*</u>	<u>Amount (phr**)</u>
PEDM 1	100
Carbon Black	8
CHIMASSORB® 2020	0.8
388 Super Fine Sulfur	2.5
Stearic acid	1
AKRO-ZINC® BAR 25	1

15 * CHIMASSORB® 2020 (high-molecular-weight, hindered amine light stabilizer, available from BASF); AKRO-ZINC® BAR 25 (French process zinc oxide in naphthenic oil, available from Akrochem Corporation); Carbon black Pre 3 available from Cabot.

* parts by weight per hundred parts of total PEDM 1

Table 3: PEDM 2 Compound formulation

<u>Component*</u>	<u>Amount (phr**)</u>
PEDM 2	100
Carbon Black	2.75
CHIMASSORB® 2020	0.8
388 Super Fine Sulfur	2.5
X 50S®	10.5

* X 50S® (bis(triethoxysilylpropyl)tetrasulfide with carbon black, available from Evonik Industries); Carbon Black Pre 3 available from Cabot

** parts by weight per hundred parts of total PEDM 2

5 **Silica Tread Compounding**

- [0096] Tread compound formulations for the controls and examples are listed in Tables 4 and 5. All components are listed in phr, or part per hundred, of polymer unit. These compounds were mixed in suitable mixers, using at least two successive passes well known to the person skilled in the art. The non-productive passes (mixing without crosslinking system) which have
- 10 mixing at high temperatures between 110°C and 190°C. The non-productive passes are followed by a productive pass where the crosslinking system is added. The temperature for this mixing is typically below 110°C.

Table 4: Tire tread formulations using PEDM 1 Compound and corresponding controls

Component*	TT-1**	TT-2**	TT-3**	TT-4**	TT-5**	TT-6**	TT-7**
Non-Productive Pass Components							
NIPOL® NS 116R	46.7	46.7	46.7	46.7	46.7	46.7	46.7
ZEOSIL® 1165MP	67	67	67	67	67	67	67
BUNA® CB 24	38.3	38.3	38.3	38.3	38.3	38.3	38.3
SMR™ 20	15	15	15	15	15	15	15
ESOREZ™ 5340	15	15	15	20	20	25	15
SANTOFLEX™ 6PPD	2	2	2	2	2	2	2
X 50S®	10.5	10.5	10.5	10.5	10.5	10.5	10.5
Steric acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PEDM 1 Compound		20	20	20	20	20	
Productive Pass Components							
AKRO-ZINC® BAR 25	2	2	2	2	2	2	2
N-cyclohexyl-2-benzothiazyl sulfenamide (CBS)	1.19	1.19	1.19	1.19	1.19	1.19	1.19
388 Super Fine Sulfur (new	1.4	1.4	1.4	1.4	1.4	1.4	1.4
diphenyl guanidine (DPG)	1.4	1.4	1.4	1.4	1.4	1.4	1.4

* NIPOL® NS 116R (styrene butadiene rubber with 21% bound styrene, available from Zeon Corporation); BUNA® CB 24 (neodymium butadiene rubber, available from Arlanxco); SMR™ 20 (natural polymer of cis-polyisoprene, available from Herman Webber & Co.);

- ZEOSIL® 1165MP (amorphous precipitated silica, available from Rhodia); ESOREZ™ 5340 (hydrocarbon polymer additive, available from ExxonMobil Chemical Company) It has a softening point of 140°C; NYTEX® 4700 (a high viscosity naphthenic black oil, available from Nynas AB); SANTOFLEX™ 6PPD (N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine, available from Eastman Chemical)

* per hundred parts of total rubber (NIPOL® NS 116R + BUNA® CB 24 + SMR™ 20)

Table 5: Tire tread formulations using PEDM 2 Compound and corresponding controls

<u>Component*</u>	<u>TT-8**</u>	<u>TT-9**</u>	<u>TT-10**</u>	<u>TT-11**</u>	<u>TT-12**</u>	<u>TT-13**</u>
Non-Productive Pass Components						
NIPOL® NS 116R	55.5	55.5	47.7	47.7	47.7	55.5
ZEOSIL® 1165MP	67	67	67	67	67	67
BUNA® CB 24	29.5	29.5	37.3	37.3	37.3	29.5
SMR™ 20	15	15	15	15	15	15
ESOREZ 5340		15	15	15	20	
NYTEX® 4700	15					15
SANTOFLEX™ 6PPD	2	2	2	2	2	2
X 50S®	10.5	10.5	10.5	10.5	10.5	10.5
Steric acid	2.5	2.5	2.5	2.5	2.5	2.5
PEDM 2 Compound				20	20	
Productive Pass Components						
AKRO-ZINC® BAR 25	2	2	2	2	2	2
CBS	1.19	1.19	1.19	1.19	1.19	1.19
388 Super Fine Sulfur (new	1.4	1.4	1.4	1.4	1.4	1.4
DPG	1.4	1.4	1.4	1.4	1.4	1.4

- ESOREZ™ 5340 (hydrocarbon polymer additive, available from ExxonMobil Chemical Company). It has a softening point of 140°C.

