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(71) **Applicants** *(for all designated States except US)*: **STYRON EUROPE GMBH** [CH/CH]; Bachtobelstrasse 3, CH-8810 Horgen (CH). **POLYMER SERVICE GMBH MERSEBURG** [DE/DE]; Grusaer Strasse, Building 131, 06217 Merseburg (DE).

(72) **Inventors; and**

(75) **Inventors/Applicants** *(for US only)*: **THIELE, Sven** [DE/DE]; Käuzchenweg 2, 06120 Halle (DE). **ILISCH, Sybill** [DE/DE]; Haackestrasse 9, 06217 Merseburg (DE). **REINCKE, Katrin** [DE/DE]; Uferstrasse 11, 06237 Leuna (DE). **FERNER, Uwe** [DE/DE]; Feldrain 25, Ortsteil Bobbau, 06766 Bitterfeld-Wolfen (DE).

(74) **Agents**: **KLUSMANN, Peter** et al.; Hoffmann · Eitle, Arabellastrasse 4, 81925 Munich (DE).

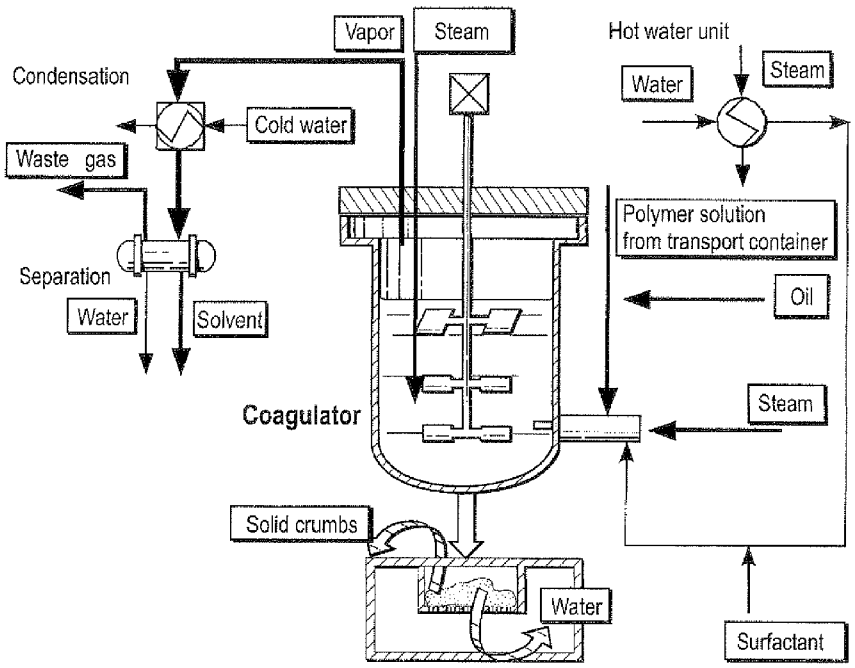
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(54) **Title**: POLYMER COMPOSITIONS

FIG. 1



[Continued on next page]

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(57) Abstract: A composition includes i) a polymer; ii) a primary filler; and iii) a secondary filler. The secondary filler includes a material selected from the group consisting of a secondary glass powder filler, a zinc-doped secondary glass powder filler, and a combination thereof.

POLYMER COMPOSITIONS

TECHNICAL FIELD

The present teachings relate generally to polymer compositions, articles prepared from polymer compositions, and methods for making polymer compositions.

BACKGROUND

It is generally accepted that increasing oil prices and national countries legislations—which require the reduction of automotive carbon dioxide emissions—force tire and rubber producers to contribute to produce "fuel efficient" and, thus, fuel-, gas- or electric energy-(for vehicles driven by electric energy) saving tires. One general approach to obtain fuel efficient tires is to produce tire formulations that have reduced hysteresis loss. A major source of hysteresis in vulcanized elastomeric polymers is believed to be attributable to free polymer chain ends—that is, the section of the elastomeric polymer chain between the last cross-link and the end of the polymer chain. This free end of the polymer does not participate in any efficient elastically recoverable process and, as a result, any energy transmitted to this section of the polymer is lost. This dissipated energy leads to a pronounced hysteresis under dynamic deformation. Another source of hysteresis in vulcanized elastomeric polymers is believed to be attributable to the type and composition of the filler material. Usually small reinforcing particles, which interact well with the polymer or with functional groups attached to the polymer during the compounding and vulcanization process lead to a low vulcanizate hysteresis. Furthermore, a source of hysteresis in vulcanized elastomeric polymers is believed to be attributable to an insufficient distribution of filler particles in the vulcanized elastomeric polymer composition. Therefore, secondary inorganic compound components which boost processing without being inactive towards polymers also contribute to a low vulcanizate hysteresis. The hysteresis loss of a cross-linked elastomeric polymer composition is related to its Tan δ, at 60 °C, value (see ISO 4664-1:2005; Rubber, Vulcanized or thermoplastic; Determination of dynamic properties – part 1: General guidance). In general, vulcanized elastomeric polymer compositions having relatively small Tan δ values, at 60 °C, are preferred as having lower hysteresis loss. In the final tire product, this translates to a lower rolling resistance and better fuel economy.

It is generally accepted that a lower rolling resistance tire can be made at the expense of deteriorated wet grip properties. For example, if, in a random solution styrene–butadiene rubber (random SSBR), the polystyrene unit concentration is relatively reduced, with respect to the total polybutadiene unit concentration, and the 1.2-polydiene unit concentration is kept constant, both the Tan δ at 60 °C and the Tan δ at 0 °C, are reduced, generally corresponding to improved rolling resistance and deteriorated wet grip performance of a tire. Similarly, if, in a random solution styrene–butadiene rubber (random SSBR), the 1,2-polybutadiene unit concentration is relatively reduced, with respect to the total polybutadiene unit concentration, and the polystyrene unit concentration is kept constant, both the Tan δ at 60 °C and the Tan δ at 0 °C are reduced, generally corresponding to improved rolling resistance and deteriorated wet grip performance of a tire. Accordingly, when assessing the rubber vulcanizate performance correctly, both the rolling resistance, related Tan δ at 60 °C, and the wet grip, related Tan δ at 0 °C, should be monitored.

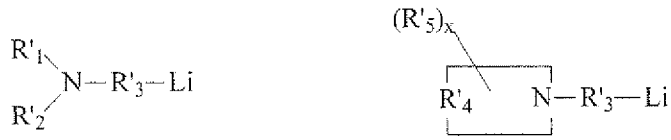
One generally accepted approach to reducing hysteresis loss is to reduce the number of free chain ends of elastomeric polymers. Various techniques are described in the open literature including the use of "coupling agents," such as tin tetrachloride, which may functionalize the polymer chain end and react with components of an elastomeric composition, such as, for example, with a filler or with unsaturated portions of a polymer. Examples of such techniques, along with other documents of interest, are described in the following U.S. patent documents: U.S. Patent Nos. 3,281,383; 3,244,664 and 3,692,874 (for example, tetrachlorosilane); U.S. Patent No. 3,978,103; U.S. Patent Nos. 4,048,206; and 4,474,908; U.S. Patent Nos. 6,777,569 (blocked mercaptosilanes) and 3,078,254 (a multi-halogen-substituted hydrocarbon, such as 1,3,5-tri(bromo methyl) benzene); U.S. Patent No. 4,616,069 (tin compound and organic amino or amine compound); and U.S. Patent Application Publication No. 2005/0124740.

One generally accepted approach to reducing hysteresis through reducing the number of free chain ends of elastomeric polymers consists in the polymer chain-end-functionalization. End-functionalization further decreases the polymer hysteresis due to polymer chain-end to polymer interactions, or to polymer chain-end to filler interaction. "Synthesis of end-functionalized polymer by means of living anionic polymerization" *Journal of Macromolecular Chemistry and Physics* **1996**, *197*, 3135-3148, describes the

synthesis of polystyrene-containing and polyisoprene-containing living polymers with hydroxy (-OH) and mercapto (-SH) functional end caps, obtained by reacting the living polymer with haloalkanes containing silyl ether and silyl thioether functions.

Furthermore, U.S. Patent No. 6,579,949 describes the use of a similar class of sulfur compounds, including tert-butyl dimethylsilyl-3-chloro-1-propylsulfide to produce a ω-chain-end modified elastomeric polymer used as a component in rubber articles having low hysteresis loss. ω-Chain-end modified elastomeric polymers are subsequently blended with fillers, vulcanizing agents, accelerators, oil extenders, and other various additives to produce tires having low hysteresis loss.

U.S. Patent No. 5,502,131 describes a method of preparing a α-chain-end modified polymer comprising polymerizing diolefin monomers and/or monovinylaromatic monomers in the presence of a polymerization initiator having the general Formula A or B:



Formula A and Formula B,

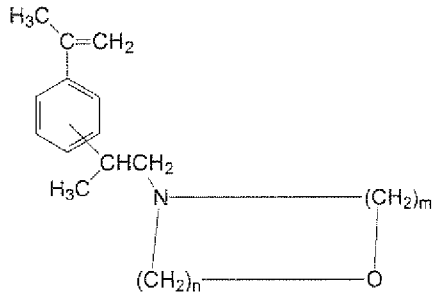
wherein R'_1 and R'_2 are same or different and are selected from alkyls, cycloalkyls and aralkyls, R'_3 is a deprotonated allyl, 2-methallyl or xylyl, R'_4 is a carbocyclic group, and R'_5 is an alkyl substituent on a methylene group.

Another method of reducing the hysteresis loss consists in a statistical backbone functionalization of polydienes. The number of functionalized positions along the rubber backbone can be higher compared with chain-end modification, where just one or two positions of one base polymer chain can be modified. Accordingly, the interaction of the polymer chain with filler particles can be more intense in the case of a backbone modification, when multiple (more than two) polymer backbone positions are modified. Thus, backbone functionalized polydienes have a potential for a lower hysteresis loss and a better compatibility with fillers, such as with carbon black and silica.

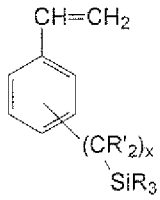
Typical examples for a polymer backbone modification include U.S. Patent Nos. 6,933,358, and U.S. Patent 7,041,761.

Polydienes prepared by using an anionic polymerization technology are usually made from butadiene, isoprene and, optionally, styrene as monomer sources.

Functionalized conjugated diene or vinylaromatic monomers can be incorporated into the growing polymer chain. Functionalized monomers, representing substituted styrene (1, 2) are shown below.

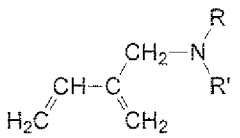


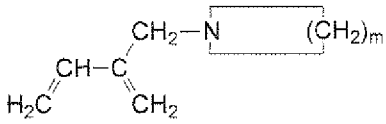
Ref. (1)



Ref. (2)

In the above structures, R and R' are individually hydrogen or an alkyl group; x is a number from 1 to 10; and m and n are individually numbers from 0 to 10. Functionalized monomers representing substituted isoprene (1) are shown below.





The substituted styrene and substituted isoprene structures as shown above were incorporated into the elastomeric polydiolefin by being copolymerized with unfunctionalized conjugated diolefin and, optionally, vinyl aromatic monomers. The functionalized polymers improved the compatibility of the rubber in tires with fillers, such as carbon black and silica. In particular, tire rolling resistance properties and, therefore, hysteresis properties of tires were stated to be improved.

United States Provisional Patent Application Nos. 61/288,697 and 61/288,519—incorporated herein by reference in their entireties—furthermore indicate that a combination of different functionalization technologies—namely, the combination of alpha modified/omega modified polymers and alpha modified/branched modified polymers—further reduce the polymer vulcanizate hysteresis.

Stated modified polymer needs to interact with filler particles comprised in rubber-filler vulcanizates efficiently. Traditionally, different carbon black and silica grades are applied as filler particle in rubber compounds used in tires.

For example, a new furnace carbon black grade was proposed in German Patent Application No. DE 19839925 A1, which leads to reduced tan δ 60 °C values in solution styrene-butadiene/polybutadiene rubber compounds compared with ASTM carbon blacks of identical CTAB-surface area.

Silica turned out to be the better reinforcement agent and, therefore, is increasingly used in high performance passenger car tires.

Depending on the silica filler particle size, surface area, surface structure and tendency for silica particle agglomeration, the rubber vulcanizate properties can be tuned up—for example, with respect to a decreased hysteresis loss and improved rolling resistance in tires. German Patent Application No. DE 10208046874 A1 reportedly solves some of the aforementioned problems and states success in minimizing the silica particle agglomeration in the rubber vulcanizate. Therefore, the application of the disclosed rubber compositions comprising at least one polar or non-polar rubber, at least one colloidal silica filler component, and further components, to tire manufacturing leads to an improved tire rolling resistance. Preferred rubbers are polyisoprene, polybutadiene and styrene-butadiene rubber. The rubber components may be optionally functionalized or non-functionalized. Exemplary rubber compounds comprising colloidal silica (of 22 nm particle size and of 138 m^2/g surface area according to the CTAB absorption method) containing 13.2 wt% TDAE oil, 0 or 1 phr silane, 50 phr Buna CB25 polybutadiene of Lanxess AG and 50 phr Nipol NS116R solution styrene-butadiene rubber of Nippon Zeon corporation was compared with a composition comprising 7 phr precipitated silica grade ULTRASIL VN3 of Evonic Industries AG and 1.2 phr A1589 silane of Momentive Performance Materials but not containing stated colloidal silica. The examples provided in DE 10208046874 A1 are at least partially in contrast to the stated invention. The use of the colloidal silica did not increase the rebound values measured as 70 °C. Increased rebound values at 70 °C are widely accepted to be an indicator for an improvement of the rolling resistance property in a tire. The reported difference of the rebound resistance at 70 °C and at room temperature reportedly representing the wet braking – rolling resistance balance only improves by 0.9 and 1.6 % versus the ULTRASIL VN3 containing

compound reference. The example incorporated in German Patent Application No. DE 10208046874 A1 demonstrates that an improved rolling resistance property of the vulcanizate in a tire can not be achieved easily. The examples provided in DE 10208046874 A1 further demonstrate that the silane coupling agent concentrations could be reduced or at least maintained at an increased silica concentration in the composition if ULTRASIL VN3 is exchanged by colloidal silica, however without significantly improving the tire rolling resistance property. The use of silica filler requires the use of relatively expensive silane coupling agents which hydrophobize the silica surface and, therefore, compatibilize the silane coupling agent surface for interaction with relatively non-polar polymer macromolecules. Therefore, it is interesting to achieve a reduction of the silane coupling agent concentration while at the same time significantly reducing the tire rolling resistance related vulcanized composition hysteresis energy loss.

A fraction of carbon black is often added to silica-rubber compositions to achieve an improved tire abrasion resistance performance. For example, Japanese Patent Application No. JP 2006036918 reports on tire compounds comprising 75.6 phr oil extended SBR (VSL 5025), 20 phr polybutadiene (Nipol 1220), 74 phr silica (Nipsil AQ), 5.9 phr silane coupling agent (Si 69), and 8 phr carbon black (Seast 7HM). The vulcanized composition was stated to have a good Lambourn abrasion resistance.

It would be beneficial if combinations of different filler materials would also lead at the same time to improved tire hysteresis properties and to improved compound processing conditions even at reduced silane coupling agent concentrations.

Rubber compounds comprising porous glass particles may be beneficial. There are only few examples demonstrating the use of specific glass particle grades in rubber compounds.

Japanese Patent No. JP 2554889B2 describes tire rubber compositions comprising (A) solution styrene-butadiene copolymer rubber and low-*cis*-polybutadiene, (B) titanium oxide coated on silica, alumina, glass flakes or on alternative inorganic materials, and (C) a filler selected from calcium carbonate, clay, talc or *syndiotactic* 1,2-polybutadiene. The optionally used (modified) glass flakes are referred to as mica and represent particles of small plate shape without significant porosity.

Japanese Patent Application No. JP2007275362 describes shoe soles and shoe bodies made from exemplary compounds comprising 85 wt% natural rubber, 15 wt% styrene-

butadiene rubber, 15 wt% Nipsil VN3 silica, and 10 wt% silane coupling agent-treated glass microsphere bubbles S60SH.

The preparation of porous glass particles is described in German Patent Application No. DE 19545065 A1. The glass particles preparation includes a high temperature extrusion process of a glass melt and coarse crushing of the resulting glass foam. Glass particles as described in DE 19545065 A1 were not applied to a rubber-filler compounding process.

Furthermore, zinc oxide is applied to the vulcanization of polymer compositions as an activator for typical vulcanization accelerators. The heavy metal containing zinc oxide is added as a powder in the course of the compounding process. Therefore, tires made by using vulcanized polymer compositions comprise zinc oxide. Zinc oxide is classified as being dangerous for the environment as well as very toxic for aquatic organisms according to EG 67/548/EEC and according to the IFA GESTIS – substance data base (http://biade.itrust.de/biade/lpext.dll?f=templates&fn=main-hit-h.htm&2.0). Accordingly, it would be beneficial if the handling of zinc oxide during rubber compounding could be avoided. Zinc oxide comprised in tires also may be released into the environment due to abrasion of tires on the road. Therefore, due to environmental and health concerns, options are sought for avoiding handling of powdery zinc oxide and for reducing the total concentration of zinc (zinc atoms or zinc ions) in tires. German Patent Application No. DE102005050764 A1 additionally states that zinc sulfide formed in the process of rubber compound vulcanization may block valves and contribute to the formation of bubbles in tires. Accordingly, the use of zinc oxide may negatively impact the rubber compounding process and cause problems with respect to the tire safety on the road. Thus, the replacement of zinc oxide or the reduction of zinc oxide concentration in the course of the rubber-filler vulcanizate and tire manufacturing is beneficial.

The preparation of vulcanized rubber compositions using a reduced zinc oxide concentration is described in German Patent Application No. DE102005050764 A1. The patent application describes a sulfur vulcanizable composition for use in tires which comprises (1) diene rubber, (2) a filler selected from carbon black and silica, (3) 0.3-2 phr zinc oxide, and (4) a process aid comprising at least one sodium or potassium soap and at least one compound from the group consisting of mono- and digycerol ester of organic carbon acids. The ratio of sodium and/or potassium soap to mono- and/or digycerol ester preferably amounts to 2 to 4. According to the example provided in DE102005050764 A1,

the zinc oxide concentration of 3 phr could be reduced to 0.9 phr through the addition of, for example, 3 phr Stuktol® HT 207 from Schill & Seilacher AG, representing a mixture of sodium- and potassium soaps and glycerol esters of the palmitin and stearin acid.

Unfortunately, the reduction of zinc oxide could only be performed through addition of a sodium/potassium soap and mono- and/or digycerol ester containing mixture. Therefore, the reduction of zinc oxide is combined with extra costs for a new component required in the rubber-filler composition. It would be beneficial if the reduction or elimination of zinc oxide could be performed without adding costs for additional components, which do not improve the mechanical properties of vulcanized rubber compositions. It also would be beneficial if the reduction of the zinc concentration could be achieved without significantly changing the vulcanization kinetic of rubber composition.

There is a need to find polymer-multi-filler compositions which enable the reduction of zinc oxide, silane coupling agent while decreasing the polymer vulcanizate hysteresis energy loss and improving the polymer compound processing performance.

SUMMARY

The scope of the present invention is defined solely by the appended claims, and is not affected to any degree by the statements within this summary.

By way of introduction, a first composition in accordance with the present teachings includes (i) a polymer; (ii) a primary filler; and (iii) a secondary filler. The secondary filler includes a material selected from the group consisting of a secondary glass powder filler, a zinc-doped secondary glass powder filler, and a combination thereof.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows a schematic illustration of a coagulator for copolymer suspension

DETAILED DESCRIPTION

A first polymer composition embodying features of the present invention comprises at least one primary filler, at least one polymer, and at least one secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler each as described herein. In some embodiments, the compositions have improved processing characteristics. In some embodiments, a first polymer composition comprises at least one secondary filler selected from the group consisting of secondary glass powder filler

and zinc-doped glass powder filler. First polymer compositions comprising zinc-doped secondary glass powder filler do not require the use of zinc oxide as a component of the vulcanization system and, therefore, are environmentally friendly. In some embodiments, these first polymer compositions are used in the preparation of second (vulcanized) polymer compositions, and articles prepared from the same. The second (vulcanized) polymer compositions are useful in the preparation of vulcanized—and, therefore, cross-linked—elastomeric compositions having relatively low hysteresis loss. Such compositions are useful in many articles, including tire treads having low rolling resistance in combination with a good balance of other desirable physical and chemical properties including but not limited to wet grip, elongation at break, and processability.

In some embodiments, a first polymer composition comprises:

i) a primary filler selected from the group consisting of silica, carbon-silica dual phase filler, carbon black, carbon nano-tube filler, lignin, and combinations thereof;

ii) a secondary filler selected from the group consisting of:

iia) a secondary glass powder filler which, in some embodiments, comprises glass fillers of mean diameter < 20 μm and BET-surface > 0.5 m^2/g, in some embodiments of mean diameter < 10 μm and BET-surface > 1.0 m^2/g, and in some embodiments of mean diameter < 5 μm and BET-surface > 2.0 m^2/g; and

iib) a secondary zinc-doped glass powder filler which, in some embodiments, comprises glass fillers of mean diameter < 20 μm, BET-surface > 0.5 m^2/g, and a zinc concentration in the pores and on the surface of the glass particles of 0.2 to 30 percent by weight of the glass powder filler, in some embodiments of mean diameter < 10 μm, BET-surface > 1.0 m^2/g, and a zinc concentration in the pores and on the surface of the glass particles of 0.5 to 20 percent by weight of the glass powder filler, and in some embodiments of mean diameter < 5 μm, BET-surface > 2.0 m^2/g, and a zinc concentration in the pores and on the surface of the glass particles of 1.0 to 10 percent by weight of the glass powder filler;

iii) a polymer selected from the group consisting of polybutadiene; modified-polybutadiene; polyisoprene; modified-polyisoprene; styrene/butadiene copolymers with styrene contents of 1 to 60, including SSBR wherein the polymer was prepared in solution; modified-styrene/butadiene copolymers (SSBR), with styrene contents of 1 to 60, including modified-SSBR wherein the polymer was prepared in solution; styrene/isoprene copolymers

with styrene contents of 1 to 60; modified- styrene/isoprene copolymers (SIR) with styrene contents of 1 to 60, including modified–SSIR wherein the polymer was prepared in solution; isobutylene/isoprene copolymers; modified–isobutylene/isoprene copolymers; isoprene/butadiene copolymers; modified-isoprene/butadiene copolymers; butadiene/C1-C4-alkyl acrylate copolymers; butadiene/acrylonitrile copolymers; partially hydrogenated or fully hydrogenated butadiene/acrylonitrile copolymers; and combinations thereof.

In some embodiments, the polymer is selected from the group consisting of polybutadiene; modified–polybutadiene; polyisoprene; modified–polyisoprene; styrene/butadiene copolymers with styrene contents of 10 to 50, including SSBR wherein the polymer was prepared in solution; modified–styrene/butadiene copolymers (SSBR), with styrene contents of 10 to 50, including modified–SSBR wherein the polymer was prepared in solution; styrene/isoprene copolymers with styrene contents of 10 to 50; modified styrene/isoprene copolymers (SIR) with styrene contents of 10 to 50, including SSIR wherein the polymer was prepared in solution; isoprene/butadiene copolymers; modified-isoprene/butadiene copolymers; and combinations thereof. In some embodiments, modified polymers are presently preferred.

In some embodiments, the first composition further comprises a silane coupling agent. In some embodiments, the first composition further comprises an oil. In some embodiments, the first composition further comprises a processing aid. In some embodiments, the first composition further comprises a vulcanization agent.

In some embodiments, the present teachings also provide a second (vulcanized) polymer composition comprising the reaction product of: (1) a vulcanization agent; and (2) a first composition as described herein.

In some embodiments, the present teachings also provide a method for making a vulcanized polymer composition comprising reacting: (1) a vulcanization agent; and (2) a first composition as described herein.

In some embodiments, a first composition in accordance with the present teachings comprises a combination of two or more embodiments as described herein.

In addition, in some embodiments, a vulcanized composition in accordance with the present teachings comprises a combination of two or more embodiments as described herein.

The following embodiments apply to aspects of the present teachings described above: In some embodiments, the primary filler comprises carbon black. In some

embodiments, the primary filler comprises silica. In some embodiments, the primary filler comprises carbon–silica dual-phase filler. In some embodiments, the secondary glass powder filler comprises a borosilicate glass. In some embodiments, the secondary glass powder filler comprises a soda-lime-glass. In some embodiments, the zinc-doped secondary glass powder filler comprises a borosilicate glass. In some embodiments, the zinc-doped secondary glass powder filler comprises a soda-lime-glass.

Polymers

Representative uncrosslinked elastomeric polymers in accordance with the present teachings include ones that are prepared from the following list of representative monomers: conjugated olefins and olefins selected from α-olefins, internal olefins, cyclic olefins, polar olefins, nonconjugated diolefins, and combinations thereof.

Representative conjugated unsaturated monomers include but are not limited to conjugated dienes, such as 1,3-butadiene, 2-alkyl-1,3-butadiene, isoprene (2-methyl-1,3-butadiene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 2-methyl-2,4-pentadiene, cyclopentadiene, 2,4-hexadiene, 1,3-cyclooctadiene, and combinations thereof.

Representative olefins include but are not limited to C_{2-20} α-olefins, including but not limited to long chain macromolecular α-olefins—especially aromatic vinyl compounds.

Representative aromatic vinyl compounds include but are not limited to styrene, including but not limited to C_{1-4} alkyl substituted styrenes, such as 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2,4-dimethylstyrene, 2,4,6-trimethylstyrene, α-methylstyrene and stilbene, 2,4-diisopropylstyrene,4-tert-butylstyrene, vinyl benzyl dimethylamine, (4-vinylbenzyl)dimethyl aminoethyl ether, N,N-dimethylaminoethyl styrene, tert-butoxystyrene, vinylpyridine, and combinations thereof.

Representative polar olefins include but are not limited to acrylonitrile, methacrylates, methylmethacrylate, and combinations thereof.

Representative nonconjugated olefins include but are not limited to C_{4-20} diolefins, especially norbornadiene, ethylidenenorbornene, 1,4-hexadiene, 1,5-hexadiene, 1,7-octadiene, 4-vinylcyclohexene, divinylbenzene including 1,2-divinylbenzene, 1,3-divinylbenzene and 1,4-divinylbenzene, and combinations thereof.

Representative conjugated dienes include but are not limited to butadiene, isoprene, cyclopentadiene, and combinations thereof. Representative aromatic α-olefins include but are not limited to styrene, 4-methylstyrene, and a combination thereof.