Loss Tangent Measurements

[0097] The compounds listed in Tables 4 and 5 were compression molded and cured into

pads. Afterward, a rectangular test specimen (12 mm wide & 30 mm long) was die cut out of the cured pads and mounted in an ARES G2 (Advanced Rheometric Expansion System, TA instruments) for dynamic mechanical testing in torsion rectangular geometry. Though the thickness of the test specimen was around 1.8 mm, the thickness of the specimens varied and was measured manually for each test. A strain sweep at room temperature up to 5.5% strains and at 10 Hz was conducted first followed by a temperature sweep at 4% strain and 10 Hz from -38°C to 100°C at 2°C/min ramp rates. Storage and loss moduli were measured along with the loss tangent values. For better wet traction, it is preferred to have higher loss tangent values at temperatures below 0°C whereas the loss tangent is preferred to be lower at 40°C for better rolling resistance.

[0098] Table 6 provides the loss tangent measurements for the tire tread formulations using PEDM 1 Compound (Table 4), and Table 7 provides the same measurements but as a percentage of the control tire tread formulation TT-1.

Table 6: Loss tangent for tire tread formulations using PEDM 1 Compound

Temperature (°C)	TT-1	TT-2	TT-3	TT-4	TT-5	TT-6	TT-7
-16	0.606	0.657	0.656	0.656	0.650	0.668	0.596
-14	0.573	0.667	0.665	0.659	0.651	0.665	0.561
-12	0.540	0.675	0.670	0.665	0.658	0.665	0.528
-10	0.508	0.673	0.661	0.674	0.665	0.668	0.496
-8	0.478	0.653	0.633	0.676	0.668	0.672	0.466
-6	0.451	0.614	0.589	0.666	0.658	0.674	0.439
-4	0.426	0.564	0.538	0.639	0.632	0.668	0.414
-2	0.402	0.513	0.487	0.597	0.589	0.650	0.391
0	0.381	0.465	0.440	0.548	0.541	0.619	0.369
2	0.362	0.423	0.401	0.500	0.489	0.578	0.352
4	0.344	0.387	0.367	0.454	0.443	0.533	0.335
6	0.328	0.356	0.337	0.412	0.402	0.487	0.321
8	0.314	0.329	0.311	0.377	0.365	0.443	0.307
10	0.302	0.307	0.291	0.345	0.335	0.405	0.296
40	0.205	0.185	0.178	0.182	0.174	0.188	0.205

15

Table 7: Loss tangent (percent of TT-1) for tire tread formulations using PEDM 1

<u>Compound</u>							
<u>Temperature</u> <u>(°C)</u>	<u>TT-1</u>	<u>TT-2</u>	<u>TT-3</u>	<u>TT-4</u>	<u>TT-5</u>	<u>TT-6</u>	<u>TT-7</u>
-16	100	108	108	108	107	110	98
-14	100	116	116	115	114	116	98
-12	100	125	124	123	122	123	98
-10	100	132	130	133	131	132	98
-8	100	136	132	141	140	141	97
-6	100	136	131	148	146	150	97
-4	100	133	126	150	148	157	97
-2	100	128	121	149	147	162	97
0	100	122	116	144	142	162	97
2	100	117	111	138	135	160	97
4	100	112	107	132	129	155	97
6	100	108	103	125	122	148	98
8	100	105	99	120	116	141	98
10	100	102	96	114	111	134	98
40	100	90	87	89	85	91	100

[0099] The addition of PEDM 1 to the tread compound improves wet traction (increased loss tangent below 0°C) and improves rolling resistance (decreased loss tangent at 40°C).

- 5 **[00100]** Table 8 provides the loss tangent measurements for the tire tread formulations using PEDM 2 Compound (Table 5), and Table 9 provides the same measurements but as a percentage of the control tire tread formulation TT-8.

Table 8: Loss tangent (A_{tangent}) for tire tread formulations using PEDM 2 Compound

<u>Temperature (°C)</u>	<u>TT-8</u>	<u>TT-9</u>	<u>TT-10</u>	<u>TT-11</u>	<u>TT-12</u>	<u>TT-13</u>
-14	0.479	0.674	0.544	0.544	0.558	0.495
-12	0.448	0.632	0.510	0.544	0.553	0.462
-10	0.421	0.589	0.478	0.548	0.552	0.433
-8	0.396	0.549	0.448	0.557	0.555	0.407
-6	0.375	0.510	0.421	0.571	0.566	0.383
-4	0.355	0.475	0.396	0.586	0.580	0.363
-2	0.338	0.442	0.373	0.600	0.597	0.345
0	0.323	0.413	0.352	0.601	0.613	0.330
2	0.310	0.387	0.334	0.582	0.619	0.315
4	0.298	0.363	0.318	0.542	0.606	0.303
6	0.287	0.342	0.303	0.491	0.572	0.292
8	0.278	0.323	0.291	0.439	0.521	0.282
10	0.269	0.306	0.279	0.389	0.466	0.273
40	0.193	0.191	0.192	0.167	0.170	0.196
60	0.166	0.162	0.166	0.143	0.142	0.169