Representative uncrosslinked elastomeric polymers include but are not limited to homopolymers of conjugated dienes, especially butadiene or isoprene, and random or block co- and terpolymers of at least one conjugated diene, especially butadiene or isoprene, with at least one conjugated diene or with at least one aromatic α-olefin, and especially styrene and 4-methylstyrene, aromatic diolefin, especially divinylbenzene. The random copolymerization, optionally terpolymerization, of at least one conjugated diene with at least one aromatic α-olefin, and optionally at least one aromatic diolefin or aliphatic α-olefin, and especially butadiene or isoprene with styrene, 4-methylstyrene and/or divinylbenzene is presently preferred. Additionally, the random copolymerization of butadiene with isoprene is presently preferred.

Examples of applicable uncrosslinked elastomeric modified polymers include but are not limited to: modified BR-polybutadiene; butadiene/C1-C4-alkyl acrylate copolymers; modified IR-polyisoprene; modified SBR-styrene/butadiene copolymers with styrene contents of 1 to 60, in some embodiments 10 to 50 weight percent, including SSBR wherein the polymer was prepared in solution; modified SIR-styrene/isoprene copolymers with styrene contents of 1 to 60, in some embodiments 10 to 50 weight percent including SSIR wherein the polymer was prepared in solution; modified IIR-isobutylene/isoprene copolymers; modified IBR-isoprene/butadiene copolymers; modified NBR-butadiene/acrylonitrile copolymers; modified HNBR-partially hydrogenated or fully hydrogenated NBR rubber; EPDM (an ethylene/propylene/diene copolymer); and combinations thereof.

In some embodiments, the modified polymer comprises a modified polybutadiene.

In some embodiments, the modified polymer comprises a modified butadiene/C1-C4-alkyl acrylate copolymer.

In some embodiments, the modified polymer comprises a modified butadiene/styrene copolymer.

In some embodiments, the modified polymer comprises a modified butadiene/styrene copolymer (SSBR) prepared in solution.

In some embodiments, the modified polymer comprises a modified isoprene/styrene

copolymer (SSIR) prepared in solution.

In some embodiments, the modified polymer comprises a modified butadiene/isoprene copolymer.

In some embodiments, the modified polymer comprises a modified polychloroprene.

In some embodiments, the modified polymer comprises a modified polyisoprene, including synthetic polyisoprene and natural rubber.

In some embodiments, the modified polymer comprises a modified styrene/butadiene copolymer with a styrene unit content from 1 to 60 weight percent, in some embodiments from 10 to 50 weight percent, based on the total weight of the copolymer.

In some embodiments, the modified polymer comprises a modified styrene/butadiene copolymer with a 1,2-polybutadiene unit content from 5 to 70 weight percent, in some embodiments from 50 to 70, or 5 to 27 weight percent, based on the total weight of polybutadiene unit fraction of the copolymer.

In some embodiments, the modified polymer comprises a modified styrene/isoprene copolymer with a styrene unit content from 1 to 60 weight percent, in some embodiments from 10 to 50 weight percent, based on the total weight of the copolymer.

In some embodiments, the modified polymer comprises a modified styrene/isoprene copolymer with a 1,2-polyisoprene unit content from 5 to 70 weight percent, in some embodiments from 50 to 70, or 5 to 25 weight percent, based on the total weight of polybutadiene unit fraction of the copolymer.

In some embodiments, the modified polymer comprises a modified butadiene/isoprene copolymer with an isoprene unit content from 0.1 to 70 weight percent, in some embodiments from 5 to 50 weight percent, based on the total weight of the copolymer.

In some embodiments, the modified polymer comprises a modified isobutylene/isoprene copolymer.

In some embodiments, the modified polymer comprises a modified partially hydrogenated butadiene.

In some embodiments, the modified polymer comprises a modified partially hydrogenated styrene–butadiene copolymer.

Such representative uncrosslinked elastomeric modified polymers comprise functional groups which, in some embodiments, are attached to one or both polymer chain

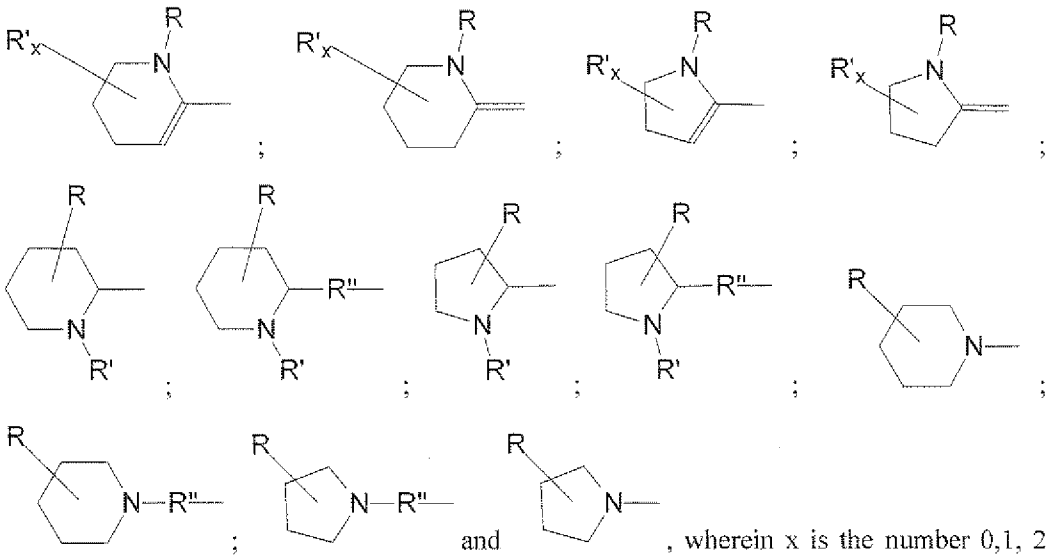
ends to the branching point of the polymer or to the polymer backbone. In some embodiments, the functional groups are selected from the following and combinations thereof:

thiol groups (HS- or HS-R''-); protected thiol groups including but not limited to hydrocarbyl thioethers (RS- or RS-R''-), trihydrocarbylsilyl-thioethers ($(R_3Si)S$- or $(R_3Si)S$-R''-), and trihydrocarbylstannyl-thioethers ($(R_3Sn)S$- or $(R_3Sn)S$-R''-);

primary amine groups (H_2N- or H_2N-R''-); protected primary amino groups including but not limited to bis-trihydrocarbylsilyl-amino groups ($(R_3Si)_2N$- or $(R_3Si)_2N$-R''-), bis-trihydrocarbylstannyl-amino groups ($(R_3Sn)_2N$- or $(R_3Sn)_2N$-R''), trihydrocarbylsilyl-amino groups ($R_3Si(H)N$- or $R_3Si(H)N$-R''-), and trihydrocarbylstannyl-amino groups ($R_3Sn(H)N$- or $R_3Sn(H)N$-R''-);

hydrocarbyl amino groups (R(H)N- or R(H)N-R''-); protected hydrocarbyl amino groups including but not limited to trihydrocarbylsilyl-hydrocarbyl-amino groups ($(R(R'_3Si)N$- or $(R(R'_3Si)N$-R''-) and trihydrocarbylstannyl-hydrocarbyl-amino groups ($(R(R'_3Sn)N$- or $(R(R'_3Sn)N$-R'');

cyclic amine groups including but not limited to the following groups



and , wherein x is the number 0,1, 2 or 3;

dihydrocarbylamino groups (R_2N- or R_2N-R''-);

primary phosphane groups (H_2P- or H_2P-R''-); protected primary phosphane groups

including but not limited to bis-trihydrocarbylsilyl-phosphane groups ($(R_3Si)_2P$- or $(R_3Si)_2P$-R''-), bis-trihydrocarbylstannyl-phosphane groups ($(R_3Sn)_2P$- or $(R_3Sn)_2P$-R''-), trihydrocarbylsilyl-phosphane groups ($(R_3Si)(H)P$- or $(R_3Si)(H)P$-R''-), and bis-trihydrocarbylstannyl-phosphane groups ($(R_3Sn)(H)P$- or $(R_3Sn)(H)P$-R''-);

hydrocarbyl phosphane groups (R(H)P- or R(H)P-R''-); protected hydrocarbyl phosphane groups including but not limited to trihydrocarbylsilyl-hydrocarbyl-phosphane groups ($(R(R'_3Si)P$- or $(R(R'_3Si)P$-R''-) and trihydrocarbylstannyl-hydrocarbyl-phosphane groups ($(R(R'_3Sn)P$- or $(R(R'_3Sn)P$-R''-);

alcohol groups (HO- or HO-R''-); protected alcohol groups including but not limited to trihydrocarbylsilyl-ethers (R_3Si-O- or R_3Si-O-R''-) and trihydrocarbylstannyl-ethers (R_3Sn-O- or R_3Sn-O-R''-);

carboxyl groups (HOOC- or HOOC-R''-) including but not limited to protected carboxy groups, including but not limited to carbon acid hydrocarbylesters (ROOC- or ROOC-R''-);

carboxy amide (H_2NOC or H_2NOC-R''-)-anhydride groups and carboxy hydrocarbyl amides ($(R)(H)N)OC$- or $(R)(H)N)OC$-R''-);

hydrocarboxysilyl groups including but not limited to trihydrocarboxysilyl groups ($(RO)_3Si$- or $(RO)_3Si$-R''-), hydrocarbyl-dihydrocarboxysilyl groups ($R'(RO)_2Si$- or $R'(RO)_2Si$-R''-), and dihydrocarbyl-hydrocarboxysilyl groups ($R'_2(RO)Si$-R''-);

dihydrocarbylsilanol groups ($(HO)(R_2)Si$- or $(HO)(R_2)Si$-R''-); hydrocarbyldisilanol groups ($(HO)_2(R)Si$- or $(HO)_2(R)Si$-R''-);

trichlorosilyl groups (Cl_3Si- or Cl_3Si-R''-); dichloro-hydrocarbylsilyl groups ($R(Cl)_2Si$- or $R(Cl)_2Si$-R''-); chloro-dihydrocarbylsilyl groups ($R_2(Cl)Si$- or $R_2(Cl)Si$-R''-); and

hydrocarbyl or dihydrocarbylolegosiloxane groups, including but not limited to groups formed through reaction of tris-dimethylsiloxane ($((CH_3)_2SiO)_3$) with living anionic polymer chains;

wherein R and R' are independently selected hydrocarbyl groups and R'' is a divalent hydrocarbon group.

One or more types of the aforementioned functional groups may be attached to the polymer.

Representative uncrosslinked elastomeric modified polymers comprising thiol groups and/or protected thiol groups are described in International Patent Publication Nos. WO 2007047943 and WO 2008076875, International Patent Application Nos. PCT/US09/045553 and PCT/US09/063961, and U.S. Provisional Application Serial Nos. 61/288,519 and 61/288,697. Representative uncrosslinked modified polymers comprising dihydrocarbylamino groups are described in DD 237513 A1; DD242232 A1; DD236321 A1; in U.S. Patent Nos. 5,502,131; 6,025,450; 7,342,070; 5,786,441; 5,736,617; 5,912,343; 5,852,189; 5,959,048; 5,866,650; 5,916,961; 5,792,820; 6,046,288; 6,080,835; 6,025,450; 5,502,131; 7,342,070; and 5,248,736; in International Patent Publication No. WO 2007/015872; and in European Patent Document Nos. EP 180141; EP 150479; EP 180853; EP 1939224; and EP 1939225. Representative uncrosslinked modified polymers comprising thioether groups are described in U.S. Patent No. 7,462,677, in U.S. Patent Application Publication No. 2009/0156751, and in the manuscript of the 170th technical meeting of the rubber division of the American chemical society (1-25, 2006; ISSN: 15471977). Representative uncrosslinked modified polymers comprising alkoxysilane groups are described in U.S. Patent No. 6,566,480 and in the manuscript of the 143rd technical meeting of the rubber division of the American chemical society at Denver, Colorado (May 18.21, 1993; title: Chemical modification of short polystyrene block-SBR with alkoxysilane, presented by I. Hattori and M. Sakalibara, Japan Synthetic Rubber Co., Ltd.).

It is believed that the functional groups of the applicable modified polymers are reactive with fillers (such as silica and/or carbon black) present. Further interaction can be referred to intermolecular reactions of functional groups or to reactions of functional groups with unsaturated portions of the polymer backbone. The condensation of polymer-chain bound silanol groups (Polymer-Si-OH groups) with silanol groups bound to different polymer chains leads to siloxane bonds (polymer-Si-O-Si-polymer) and can be referred to as an intermolecular polymer reaction of functional groups. The reaction of the functional groups with fillers is believed to result in the formation of bonds with filler particles or, in the case of some filler particles, in electrostatic interactions, which result in more homogeneous distributions of filler within the polymer compositions. Intermolecular interaction of polymer bound functional groups with other polymer-chain backbones or with functional groups attached to other polymer chains leads to deteriorated processing

characteristics of the polymers in polymer compounds. Traditionally, processing difficulties were counteracted through the use of processing aids.

Representative uncrosslinked modified polymers exclusively comprising functional groups at one or more of the alpha-chain-end position, the omega-chain-end position, and at the branching point of polymer chains, comprise functional groups typically in a total amount from 0.0001 to 1.50 mmol/gram of polymer, in some embodiments from 0.0005 to 0.75 mmol/gram, in some embodiments from 0.0010 to 0.45 mmol/gram, and in some embodiments from 0.0020 to 0.18 mmol/gram of polymer. Representative uncrosslinked modified polymers comprising functional groups at positions different to the alpha-chain-end position, the omega-chain-end position or to the branching point of polymer chains are modified at the polymer backbone. Backbone modified polymers comprise functional groups typically in a total amount up to 5 wt%, in some embodiments up to 2.5 wt%, in some embodiments up to 1.5 wt%, and in some embodiments up to 0.75 wt% of the total polymer molecular weight.

For most applications, the modified polymer is preferably a homopolymer derived from a conjugated diolefin, a copolymer derived from a conjugated diolefin monomer with an aromatic vinyl monomer, and/or a terpolymer of one or two types of conjugated diolefins with one or two types of aromatic vinyl compounds.

Although there are no specific limitations regarding the content of 1,2-bonds and/or 3,4-bonds (hereinafter called "vinyl bonds") of the conjugation diolefin portion of the (elastomeric) polymer, for most applications, the vinyl bond content is from 10 to 90 weight percentage, and in some embodiments from 15 to 80 weight percentage (based on total weight of polymer). If the vinyl bond content in a polymer is less than 10 weight percentage, the resulting product may have inferior wet skid resistance. If the vinyl content in the (elastomeric) polymer exceeds 90 weight percentage vinyl bonds, the product may exhibit compromised tensile strength and abrasion resistance, and relatively large hysteresis loss.

Although there are no specific limitations regarding the amount of aromatic vinyl monomer used in the modified polymer, in most applications, the aromatic vinyl monomers comprise from 5 to 60 weight percentage of the total monomer content, and in some embodiments from 10 to 50 weight percentage (based on total weight of polymer). Values less than 5 weight percentage may lead to reduced wet skid properties, abrasion resistance,

and tensile strength; whereas values more than 60 weight percentage may lead to increased hysteresis loss. The modified (elastomeric) polymer may be a block or random copolymer, and in some embodiments 40 weight percentage or more of the aromatic vinyl compound units are linked singly, and 10 weight percentages or less are of "blocks" in which eight or more aromatic vinyl compounds are linked successively. Copolymers falling outside this range often exhibit increased hysteresis. The length of successively linked aromatic vinyl units can be measured by an ozonolysis-gel permeation chromatography method developed by Tanaka, et al. (*Polymer*, **1981**, *22*, 1721-1723).

While dependent upon the specific polymer(s) and upon the desired end use application, polymers including the group of modified polymers in accordance with the present teachings have, in some embodiments, a Mooney viscosity (ML 1+4, 100 °C, as measured in accordance with ASTM D 1646 (2004)), in the range from 20 to 150, and in some embodiments from 30 to 100, using a Monsanto MV2000 instrument. If the Mooney viscosity (ML 1+4, 100 °C) is less than 20, abrasion resistance and hysteresis loss properties may be compromised. Moreover, tack and cold flow of the uncrosslinked elastomeric polymer are increased, resulting in difficult handling, poor green strength, and poor dimensional stability during storage. If the Mooney viscosity (ML 1+4, 100 °C) of the polymer is more than 150 MU, processability (filler incorporation and heat build up in the internal mixer, banding on the roll mill, extrusion rate, extrudate die swell, smoothness, etc.) is negatively impacted because compounding machinery used at the manufacturer of tires are not designed to handle such high Mooney rubber grades, and the cost of processing increases.

The preferred molecular weight distribution of the modified polymer, represented by the ratio of the weight average molecular weight to the number average molecular weight, (M_w/M_n), ranges in some embodiments from 1.2 to 3.0.

In some embodiments, the one or more uncrosslinked elastomeric polymer(s)—including but not limited to the group of modified polymers—is (are) combined and reacted with secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, primary filler component(s) selected from the group consisting of silica, carbon-silica dual phase filler, carbon black, carbon nano-tube filler, lignin, in some embodiments silica and vulcanization agent, and, optionally, additional constituents including but not limited to oils, accelerators and silane coupling agents.

In some embodiments, the total elastomeric polymer present (including oil extended embodiments) in the glass powder and alternative filler comprising polymer compound comprises at least 30 weight percentage, and more preferably at least 50 weight percentage of modified elastomeric polymer. The remaining portion of the total elastomeric polymer present in the polymer compound is unmodified elastomeric polymer. Examples of preferred unmodified elastomeric polymers are listed in International Patent Publication No. WO 2009/148932 (Attorney Docket No. 66798), and in some embodiments include styrene-butadiene copolymer, natural rubbers, polyisoprene, and polybutadiene. It is desirable that non-modified polymers have a Mooney viscosity (ML 1 +4, 100 °C as measured in accordance with ASTM D 1646 (2004), as discussed above) in the range from 20 to 200, and in some embodiments from 25 to 150. In some embodiments, the composition in accordance with the present teachings includes secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler and primary fillers, which serve as reinforcement agents.

Oils

Oils may be used in combination with the uncrosslinked elastomeric polymers to reduce viscosity or Mooney values, or to improve processability of first polymer compositions in accordance with the present teachings and various performance properties of (vulcanized) second polymer compositions products in accordance with the present teachings.

The oil(s) can be added to the polymer prior to the end of the polymer preparation process and as a separate component of the first or second polymer composition preparation process in accordance with the present teachings. For representative examples and classification of the oils see International Patent Application No. PCT/US09/045553 and U.S. Patent Application Publication No. 2005/0159513, each of which is incorporated herein by reference in its entirety.

Representative oils include but are not limited to MES (Mild Extraction Solvate), TDAE (Treated Distillate Aromatic Extract), RAE (Residual Aromatic Extract) including but not limited to T-RAE and S-RAE, DAE including T-DAE and NAP (light and heavy naphthenic oils), including but not limited to Nytex 4700, Nytex 8450, Nytex 5450, Nytex 832, Tufflo 2000, and Tufflo 1200. In addition, native oils, including but not limited to

vegetable oils, can be used as extender oils. Aforementioned oils comprise different concentrations of polycyclic aromatic compounds, parafinics, naphthenics and aromatics, and have different glass transition temperatures. The above mentioned types of oil have been characterized (*Kautschuk Gummi Kunststoffe*, vol. *52*, pages 799-805). In some embodiments, the MES, RAE and TDAE are extender oils for rubber.

Processing Aids

Processing aids can be optionally added to the first polymer compositions in accordance with the present teachings. Processing aids are usually added to reduce the first polymer composition viscosity. As a result, the mixing period is decreased and/or the number of mixing steps is reduced and, consequently, less energy is consumed and/or a higher throughput in the course of the rubber compound extrusion process is achieved. Representative processing aids which can optionally be used as a component in the first polymer compositions in accordance with the present teachings are described in the *Rubber Handbook, SGF, The Swedish Institution of Rubber Technology 2000* and in Werner Kleemann, Kurt Weber, *Elastverarbeitung-Kennwerte und Berechnungsmethoden*, Deutscher Verlag für Grundstoffindustrie (Leipzig, 1990), each of which is incorporated herein by reference in its entirety. Examples of representative possessing aids which can optionally be used as component in the first polymer compositions in accordance with the present teachings can be classified as follows:

(A) fatty acids including but not limited to oleic acid, priolene, pristerene and stearinsyra;

(B) fatty acid salts including but not limited to Aktiplast GT, PP, ST, T, T-60, 8, F; Deoflow S; Kettlitz Dispergator FL, FL Plus; Dispergum 18, C, E, K, L, N, T, R; Polyplastol 6, 15, 19, 21, 23; Struktol A50P, A60, EF44, EF66, EM16, EM50, WA48, WB16, WB42, WS180, WS280 and ZEHDL;

(C) dispersing agents and processing aids including but not limited to Aflux 12, 16, 42, 54, 25; Deoflow A, D; Deogum 80; Deosol H; Kettlitz Dispergator DS, KB, OX; Kettlitz-Mediaplast 40, 50, Pertac/GR; Kettlitz-Dispergator SI; Struktol FL and WB 212; and

(D) dispersing agents for highly active white fillers including but not limited to Struktol W33 and WB42.

Bifunctionalized silanes and monofunctional silanes (herein also called "silane coupling agents") are also occasionally referred to as processing aids but are separately described below.

Silane Coupling Agent

In some embodiments, a silane coupling agent (used for compatibilization of polymer and stated fillers) is added to the composition containing modified polymer as described herein and silica or carbon-silica dual-phase filler, which is used as filler component. The typical amount of a silane coupling agent added is from about 1 to about 20 parts by weight and, in some embodiments, from about 5 to about 15 parts by weight for 100 parts by weight of the total amount of silica and/or carbon-silica dual-phase filler.

Silane coupling agents can be classified according to the *Fritz Röthemeyer, Franz Sommer: Kautschuk Technologie*, (Carl Hanser Verlag 2006):

(A) bifunctionalized silanes including but not limited to Si 230 $(EtO)_3Si(CH_2)_3Cl$, Si 225 $(EtO)_3SiCH{=}CH_2$, A189 $(EtO)_3Si(CH_2)_3SH$, Si 69 $[(EtO)_3Si(CH_2)_3S_2]_2$, Si 264 $(EtO)_3Si$-$(CH_2)_3SCN$ and Si 363 $(EtO)Si((CH_2\text{-}CH_2\text{-}O)_5\ (CH_2)_{12}\ CH_3)_2\ (CH2)_3\ SH)$ (Evonic Industries AG); and

(B) monofunctional silanes including but not limited to Si 203 $(EtO)_3$-Si-C_3H_7, and Si 208 $(EtO)_3$-Si-C_8H_{17}.

Further examples of silane coupling agents are given in International Patent Application No. PCT/US2009/045553, and include but are not limited to bis-(3-hydroxy-dimethylsilyl-propyl)tetrasulfide, bis-(3-hydroxy-dimethylsilyl-propyl)-disulfide, bis-(2-hydroxy-dimethylsilyl-ethyl)tetrasulfide, bis-(2-hydroxy-dimethylsilyl-ethyl)disulfide, 3-hydroxy-dimethylsilyl-propyl-N,N-dimethylthiocarbamoyltetrasulfide, and 3-hydroxy-dimethylsilyl-propylbenzothiazole tetrasulfide.

Vulcanization Agent

Sulfur, sulfur-containing compounds acting as sulfur-donors, sulfur-accelerator systems, and peroxides are the most common vulcanizing agents. Examples of sulfur-containing compounds acting as sulfur-donors include but are not limited to dithiodimorpholine (DTDM), tetramethylthiuramdisulphide (TMTD), tetraethylthiuramdisulphide (TETD), and dipentamethylenthiuramtetrasulphide (DPTT).

Examples of sulfur accelerators include but are not limited to amine derivates, guanidine derivates, aldehydeamine condensation products, thiazoles, thiuram sulphides, dithiocarbamates and thiophospahtes. Examples of peroxides used as vulcanizing agents include but are not limited to di-*tert.*-butyl-peroxides, di-(*tert.*-butyl-peroxy-trimethyl-cyclohexane), di-(*tert.*-butyl-peroxy-isopropyl-)benzene, dichloro-benzoylperoxide, dicumylperoxides, *tert.*-butyl-cumyl-peroxide, dimethyl-di(*tert.*-butyl-peroxy)hexane and dimethyl-di(*tert.*-butyl-peroxy)hexine and butyl-di(*tert.*-butyl-peroxy)valerate (*Rubber Handbook, SGF, The Swedish Institution of Rubber Technolgy 2000*).

Further examples and additional information regarding vulcanizing agents can be found in Kirk-Othmer, *Encyclopedia of Chemical technology 3rd, Ed.*, (Wiley Interscience, N.Y. 1982), volume 20, pp. 365-468, (specifically "Vulcanizing Agents and Auxiliary Materials" pp. 390-402).

A vulcanizing accelerator of sulfene amide-type, guanidine-type, or thiuram-type can be used together with a vulcanizing agent as required. Other additives such as zinc white, vulcanization auxiliaries, aging preventives, processing adjuvants, and the like may be optionally added. A vulcanizing agent is typically added to the polymer composition in an amount from 0.5 to 10 parts by weight and, in some embodiments, from 1 to 6 parts by weight for 100 parts by weight of the total elastomeric polymer. Examples of vulcanizing accelerators, and the amount of accelerator added with respect to the total polymer, are given in International Patent Publication No. WO 2009/148932.

Primary Fillers

The elastomeric composition in accordance with the present teachings includes primary fillers, which serve as reinforcement agents. Carbon black, silica, carbon-silica dual-phase filler, clay, calcium carbonate, magnesium carbonate, lignin, starch based fillers, and the like, and combinations thereof, are examples of suitable primary fillers. In some embodiments, the combined use of carbon black and silica, the use of carbon-silica dual-phase-fillers alone, or the combined use of carbon-silica dual-phase-filler and carbon black and/or silica are employed. Carbon black is manufactured by a furnace method and in some embodiments a nitrogen adsorption specific surface area of 50-200 m^2/g and DBP oil absorption of 80-200 ml/100 grams, for example, FEF; HAF, ISAF, or SAF class carbon black, is used. In some embodiments, high agglomeration type carbon black is used.

Carbon black is typically added in an amount from 2 to 100 parts by weight, in some embodiments from 5 to 100 parts by weight, in some embodiments from 10 to 100 parts by weight, and in some embodiments from 10 to 95 parts by weight for 100 parts by weight of the total elastomeric polymer.