Table 9: Loss tangent (percent of TT-8) for tire tread formulations using PEDM 2

<u>Compound</u>						
<u>Temperature (°C)</u>	<u>TT-8</u>	<u>TT-9</u>	<u>TT-10</u>	<u>TT-11</u>	<u>TT-12</u>	<u>TT-13</u>
-14	100	141	114	114	117	103
-12	100	141	114	121	124	103
-10	100	140	114	130	131	103
-8	100	138	113	140	140	103
-6	100	136	112	152	151	102
-4	100	134	111	165	163	102
-2	100	131	110	177	177	102
0	100	128	109	186	190	102
2	100	125	108	188	200	102
4	100	122	107	182	203	102
6	100	119	106	171	199	102
8	100	116	105	158	188	101
10	100	114	104	145	173	101
40	100	99	100	86	88	101
60	100	98	100	86	85	101

- [00101] The addition of PEDM 2 to the tread compound (TT-11 and TT-12) improves wet traction (increased loss tangent at 0°C) and improves rolling resistance (decreased loss tangent at 40°C and 60°C).

Stress/Strain Measurements

- [00102] Five test specimens were dies out with ASTM D4482 die and conditioned in the lab for 16 hours before testing. Specimens were tested on an Instron 5565 with a long travel mechanical extensometer. The load cell and extensometer were calibrated before each day of testing. Extensometer was calibrated at 20mm as the gauge length. The sample information, operator name, date, lab temperature, and humidity were all recorded. Specimen thickness was measured at three places in the test area, average value is entered when prompted, and lab temperature and humidity are measured. Specimen was carefully loaded in the grips to ensure grips clamp on the specimen symmetrically. The extensometer grips were then attached to the sample in the test area. The test was prompted to start. A pre-load of 0.1N was applied. Testing

began with the crosshead moving at 20 inches/minute until a break is detected. Five specimens from each sample were tested and median values were used for reporting.

- [00103] Table 10 provides the stress/strain measurements for the tire tread formulations using PEDM 1 Compound (Table 4), and Table 11 provides the same measurements but as a percentage of the control tire tread formulation TT-8.

Table 10: Stress/strain measurements for tire tread formulations using PEDM 1 Compound

<u>Property</u>	<u>TT-1</u>	<u>TT-2</u>	<u>TT-3</u>	<u>TT-4</u>	<u>TT-5</u>	<u>TT-6</u>	<u>TT-7</u>
300% Modulus (MPa)	14.7	14.3	14.4	13.2	13.1	12.3	14.4
Tensile Strength (MPa)	21.9	19.3	20.5	20.3	19.6	20.8	21.7
Elongation (%)	417	392	405	422	416	464	418

Table 11: Stress/strain measurements (percent of TT-1) for tire tread formulations using PEDM 1 Compound

<u>Property</u>	<u>TT-1</u>	<u>TT-2</u>	<u>TT-3</u>	<u>TT-4</u>	<u>TT-5</u>	<u>TT-6</u>	<u>TT-7</u>
300% Modulus (% of TT-1)	100	97	98	90	89	84	98
Tensile Strength (% of TT-1)	100	88	94	93	89	95	99
Elongation (% of TT-1)	100	94	97	101	100	111	100

- 10 [00104] The addition of PEDM 1 improves rolling resistance wet braking trade-off without adversely affecting wear resistance.

[00105] Table 10 provides the stress/strain measurements for the tire tread formulations using PEDM 1 Compound (Table 4), and Table 11 provides the same measurements but as a percentage of the control tire tread formulation TT-8.

Table 12: Stress/strain measurements for tire tread formulations using PEDM 2**Compound**

<u>Property</u>	<u>TT-8</u>	<u>TT-9</u>	<u>TT-10</u>	<u>TT-11</u>	<u>TT-12</u>	<u>TT-13</u>
300% Modulus (MPa)	13	14.1	13.8	15.3	14.1	12.8
Tensile Strength (MPa)	17.3	20	20.3	19	19.8	18
Elongation (%)	378	398	414	362	396	410

Table 13: Stress/strain measurements (percent of TT-8) for tire tread formulations**using PEDM 2 Compound**

<u>Property</u>	<u>TT-8</u>	<u>TT-9</u>	<u>TT-10</u>	<u>TT-11</u>	<u>TT-12</u>	<u>TT-13</u>
300% Modulus (% of TT-8)	100	108	106	118	108	98
Tensile Strength (% of TT-8)	100	116	117	110	114	104
Elongation (% of TT-8)	100	105	110	96	105	108

5 [00106] The addition of PEDM 2 (TT-11 and TT-12) to the tread has improved modulus, which indicates enhanced durability and handling.

[00107] Also disclosed is the use of the propylene-ethylene-diene terpolymer in a tire tread composition as described.

[00108] In the specification and in the claims, the terms “including” and “comprising” are open-ended terms and should be interpreted to mean “including, but not limited to”. These terms encompass the more restrictive terms “consisting essentially of” and “consisting of”.

10 [00109] It must be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise. As well, the terms “a” (or “an”), “one or more” and “at least one” can be used interchangeably

15 herein. It is also to be noted that the terms “comprising”, “including”, “characterized by” and “having” can be used interchangeably.