Examples of silica fillers include but are not limited to wet process silica, dry process silica, synthetic silicate-type silica, and combinations thereof. Silica with a small particle diameter exhibits a high reinforcing effect. Small diameter, high agglomeration-type silica (i.e., having a large surface area and high oil absorptivity) exhibits excellent dispersability in the elastomeric polymer composition, representing desirable properties and superior processability. An average particle diameter of silica, in terms of a primary particle diameter, is in some embodiments from 5 to 60 nm, and in some embodiments from 10 to 35 nm. Moreover, the specific surface area of the silica particles (measured by the BET method) is in some embodiments from 35 to 300 m^2/g. Silica is added in an amount from 10 to 100 parts by weight, in some embodiments from 30 to 100 parts by weight, and in some embodiments from 30 to 95 parts by weight for 100 parts by weight of the total elastomeric polymer.

Carbon black and silica may be added together; in which case the total amount of carbon black and silica added is from 30 to 100 parts by weight and, in some embodiments, from 30 to 95 parts by weight for 100 parts by weight of the total elastomeric polymer. So long as such fillers are homogeneously dispersed in the elastomeric composition, increasing quantities (within the above cited ranges) result in compositions having excellent rolling and extruding processability, and vulcanized products exhibiting favorable hysteresis loss properties, rolling resistance, improved wet skid resistance, abrasion resistance, and tensile strength.

Carbon-silica dual-phase-filler may be used either independently or in combination with carbon black and/or silica in accordance with the present teachings. Carbon-silica dual-phase-filler can exhibit the same effects as those obtained by the combined use of carbon black and silica, even in the case where it is added alone. Carbon-silica dual-phase-filler is so called silica-coated-carbon black made by coating silica over the surface of carbon black, and is commercially available under the trademark CRX2000, CRX2002, or CRX2006 (products of Cabot Co.). Carbon-silica dual-phase-filler is added in the same amounts as previously described with respect to silica. Carbon-silica dual-phase-filler can be used in

combinations with other fillers including but not limited to carbon black, silica, clay, calcium carbonate, magnesium carbonate, and combinations thereof. In some embodiments, carbon black and silica, either individually or in combination, are used.

Silica, carbon black or carbon black-silica dual-phase-fillers or combinations thereof can be used in combination with natural fillers including but not limited to starch or lignin.

Examples of primary fillers are described in International Patent Application No. PCT/US2009/045553, which is incorporated herein by reference in its entirety.

In some embodiments, the silica incorporated in the rubber compound has a surface area by nitrogen adsorption (hereinafter referred to as "N2A") of from 150 to 300 m^2/g. A silica having N2A of less than 150 m^2/g leads to an unfavorably low reinforcing effect. A silica having N2A of more than 300 m^2/g provides a rubber compound with an increased viscosity and a deteriorated processability. In the case of carbon black incorporated into the rubber compound, a N2A from 60 to 150 m^2/g is suitable. A carbon black having N2A of less than 60 m^2/g leads to a low reinforcing effect. A carbon black having N2A of more than 150 m^2/g provides a rubber compound with an increased hysteresis loss and a deteriorated processability. Carbon black is typically added in an amount from 2 to 100 parts by weight, in some embodiments from 5 to 100 parts by weight, in some embodiments from 10 to 100 parts by weight, and in some embodiments from 10 to 95 parts by weight for 100 parts by weight of the total polymer.

For examples of silica filler diameters, particle sizes, and BET surfaces, see International Patent Application No. PCT/US2009/045553. In some embodiments, silica is added in an amount from 10 to 100 parts by weight, in some embodiments from 30 to 100 parts by weight, and in some embodiments from 30 to 95 parts by weight for 100 parts by weight of the total polymer.

In some embodiments, carbon black and silica are added together, in which case the total amount of carbon black and silica added is from 30 to 100 parts by weight and, in some embodiments, from 30 to 95 parts by weight for 100 parts by weight of the total polymer.

Secondary Filler

Secondary fillers are selected from the group consisting of (A1) secondary glass powder filler and (A2) zinc-doped glass powder filler.

(A1) Secondary Glass Powder Filler

Secondary glass powder fillers are made from glass foam. The glass powder filler is manufactured as a result of a high-temperature extrusion process of glass to porous, amorphous glass foam according to a method described in German Patent Application No. DE 19545065 C2, which is incorporated herein by reference in its entirety. After coarse crushing of the glass foam, the resulting intermediate product is ground and classified. There is no limitation with respect to the types of glass which can be applied to the method of secondary glass powder filler preparation and representative types include but are not limited to those types of glass described in DE 19545065 C2. In some embodiments, the type of glass is soda-lime-glass, borosilicate glass or glass compositions comprising soda-lime-glass or borosilicate glass. In some embodiments, soda-lime-glass or borosilicate glass is used. In some embodiments, borosilicate glass is used. In some embodiments, borosilicate glass filler comprises 55.0 to 60.0 percent by weight SiO_2, 8.0 to 11.0 percent by weight B_2O_3, 9.5 to 13.5 percent by weight Na_2O, 1.0 to 4.0 percent by weight K_2O, 0 to 2.0 percent by weight MgO, 1.0 to 5.0 percent by weight CaO, 4.0 to 7.0 percent by weight Al_2O_3, 2.0 to 5.0 percent by weight ZnO, and 3.0 to 6.0 percent by weight BaO. The mean diameter (d_{50}) of the glass particles made from glass foam according to DE 19545065 C2 is < 20 µm, in some embodiments < 10 µm, in some embodiments < 5 µm and in some embodiments < 3 µm. The moisture content of the glass powder filler is lower than 0.5 percent by weight. Soda-lime-glass in some embodiments comprises 71.0 to 74.0 percent by weight SiO_2, 9.0 to 14.0 percent by weight Na_2O, 0 to 1.0 percent by weight K_2O, 1.5 to 4.0 percent by weight MgO, 9.0 to 13.5 percent by weight CaO, and 1.0 to 2.5 percent by weight Al_2O_3. The mean diameter (d_{50}) of the glass particles made from glass foam according to DE 19545065 C2 is < 20 µm, in some embodiments < 10 µm, in some embodiments < 5 µm and in some embodiments < 3 µm. The moisture content of the glass powder filler is lower than 0.5 percent by weight. The BET-surface of the glass particles made from glass foam according to DE 19545065 C2 is > 0.5 m^2/g, in some embodiments > 1 m^2/g and in some embodiments > 2 m^2/g.

Secondary glass powder filler is typically added in an amount from 0.1 to 100 parts by weight and, in some embodiments, from 0.5 to 60 parts by weight for 100 parts by weight of the total polymer.

In some embodiments, secondary glass powder filler is typically added in an amount

from 0.5 to 30 parts by weight for 100 parts by weight of the total polymer.

In some embodiments, secondary glass powder filler is typically added in an amount from 30 to 60 parts by weight for 100 parts by weight of the total polymer.

In some embodiments, zinc-doped secondary glass powder filler is added in an amount from 0.5 to 15 parts by weight for 100 parts by weight of the total polymer.

Optionally, the glass particles can be doped with aluminium salt to (i) change the silanol group density on the secondary glass powder filler surface or to (ii) change the pH value of the secondary glass powder filler. Optionally, secondary glass powder fillers can be used as support for vulcanization accelerators including but not limited to CBS (N-cyclohexyl-2-benzothiazylsulfenamid sold under the tradename Vulcacit CZ/EG), and subsequently applied to the preparation of the first polymer compound or to the preparation of the second polymer compound.

(A2) Secondary Zinc-Doped Glass Powder Filler

Secondary zinc-doped glass powder fillers comprise an increased concentration of zinc-ions with the additional zinc-ions in some embodiments being located in the pores of the filler. The secondary zinc-doped glass powder fillers are made from secondary glass powder fillers of relatively lower zinc concentration or from secondary glass powder fillers not comprising zinc. Therefore, the choice of glass subsequently used for the preparation of secondary glass powder filler of relatively lower zinc-ion concentration also applies for zinc-doped secondary glass powder filler with relatively higher zinc-ion concentration. Thus, there is once again no limitation with respect to the types of glass which can be applied to the preparation of zinc-doped secondary glass powder filler of relatively high zinc-ion concentration via secondary glass powder filler with relatively low zinc-ion concentration as an intermediate. In some embodiments, soda-lime-glass, borosilicate glass or glass compositions comprising soda-lime-glass or borosilicate glass are used. In some embodiments, soda-lime-glass or borosilicate glass is used. In some embodiments, borosilicate glass is used.

The secondary zinc-doped glass powder fillers can be made, for example, from secondary glass powder fillers of relatively lower zinc concentration through subsequent treatment with an aqueous zinc salt solution. The selected secondary glass powder filler of relatively low zinc-ion concentration is mixed with a solution of a water soluble zinc salt. Zinc salts useful for the glass powder modification include all soluble zinc salts, with

representative examples including but not limited to zinc bromide, zinc sulphate, zinc iodide, zinc fluoride, zinc nitrate, zinc chloride and organic zinc salts including but not limited to zinc acetate. In some embodiments, zinc chloride solution is used. The concentration of the zinc salt in water, given as an example for zinc chloride, ranges in some embodiments from 5 to 1000 mmol (zinc chloride)/mL of water, and in some embodiments from 50 to 200 mmol (zinc chloride) / mL of water. After mixing, the aqueous zinc solution comprising glass powder is dried in an oven. After drying, the moisture content of the resulting zinc-doped secondary glass powder filler is lower than 0.5 percent by weight. The zinc fraction which has been added as aqueous zinc salt solution is in some embodiments accumulated in the pores and on the surface of the glass particles. The concentration of zinc located in pores and on the surface of the glass particles amounts to 0.2 to 30 percent by weight, in some embodiments to 0.5 to 20 percent by weight, and in some embodiments to 1 to 10 percent by weight of the glass. Zinc potentially located in the bonding structure of glass is not soluble and not derived from zinc added as aqueous solution. In the case of borosilicate glass or soda-lime-glass, the composition corresponds to those described above in the section entitled "Secondary Glass Powder Filler". The mean diameter (d_{50}) of the zinc-doped secondary glass powder filler particles comprising zinc is < 20 µm, in some embodiments < 10 µm, in some embodiments < 5 µm, and in some embodiments < 3 µm. The BET-surface of the zinc-doped secondary glass powder filler particles comprising zinc is > 0.5 m^2/g, in some embodiments > 1 m^2/g, and in some embodiments > 2 m^2/g.

Those zinc-ions in zinc-doped secondary glass powder fillers located in the filler pores are relatively well distributed and act as activator of typical vulcanization accelerators. Therefore, state of the art zinc oxide can be replaced as a component in the first polymer compositions in accordance with the present teachings. Due to the relatively higher activity of the zinc-ions in zinc-doped secondary glass powder filler with respect to the relatively lower activity of zinc added to the first polymer composition as zinc oxide, the total zinc concentration can be reduced in the process of the preparation of the second polymer composition (vulcanized polymer composition) in accordance with the present teachings. The more uniform distribution of the zinc-ions in the pores of zinc-doped secondary glass powder filler with respect to the less uniform distribution of zinc added as zinc oxide can be an explanation for the increased activation efficiency towards typical vulcanization accelerators in the course of the vulcanization process.

Polymer Composition

The polymer composition in accordance with the present teachings can be prepared by kneading the above-described polymers (including oil extended varieties), in some embodiments comprising modified polymers (including oil extended varieties), primary fillers (carbon black, silica, carbon-silica dual-phase filler, etc.), secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, optionally processing aids, oils, silane coupling agents, and other additives, in a kneader at 140 °C to 180 °C, to form a filler containing formulation.

Alternatively, polymer compositions in accordance with the present teachings can be prepared by kneading the above-described polymers (including oil extended varieties) already comprising the secondary fillers selected from the group consisting of secondary glass powder fillers and zinc-doped glass powder fillers with primary fillers (carbon black, silica, carbon-silica dual-phase filler, etc.) and, optionally, with processing aids, oils, silane coupling agents, and other additives in a kneader at 140 °C to 180 °C to form a filler containing formulation. In some embodiments, the polymer composition can be prepared by kneading the above-described modified polymers (including oil extended varieties) already comprising the secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler with primary fillers (carbon black, silica, carbon-silica dual-phase filler, etc.) and, optionally, with processing aids, oils, silane coupling agents, and other additives in a kneader at 140 °C to 180 °C to form a filler containing formulation.

Polymer compositions already comprising the secondary fillers selected from the group consisting of secondary glass powder fillers and zinc-doped glass powder fillers are prepared by adding the secondary fillers into a polymer solution (e.g., during agitation) followed by an azeotropic (solvent/water-steam) solvent removal process, followed by drying the secondary filler comprising polymer at an elevated temperature.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 30-60 parts by weight, in some embodiments 30-45 parts by weight, for 100 parts by weight of the total polymer of a secondary glass powder filler, 10-100 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of silica, 30-90 parts by weight, in some embodiments 40-80 parts by

weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene, and 1-25 parts by weight, in some embodiments 3-15 parts by weight, of a silane coupling agent.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 0.5-30 parts by weight, in some embodiments 3-20 parts by weight, for 100 parts by weight of the total polymer of a secondary glass powder filler, 10-110 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of silica, 30-95 parts by weight, in some embodiments 40-80 parts by weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-25 parts by weight, in some embodiments 3-15 parts by weight of a silane coupling agent.

In another embodiment a polymer composition in accordance with the present teachings comprises at least 0.1-25 parts by weight, in some embodiments 0.5-15 parts by weight, for 100 parts by weight of the total polymer of a zinc-doped secondary glass powder filler, 10-110 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of silica, 30-95 parts by weight, in some embodiments 40-80 parts by weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-25 parts by weight, in some embodiments 3-15 parts by weight, of a silane coupling agent.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 0.5-30 parts by weight, in some embodiments 3-20 parts by weight, for 100 parts by weight of the total polymer of a secondary glass powder filler, 10-110 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of

the total polymer of carbon black, 30-95 parts by weight, in some embodiments 40-80 parts by weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, preferably 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-50 parts by weight, in some embodiments 3-30 parts by weight, of an oil.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 0.5-30 parts by weight, in some embodiments 3-20 parts by weight, for 100 parts by weight of the total polymer of a zinc-doped secondary glass powder filler, 10-110 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of carbon black, 30-95 parts by weight, in some embodiments 40-80 parts by weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-50 parts by weight, in some embodiments 3-30 parts by weight, of an oil.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 30-60 parts by weight, in some embodiments 30-45 parts by weight, for 100 parts by weight of the total polymer of a secondary glass powder filler, 10-100 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of carbon black, 30-90 parts by weight, in some embodiments 40-80 parts by weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-50 parts by weight, in some embodiments 3-30 parts by weight, of an oil.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 0.5-30 parts by weight, in some embodiments 3-20 parts by weight, for 100 parts by weight of the total polymer of a secondary glass powder filler, 10-100 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of

the total polymer of silica and carbon black, 30-95 parts by weight, in some embodiments 40-80 parts by weight for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-20 parts by weight, in some embodiments 3-12 parts by weight, of a silane coupling agent.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 0.5-30 parts by weight, in some embodiments 3-20 parts by weight, for 100 parts by weight of the total polymer of a zinc-doped secondary glass powder filler, 10-100 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of silica and carbon black, 30-95 parts by weight, in some embodiments 40-80 parts by weight for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-20 parts by weight, in some embodiments 3-12 parts by weight, of a silane coupling agent.

In some embodiments, a polymer composition in accordance with the present teachings comprises at least 30-60 parts by weight, in some embodiments 30-45 parts by weight, for 100 parts by weight of the total polymer of a secondary glass powder filler, 10-100 parts by weight, in some embodiments 30-95 parts by weight, for 100 parts by weight of the total polymer of silica and carbon black, 30-90 parts by weight, in some embodiments 40-80 parts by weight, for 100 parts by weight of the total polymer content of a polymer selected from the group consisting of SBR, SIR, S-SBR or S-SIR; 5-60 parts by weight, in some embodiments 10-50 parts by weight, for 100 parts by weight of the total polymer of a polymer selected from the group consisting of polybutadiene, polyisoprene or natural rubber or conjugated polydiene and 1-20 parts by weight, in some embodiments 2-10 part by weight of a silane coupling agent.

Optionally, the typical primary filler content is reduced when secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler is added to the polymer composition. By way of example and not limitation, if

20 parts by weight of secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler is added as a component to the polymer composition, the primary filler content (silica, carbon black, silica-carbon black dual filler) in the polymer composition can be optionally reduced by 20 parts by weight for 100 parts by weight of the total polymer content in a polymer composition. If, in a polymer composition, the silica filler content is reduced as result of the secondary filler addition, there is the option to reduce the silane coupling agent concentration of the polymer composition as well. The silane coupling agent concentration is usually calculated with respect to the surface area of all silicon-hydroxy (Si-OH) groups containing fillers comprised in the polymer composition. Therefore, in an exemplary polymer composition in accordance with the present teachings comprising silica and secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, the silane coupling agent concentration can be calculated with respect to the surface area of the total silica and secondary glass powder filler present in the polymer composition. Due to the reduced surface area of the secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler compared with the silica surface area, the silane coupling agent concentration can be reduced. Therefore, beneficially, expenses on silane coupling agents can be saved, when secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler is applied as a constituent to a silica-containing polymer composition.

After cooling, vulcanizing agents, such as sulfur, vulcanizing accelerators, and the like, are added to the aforementioned filler-containing formulation, and the resulting mixture is blended using a Brabender mixer, Banbury mixer or open roll mill to form the desired shape, and the mixture is vulcanized at 140 °C to 180 °C, to obtain a vulcanized article.

Because the vulcanized elastomeric second polymer compositions in accordance with the present teachings exhibit low rolling resistance, low dynamic heat build up, and superior wet skid performance, the secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, and primary fillers comprising polymer compositions in accordance with the present teachings, and preferably compositions containing modified polymers as described herein, secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, and primary filler, vulcanization agents, and the vulcanized elastomeric second polymer compositions,

are well suited for use in preparing tires, tire treads, side walls, and tire carcasses, as well as other industrial products such as belts, hoses, vibration dampers, and footwear components.

In some embodiments, a composition in accordance with the present teachings comprising at least (A) secondary filler selected from the group consisting of (A1) secondary glass powder filler and (A2) zinc-doped glass powder filler, (B) primary filler component(s) selected from the group consisting of silica, carbon-silica dual-phase filler, carbon black, carbon nano-tube filler, lignin (in some embodiments silica), and (C) one or more types of polymers including but not limited to the group of modified polymers is used for vulcanized (or cross-linked) elastomeric polymer compositions, and articles made from such compositions, such as pneumatic tires, tire treads, belts, footwear components, and the like.

The second polymer compositions (or cross-linked polymer compositions or vulcanized polymer compositions) in accordance with the present teachings comprising secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler exhibit lower Tan δ at 60 °C values or higher Tan δ at 0 °C values, and a good balance of physical properties including but not limited to one or more of abrasion resistance, tensile and tear strength, modulus, and heat buildup when compared with second polymer compositions (or cross-linked polymer compositions) not comprising secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler.

The second polymer compositions in accordance with the present teachings also exhibit lower Tan δ at 60 °C values, higher Tan δ at 0 °C values or higher Tan δ at -10 °C values, and a good balance of physical properties including but not limited to one or more of abrasion resistance, tensile and tear strength, modulus, and heat buildup when in the first polymer compositions in accordance with the present teachings at the same time silica is partially replaced by secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, and the silane coupling agent concentration is reduced. Therefore, the second polymer compositions in accordance with the present teachings can be manufactured by using a reduced amount of relatively expensive silane coupling agent.

The compositions in accordance with the present teachings are useful in preparing tire treads having lower rolling resistance, higher wet grip, higher ice grip, and/or lower heat buildup while maintaining good wear properties. Therefore, compositions in accordance

with the present teachings are useful in preparing tires with improved fuel economy and safety in terms of a reduced braking distance.

Furthermore, first polymer compositions (compositions prior to vulcanization comprising uncrosslinked elastomeric polymers) in accordance with the present teachings comprising secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler exhibit improved processing characteristics as represented by decreased first polymer composition Mooney value, when compared with first polymer compositions not comprising secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler. Therefore, the composition in accordance with the present teachings exhibits improved processing characteristics for tire manufacturers. The improved processing characteristic leads to a reduced mixing period and a higher throughput in the course of the rubber compound extrusion process. The compositions in accordance with the present teachings including secondary filler selected from the group consisting of secondary glass powder filler and zinc-doped glass powder filler, primary fillers such as silica, carbon black, carbon nano-tube, carbon-silica dual, phase filler, softener, vulcanizing agents and the like, and the (vulcanized elastomeric) second polymer compositions in accordance with the present teachings are particularly useful in the preparation of tires.

The present teachings also provide a method to replace zinc oxide added in powder form to first polymer compositions through the application of zinc-doped secondary glass powder filler. Therefore, the handling of powdery zinc oxide, which is classified as environmentally dangerous according to EG 67/548/EEC, in the process of the preparation of first polymer compositions can be avoided.

The present teachings further provide second polymer compositions (and first polymer compositions) with reduced zinc concentration. Zinc, provided through the application of zinc-doped secondary glass powder filler in the first polymer compositions in accordance with the present teachings more efficiently activates typical vulcanization accelerators. Therefore, the total zinc concentration required for performing the vulcanization of first polymer compositions can be reduced if zinc oxide is replaced by zinc-doped secondary glass powder filler.

The present teachings also provide an article comprising at least one component formed from a composition in accordance with the present teachings. In some embodiments,

the article comprises a tire. In some embodiments, the article comprises a tire tread. In some embodiments, the article comprises a tire side wall. In some embodiments, the article comprises an automotive part. In some embodiments, the article comprises a footwear component. In some embodiments, the inventive article comprises a belt, a gasket, a seal, or a hose.

For producing vehicle tires, the following polymers are of particular interest: natural rubber; emulsion SBR and solution SBR rubbers with a glass transition temperature above -50 °C; polybutadiene rubber with a high cis 1,4-unit content (>90%), which has been prepared using catalysts based on nickel, cobalt, titanium, vanadium, gadolinium or neodymium; and polybutadiene rubber with a vinyl content of 0 to 75%; and combinations thereof.

Furthermore, for producing vehicle tires, the following polymers are of particular interest: polybutadiene rubber with a high trans 1,4-unit content (>75%), or SBR containing in some embodiments between 5 and 40 wt% styrene and a high trans 1,4-polybutadiene content (>75%) of the polybutadiene fraction of the copolymer, and in which each type of polymer (SBR or BR) has been prepared with one or more initiator compounds comprising earth alkaline metal compounds, such as described for example in U.S. Patent Nos. 6,693,160; 6,627,715; 6,489,415; 6,103,842; 5,753,579; 5,086,136; and 3,629,213—each of which is hereby incorporated herein by reference in its entirety—or by using catalysts based on cobalt, such as described for example in U.S. Patent Nos. 6310152; 5,834,573; 5,753,761; 5,448,002 and 5,089,574, and U.S. Patent Application Publication No. 20030065114—each of which is hereby incorporated herein by reference in its entirety—or by using catalysts based on vanadium, such as described for example in European Patent Application No. 1367069; Japanese Patent Application No. 11301794 and U.S. Patent No. 3951936—each of which is hereby incorporated herein by reference in its entirety—or by using catalysts based on neodymium, such as described, for example, in European Patent Application Nos. EP0964008 and EP0924214 and in U.S. Patent Nos. 6,184,168; 6,018,007; 4931376; 5,134,199 and 4,689,368—each of which is hereby incorporated herein by reference in its entirety.

For a vulcanized polymer, the gel content in some embodiments is greater than 50 weight percent, in some embodiments greater than 75 weight percent, and in some embodiments greater than 90 weight percent based on the weight of the polymer. Gel

content can be determined by dissolving about 0.2 grams of polymer in 150 ml of toluene for 24 hours at ambient temperature, separating the insolubles, drying the insolubles, and measuring the amount of insolubles.

As used herein, the term "alkyl" refers to at least one aliphatic group, and may also refer to two or more aliphatic groups. The alkyl group may be linear, branched, cyclic, or a combination thereof, and saturated or unsaturated. In some embodiments, the alkyl group is linear, branched, cyclic or a combination thereof, and saturated. In some embodiments, the alkyl group is linear and saturated or branched and saturated. The term "alkyl" is understood to include both straight chain aliphatic hydrocarbon groups, (for example, methyl (Me), ethyl (Et), n-propyl (Pr), n-butyl (Bu), n-pentyl, n-hexyl, etc.), branched aliphatic hydrocarbon groups (for example, isopropyl, tert-butyl, etc.), and carbon-based non-aromatic rings aliphatic hydrocarbon groups. In some embodiments, "alkyl" refers to saturated linear, branched, cyclic, or combinations thereof, aliphatic hydrocarbon groups, and unsaturated, linear, branched, cyclic, or combinations thereof, aliphatic hydrocarbon groups.

The term "alkoxy" is understood to include methoxy (MeO), ethoxy (EtO), propoxy (PrO), butoxy (BuO), isopropoxy (*i*PrO), isobutoxy (*i*BuO), pentoxy, and the like.

As used herein, the term "aralkyl" refers to at least one aromatic ring, and also at least one alkyl group. The term "aralkyl" is understood to mean an aryl group bonded to an alkyl.

The phrase "hydrocarbon groups" is understood to include any group, including saturated, unsaturated, linear, branched, cyclic, aromatic groups, which only consist of the elements hydrogen and carbon.

EXAMPLES

The following examples and representative procedures illustrate features in accordance with the present invention, and are provided solely by way of illustration. They are not intended to limit the scope of the appended claims or their equivalents. The Examples include the preparation of the glass fillers, the preparation of polymers, and the preparation and testing of uncrosslinked, as well as cross-linked, polymer compositions. Unless stated to the contrary, all parts and percentages are expressed on a weight basis. The polymerizations were performed under the exclusion of moisture and oxygen, in a nitrogen

atmosphere. Various methods were used to test and measure the examples. A brief description of each technique is provided.

(I) Polymer Analysis & Characterization

The ratio between the 1.4-cis-, 1.4-trans-, and 1.2-polydiene content of the butadiene polymers or styrene-butadiene copolymers was determined by IR, ^{1}H-NMR- and ^{13}C-NMR-spectroscopy [NMR (Avance 400 device (^{1}H = 400 MHz; ^{13}C = 100 MHz) of Bruker Analytic GmbH]. The vinyl content in the conjugated diolefin part was additionally determined by IR absorption spectrum (Morello method, IFS 66 FT-IR spectrometer of Bruker Analytic GmbH). The IR samples were prepared using CS_2 as swelling agent.

Bonded styrene content: A calibration curve was prepared by IR absorption spectrum (IFS 66 FT-IR spectrometer of Bruker Analytik GmbH). The IR samples were prepared using CS_2 as swelling agent. For the IR determination of the bound styrene in styrene-butadiene copolymers are four bands viewed: a) band for trans-1.4-polybutadiene units at 966 cm^{-1}, b) band for cis-1.4-polybutadiene units at 730 cm^{-1}, c) band for 1.2-polybutadiene units at 910 cm^{-1} and band for bound styrene (styrene aromatic bond) at 700 cm^{-1}. The band heights are normed according to the appropriate extinction coefficients and summarized to a total of 100%. The normation is done via ^{1}H- and ^{13}C-NMR. The styrene content was alternatively determined by NMR technique [Avance 400 device (^{1}H = 400 MHz; ^{13}C = 100 MHz) of Bruker Analytik GmbH].

Aromatic vinyl content was determined by NMR technique [Avance 400 device (^{1}H = 400 MHz; ^{13}C = 100 MHz) of Bruker Analytik GmbH].

The 1D NMR spectra were collected on a Bruker Avance 200 NMR spectrometer (BRUKER BioSpin GmbH) using a 5 mm dual detection probe. The field homogeneity was optimized by maximizing the deuterium lock signal. The samples were shimmed by optimizing the deuterium lock signal. The samples were run at room temperature (298 K). The following deuterated solvents were used: C6D6 (7.15 ppm for 1H; 128.02 ppm for 13C), $CDCl_3$ (7.24 ppm for 1H; 77.03 ppm for 13C), d_8-THF (1.73, 3.58 ppm for 1H; 25.35 ppm for 13C), the signals of the remaining protons of deuterated solvents were each used as an internal reference.

For spectral processing, the BRUKER 1D WINNMR software (version 6.0) was used. Phasing, base line correction, and spectral integration of the resulting spectra were done in the manual mode. For acquisition parameters see Table 1.

Table 1: 1D-NMR Acquisition Parameters Using BRUKER Standard Pulse Sequences

	1H-NMR	13C-NMR
Observe frequency	200.130 MHz	50,323 MHz
Spectral width	4139.073 Hz	12562.814
BRUKER Pulse program	Zg30	Zgpg30
Pulse angle	30°	30°
Relaxation delay	1.0 s	2.0 s
Number of Data points for FT	32 K	32 K
Line broadening	0.5 Hz	1 Hz
Number of accumulated scans	64	> 1000

GPC-Method: SEC calibrated with narrow distributed polystyrene standard.

Sample preparation:

a1) Oil free polymer samples:

About 9-11 mg dried polymer sample (moisture content < 0.6%) was dissolved in 10 mL tetrahydrofurane, using a brown vial of 10 mL size. The polymer was dissolved by shaking the vial for 20 min at 200 rpm.

a2) oil containing polymer samples:

About 12-14 mg dried polymer sample (moisture content < 0.6%) was dissolved in 10 mL tetrahydrofurane, using a brown vial of 10 mL size. The polymer was dissolved by shaking the vial for 20 min at 200 u/min.

b) Polymer solution was transferred into a 2 mL vial using a 0.45 µm disposable filter.

c) The 2 mL vial was placed on a sampler for GPC-analysis.

Elution rate: 1.00 mL/min

Injection volume: 100.00 µm (GPC-method B 50.00 µm)

The measurement was performed in THF at 40 °C. Instrument: Agilent Serie 1100 /1200; Module setup: Iso pump, autosampler, thermostate, VW - Detector, RI - Detector, Degasser; Columns PL Mixed B / HP Mixed B.

In each GPC-device three columns were used in a connected mode. The length of each of the columns: 300 mm; Column Type: 79911 GP- MXB, Plgel 10 µm MIXED-B GPC/SEC Columns, Fa. Agilent Technologies

GPC Standards: EasiCal PS-1 Polystyrene Standards, Spatula A + B

Styrene Standard Manufacturer:

Polymer Laboratories

Now entity of Varian, Inc. Varian Deutschland GmbH

Website: http://www.polymerlabs.com

Polydispersity (Mw/Mn) was used as a measure for the width of molecular weight distribution. The calculation of Mw and Mn (weight average molecular weight (Mw) and number average molecular weight (Mn)), was based on one of two procedures.

The Mp1, Mp2, Mp3 correspond to the (maximum peak) molecular weight measured at the first, second or third peaks of the GPC curve [the first peak Mp1 (lowest molecular weight) is located on the right side of the curve, and the last peak (highest molecular weight) is located on the left side of the curve], respectively. Maximum peak molecular weight means the molecular weight of the peak at the position of maximum peak intensity. The Mp2 and Mp3 are two or three polymer chains coupled to one macromolecule. Mp1 is one polymer chain (base molecular weight—no coupling of two or more polymer chains to one macromolecule).

The total coupling rate represents the sum of the weight fractions of coupled polymers relative to the total polymer weight, including the sum of the weight fractions of all coupled polymers and the uncoupled polymer. The total coupling rate is calculated as shown below.

CR(total) = (∑Area fraction of all coupled peaks [Peak with maximum Mp2 to peak with highest indexed peak maximum])/(∑Area fraction of all peaks [Peak with peak maximum Mp1 to peak with highest indexed peak maximum]).

The individual coupling rate (e.g. two polymer arms coupled corresponding to the peak with peak maximum Mp2) is calculated as depicted below

CR(2arms) = (Area fraction of peak with peak maximum Mp2)/ (∑Area fraction of all peaks [Peak with peak maximum Mp1 to peak with highest indexed peak maximum]).

The Mooney viscosity of the polymer was measured according to ASTM D 1646 (2004), with a preheating time of one minute and a rotor operation time of 4 minutes, at a temperature of 100 °C [ML1+4(100 °C)], on a MV 2000E from Alpha Technologies UK. The rubber Mooney viscosity measurement is performed on dry (solvent free) raw polymer (*non*-vulcanized rubber).

(II) Secondary Glass Powder Filler and Zinc-Doped Glass Powder Filler Grade Analysis and Characterization

The composition of the glass grades was determined through atomic absorption spectroscopy on a Nova AA 350 from Analytik Jena AG and X-ray fluorescence analysis using a SEA 1200VX from Seiko Instruments Inc. according to DIN ISO 52340.

The particle size of the glass particles was determined through application of laser diffraction using a Sympatec Helos device (Type H2023) according to DIN ISO 1332-1. D50 is the particle size, when 50 percent of the particles have smaller or equal size. D99 is the particle size, when 99 percent of the particles have smaller or equal size.

The pH-value was determined by using an aqueous solution (also called eluate) prepared from 10 g glass powder and 90 g distilled water. The pH-value measurement was performed at room temperature following DIN EN ISO 787-9. The pH-value was determined using a PM 2000 with pH-electrode from the company Ingenieurgesellschaft GmbH.

The conductivity was determined by using an aqueous solution (also called eluate) prepared from 10 g glass powder and 90 g distilled water. The conductivity was measured at room temperature according to DIN EN ISO 787-14 using the device PM 2000 with a conductivity-measuring cell from the company Ingenieurgesellschaft mbH.

The moisture content of the glass particles was determined according to ISO 787-2 after two hours drying of the glass samples in a drying chamber of VEB Elektroindustrieofenbau Römhild type RE 100 at a temperature of 105 °C.

BET (Brunauer, Emmett and Teller) nitrogen surface area of glass was determined with a gas adsorption meter of Ströhlein Kaarst, model Bb, according to DIN ISO 9277. Void volume and pore diameter of the glass particles were determined with mercury porosimetry of Thermo Electro Corporation Mailand, Type Pascal 140.

The density of silanol groups on the glass surface was determined by acid-base-titration, according to the description by G. W. Sears (see analytical Chemistry, Volume 28, No. 12, 1956). The determination method is based on the chemical reaction below, "Si-OH" representing silanol groups on the glass particle surface:

$$Si\text{-}OH + NaCl \Rightarrow Si\text{-}ONa + HCl\ ;\ HCl + KOH \Rightarrow KCl + H2O.$$

The OH groups are detected according to the above stated method, also called SEARS number (titration).

(III) Polymer Compound Preparation Equipment, Analysis and Characterization

Rubber compounds were prepared by combining the constituents listed below in Tables 6 to 17, in a laboratory mixer Brabender Plasticorder PL 2000 (Brabender GmbH & Co. KG, Duisburg, Germany) with a thermostat heated mixing chamber N50 with Banbury rotors and a chamber volume of 75 cm^3 following a two-stage mixing process.

During stage 1, all components were mixed together, except the components of the vulcanization package, to form a stage 1 formulation. In stage 2, the components of the vulcanization package were mixed into the stage 1 formulation to form a stage 2 formulation. The energy input W5 measured in kJ during the two mixing steps is listed in Tables 20, 23, 25 and 28.

The vulcanization curve and rubber compound viscosity was measured with a rotorless vulcameter Goettfert Elastograph, type: Vario according to ASTM D5269 and ISO 6502 (Goettfert Werkstoffprüfmaschinen GmbH, Buchen, Germany, Frequency 50 min^{-1}, operation angle 0.5°, gap 150 micrometer, temperature 160 °C). The scorch time (TS2) and time to cure (TC90) are listed in Tables 20, 23, 25 and 28.

The rheometer measurements were performed at a constant temperature of 160 °C on the unvulcanized second stage polymer formulations, according to Tables 20, 23, 25 and 28. The amount of polymer sample is about 4.6 g. Sample shape and shape preparation are standardized and defined by the measurement device (vulcameter Goettfert Elastograph, type Vario, see above).

Measurement of unvulcanized rheological properties according to Table 31 was performed according to ASTM D 5289-95 (reapproved 2001), using a rotor-less shear rheometer (MDR 2000 E from Alpha Technologies UK) to measure Scorch Time (TS) and Time to Cure (TC).

The "TC 90" is the respective time required to achieve 90% conversion of the vulcanization reaction. The torque is measured as a function of time of reaction. The vulcanization conversion is automatically calculated from the generated torque versus time curve. The "TS 2" is the respective time required to increase the torque by 0.02 Nm above the respective torque minimum (ML) during vulcanization. Preferably TS 2 is > 2.5 minute (listed in Tables 20, 23, 25 and 28) and TC 90 (listed in Tables 20, 23, 25 and 28) is from 8 to 19 minutes.

All mechanical property tests on cured (vulcanized) materials were performed with specimens from vulcanized plates. The rubber mixtures were prepared during a two-stage process with compositions according the Tables 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 and 17. The vulcanization of plates was performed for a period of 16 to 25 minutes at a temperature of 160 °C to TC 90 (90% vulcanization conversion; see cure data in Tables 20, 23, 25 and 28). The process leads to the formation of visually "bubble free," homogeneous cured rubber plates of 100 mm x 100 mm x 2 mm for DMA tests, tensile tests, tear tests, instrumented tensile-impact tests and Shore A hardness testing and discs of 60 mm diameter and 10 mm height for abrasion tests. The specimens of the necessary geometry were prepared out of the aforementioned plates by punching and drilling out (abrasion test), respectively. Tables 21, 24, 26 and 29 summarize the results of the tensile and tear tests, of hardness testing, as well as of toughness tests.

Tensile strength σ_M, elongation at break ε_R and stress at 100% and 300% strain ("modulus 100" and "modulus 300"; σ_{100}, σ_{300}) were determined by tensile tests according to ISO 37 (2005-07), using S2 dumbbell test specimens on a ZWICK Z020 universal testing machine. Furthermore, the maximum stress σ_M (tensile strength) as well as the tensile strain at break ε_R were determined for each specimen. The tensile tests were performed at room temperature with five (5) specimens for each material. The tensile strength should be at least 12 MPa and the tensile strain at break at least 400%. Tables 21, 24, 26 and 29 summarize the results of the tensile tests.

The hardness testing was performed according to DIN 53505 (2000-08) at room temperature with the Shore A tester ZWICK 3150. As a result, the Shore A hardness was determined as the mean value of 10 single measurements for each material. For the tests, 3 pieces of the material were stacked to reach the minimum thickness for the test of 6 mm. The minimum value of the Shore A hardness should be 60. Tables 21, 24, 26 and 29 summarize the results of the hardness testing.

The tear resistance T_S was determined at room temperature according to ISO 34-1 (2005-07) by using the universal testing machine ZWICKI. The crosshead speed was 100 mm/min, and for each material, 5 trouser specimens with a thickness of 2 mm were used. Tables 21, 24, 26 and 29 summarize the results of the tear tests.

For a complete description of the mechanical property level, also the toughness of the materials expressed as a J_d value was characterized. For this purpose, instrumented tensile-

impact tests were performed by using the instrumented pendulum device CEAST RESIL IMPACTOR Junior 25 with the data acquisition system DAS 4000 and the software DAS4win. For the tests, strips with the dimensions 64 mm x 10 mm x 2 mm (length, width and thickness) were cut from plates. Afterwards, razor blade notches of 2 mm depth were made on each side of the specimen to get the typical double-edge notched tension specimen geometry. For each material, 10 specimens were prepared. For the performance of the test, the specimen was clamped so that it lay horizontally in the direction of the pendulum hammer motion between the unsecured crosshead and the fixed clamping device. The specimens were loaded indirectly by the impact of the unsecured crosshead by the pendulum hammer. The pendulum hammer speed was 3.7 m/s. As a result of the test, a load-extension diagram was recorded for each specimen. These diagrams were analyzed as follows. The maximum load F_{max} and the corresponding extension l_{max} were determined as measuring values. From the area under the load-extension curve up to F_{max} the energy value A_{max} was determined which is the basis for the calculation of the J_d value according to the following equation:

$$J_d = \frac{\eta A_{max}}{B(W-a)}$$

with the geometry function

$$\eta = -0.06 + 5.99\left(\frac{a}{W}\right) - 7.42\left(\frac{a}{W}\right)^2 + 3.29\left(\frac{a}{W}\right)^3.$$

Tan δ at 60 °C and Tan δ at 0 °C measurements were performed on rectangular specimens (10 mm x 2 mm) using a dynamic mechanical thermal spectrometer Eplexor 500 N manufactured by Gabo Qualimeter Testanlagen GmbH, Ahlden, Germany, by applying a tensile pre-strain of 10%, a dynamic tensile strain of 1%, a heating rate of 1 K/min and frequency 10 Hz, at the respective temperatures. The smaller the index at a temperature of 60 °C, the lower is the rolling resistance (lower = better). Tan δ (0 °C) was measured using the same equipment and load conditions at 0 °C. The larger the index at this temperature, the better the wet skid resistance (higher = better). Tan δ at 60 °C and Tan δ at 0 °C index values are summarized in Tables 22, 25, 27 and 30.

For rubber compounds listed in Table 19, vulcanization characteristics listed in Table 30 and mechanical properties of rubber compounds vulcanizates listed in Table 31 were different mixing equipment, test instruments or test conditions applied. Deviations in terms

of rubber compound or rubber compound vulcanizate preparation or different measurement or testing conditions are listed below when applicable.

Rubber compounds were prepared by combining the constituents listed below in Table 18 and 19 in a "380 cc Banbury mixer (Labstation 350S from Brabender GmbH&Co KG)," following a two-stage mixing process.

The Mooney viscosity of the rubber compound was measured according to ASTM D 1646 (2004), with a preheating time of one minute and a rotor operation time of 4 minutes, at a temperature of 100 °C [ML1+4(100 °C)], on a MV 2000E shear disc-viscosimeter from Alpha Technologies UK. The rubber Mooney viscosity measurement is performed on an uncured (unvulcanized) second state polymer compound sample prepared according to Tables 18 and 19. The Compound Mooney values are listed in Table 31.

Measurement of unvulcanized rheological properties on finalized first stage rubber compounds prepared according to Tables 18 and 19 was performed according to ASTM D 5289-95 (reapproved 2001) using a rotor-less shear rheometer (MDR 2000 E from Alpha Technologies UK; MDR = Moving Disc Rheometer) to measure Scorch Time (TS) and Time to Cure (TC). The rheometer measurement was performed at a constant temperature of 160 °C on an unvulcanized second stage polymer formulation, according to Table 31.

The unvulcanized first stage rubber compound rheological properties are listed in Table 31. The "TC 50" is the respective time required to achieve 50% conversion of the vulcanization reaction. The "TS 1" is the respective time required to increase the torque by 0.01 Nm above the respective torque minimum (ML) during vulcanization. Preferably TS 1 is > 1.5 minute, and TC 50 is from 3 to 8 minutes.

Tensile strength σ_M, elongation at break ε_R and stress at 300% strain ("modulus 300"; σ_{300}) were determined by tensile tests according to ASTM D 412-98A (reapproved 2002), using a dumbell die C test pieces on a Zwick Z010. Of the standardized dumbbell die C test pieces, those of "2 mm thickness" were used. The tensile strength measurement was performed at room temperature on a cured (vulcanized) second stage polymer sample prepared according to Table 18. Stage 2 formulations were vulcanized within 16-25 minutes at 160 °C to TC 95 (95% vulcanization conversion) (see cure data in Table 31). Rubber compound tensile strength σ_M, elongation at break ε_R and stress at 300% strain data are listed in Table 32.

DIN abrasion values as listed in Table 33 were measured according to DIN 53516 (1987-06-01) and DIN ISO 4649 (2006). The larger the index, the lower the wear resistance is (lower = better). The abrasion measurement was performed on a vulcanized, second stage polymer formulation according to Tables 18 and 19. Stage 2 formulations were vulcanized at 160 °C to TC 95 (95% vulcanization conversion) (see cure data in Table 31).

Tan δ at 60 °C and Tan δ at 0 °C measurements were performed cylindrical specimens using a dynamic mechanical thermal spectrometer Eplexor 150N manufactured by Gabo Qualimeter Testanlagen GmbH, Ahlden, Germany, by applying a compression dynamic strain of 0.2%, at a frequency of 2 Hz, respectively, at the respective temperatures. Rubber compound vulcanizate Tan δ at 60 °C and Tan δ at 0 °C are listed in Table 32.

The smaller the index at a temperature of 60 °C, the lower is the rolling resistance (lower = better). Tan δ (0 °C) and Tan δ (-10 °C) were measured using the same equipment and load conditions at 0 °C and -10 °C, respectively. The larger the index at 0 °C and -10 °C, the better the wet skid resistance (higher = better) and the better the ice skid resistance (higher = better). Tan δ at 60 °C, Tan δ at 0 °C and Tan δ at -10 °C index values are listed in Tables 32).

In general, the higher the values of elongation at break ε_R, tensile strength σ_M, tensile stress at 300 % strain (modulus 300) σ_{300}, and Tan δ at 0 °C, the better the sample performance; whereas the lower the Tan δ at 60 °C and the higher the Tan δ at 0 °C as well as Tan δ at -10 °C, the better the sample performance.

(IV) Glass Particle Grade Preparation Technique and Glass Particle Grade Characteristics

(IV-A) Glass Particle Grad Preparation Technique

Glass is transferred into a porous, amorphous glass foam according to patent DE 19545065 C2 incorporated herein by reference in its entirety. The reference describes that glass is first melted and then extruded using a high temperature extrusion process. Subsequently, the resulting glass foam is coarse crushed and subsequently ground. In a last step according to DE 02452693 B4. the glass particles are classified with respect to resulting average particle size.

(IV-B) Zinc-doped Glass Particle Grad Preparation Technique (Type G4 and G5)

The preparation of the zinc-doped glass powder fillers G4 and G5 is described below:

Zinc-(II)-chloride is dissolved in distilled water. TROVO® powder (952 g) is exposed to a solution of 48 g zinc chloride in 56 mL water to get free-flowing glass powder with even distribution of zinc (Type G4). For the preparation of glass grade G4 and G5, exemplary concentrations of zinc are 2.3 (G4) and 4.6 (G5) percent by weight.

First, 952 g TROVO® powder were mixed in a 5000 mL plastic container using one or more stirrers (400 rpm). Then, the zinc chloride solution is added gradually to the mixing powder phase. After completion of the addition of the $ZnCl_2$-solution to the powder bed the mixing process is continued for two minutes.

Then, the resulting mixture is distributed on a stainless steel sheet (thickness of the sheet ≤5 mm) and stored in an oven at a temperature of 190 °C for two hours. Subsequently the dried glass powder was deagglomerated in a split mill.

(IV-C) Glass Particle Grad Characteristics

The glass particle grade characteristics are described in Table 2.

Table 2: Glass Particle Grade Characteristics

Glass Grade	**G1**	**G2**	**G3**	**G4**	**G5**
General Glass Type Classification	Borosilicate Glass 3	Borosilicate Glass 1	Soda-Lime-Silica Glass	Zinc-Doped Borosilicate Glass	Zinc-Doped Borosilicate Glass
Chemical Composition [wt%]					
Na_2O[1)]	9.5 - 13.5	9.5 - 13.5	9.0 - 14.0	9.3 - 13.2	9.0 - 12.9
K_2O[1)]	1.0 - 4.0	1.0 - 4.0	0 - 1.0	1.0 - 4.0	1.0 - 3.8
MgO[1)]	0 - 2.0	0 - 2.0	1.5 - 4.0	0 - 2.0	0 - 1.9
CaO[1)]	1.0 - 5.0	1.0 - 5.0	9.0 - 13.5	1.0 - 4.9	1.0 - 4.8
Al_2O_3[1)]	4.0 - 7.0	4.0 - 7.0	1.0 - 2.5	3.9 - 6.9	3.8 - 6.6
SiO_2[1)]	55.0 - 60.0	55.0 - 60.0	71.0 - 74.0	53.9 - 58.8	52.3 - 57.2
B_2O_3[1)]	8.0 - 11.0	8.0 - 11.0	n.dt.[7]	7.8 - 10.8	7.6 - 10.5
Fe_2O_3[1)]	< 0.2	< 0.2	n.dt.[7]	< 0.2	< 0.2
ZnO[1,8)] Located in Glass Matrix	2.0 - 5.0	2.0 - 5.0	n.dt.[7]	2.0 - 4.9	1.9 - 4.8
Zn[1)] Located in Pores	< 0.2	< 0.2	n.dt.[7]	2.0 - 2.3	4.4 - 4.6
BaO[1)]	3.0 - 6.0	3.0 - 6.0	n.dt.[7]	3.0 - 5.9	2.9 - 5.7
F_2[1)]	< 1.0	< 1.0	n.dt.[7]	< 1.0	< 1.0
	G1	G2	G3	G4	G5
Particle-Size					
D_{50} [µm]	3.0 – 3.6	1.1 – 1.5	3.0 – 3.5	3.0 – 3.6	3.0 – 3.6
D_{99} [µm]	10.0 – 11.0	4.5 – 6.0	9.0 – 11.0	10.0 – 11.0	10.0 – 11.0
Eluate-pH[2)]	10.6 – 11.0	10.5 – 10.7	11.5 – 12.0	6.3 – 6.6	6.0 – 6.3
Eluate-Conductivity [mS][2)]	0.3 – 0.6	0.5 – 0.9	0.9 – 1.2	6.3 – 6.7	11.8 – 12.0
Eluate Zn^{2+} Concentration [mg/l]	n.dt.[7]	n.dt.[7]	n.dt.[7]	1920	3810
OH-Groups in Number/g Glass Powder[3)]	4.0×10^{19} – 6.0×10^{19}	1.0×10^{20} – 2.5×10^{20}	3.0×10^{20} – 4.5×10^{20}	n.d.[6]	n.d.[6]
Moisture Content in Weight cent[4)]	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
BET-Surface in m^2/g[5)]	3.0 – 6.0	12 - 15	3.0 – 6.0	3.0 – 6.0	3.0 – 6.0

1) X-ray fluorescence analysis was used

2) pH-value and conductivity in the eluate determined by calibrated meter PM 2000 from the Ingenieurgesellschaft mbH. The eluate is made from 10 g glass-powder and 90 g distilled water.

3) The OH groups are determined with the method for the SEARS number (titration).

4) Moisture content is determined with thermogravimetric analyses (drying furnace and scales) according to DIN EN ISO 3146.

5) BET nitrogen surface area are determined with area meter (company Ströhlein from Kaarst, model Bb) according to DIN ISO 9277.

6) n.d. means not determined

7) n.dt. means not detectable

8) Zinc oxide concentrations are calculated from zinc concentrations measured using X-ray fluorescence analysis

(V) Polymer Preparation, Polymer Composition and Polymer Characteristics

The following commercial polymer grades of the Styron Deutschland GmbH were used for the compound preparation: Buna cis 132-Schkopau, SE SLR-4601, SE SLR-4602 and SE SLR-4630. The characteristics of the polymer grades are summarized in Table 3. Two other polymers P5 and P6 were prepared as polymer solution in cyclohexane (amounts of components for the reaction see Table 4). Samples of the solvent-free polymers P5 und P6 were prepared to determine the polymer characteristics (polymer characteristics see Table 5).

Table 3: Polymer Grad Characteristics

Code	Polymer Grade	Butadiene Unit Concentration[1] [wt%]	Vinyl Concentraton[2] [wt%]	Styrene Concentration[3] [wt%]	TDAE[4]-oil [phr]	Mooney Viscosity [MU]	Modification
P1	Buna cis 132-Schkopau	100[5]	<2	0	0	45	no
P2	SE SLR-4601	79	63	21	0	50	Sn-coupled & modified
P3	SE SLR-4602	79	63	21	0	62	Sn-coupled & modified
P4	SE SLR-4630	75	63	25	37.5	55	Si-coupled

[1] Butadiene unit concentration is referred to the total homopolymer or copolymer

[2] Vinyl Concentration means the 1,2-polybutadiene unit concentration is referred to the total butadiene fraction of the copolymer or to the total homopolymer

[3] Styrene unit concentration is referred to the total homopolymer or copolymer

[4] phr means parts per weight per hundred parts per weight of rubber

[5] 95 wt% of the total butadiene unit concentration are 1,4-*cis*-polybutadiene units

Coupling agents: The following coupling agents were applied to polymer P001 and P002 preparation:

Coupling agent 1 (C1): tin tetrachloride

Coupling agent 2 (C2): n-methylpyrrolidine

Coupling agent 3 (C3): 3-methoxy-3-methyl-8,8-dioctyl-2-oxa-7-thia-3,8-disila-octadecane

Preparation of the polymer solution P001: The co-polymerizations of styrene and butadiene were performed in a double wall, 40 liter steel reactor, which was first purged with nitrogen, before the addition of organic solvent, monomers, polar coordinator compound, initiator compound or other components. The polymerization reactor was tempered to 60 °C, unless stated otherwise. The following components were than added in the following order: cyclohexane solvent (22.43 kilograms); butadiene monomer, styrene monomer, and tetramethylethylene diamine (TMEDA). The mixture was stirred for one hour, followed by titration with n-butyl lithium to remove traces of moisture or other impurities. The polymerization initiator n-butyl lithium was added to initiate the polymerization reaction. The polymerization was performed for 80 minutes, not allowing the polymerization temperature to exceed 60 °C. Afterwards, 0.5% of the total butadiene monomer amount were added, followed by the addition of coupling agent 1. The mixture was stirred for 20 minutes. Subsequently, 1.8% of the total butadiene monomer amount were added, followed by the addition of the coupling agent 2 (in case of P1) or of coupling agent 3 (in case of P2). For the termination of the polymerization process, the polymer solution was transferred, after 45 minutes, into a separate double wall, steel reactor, containing 100 mL ethanol, and 5 g IRGANOX 1520 as stabilizer for the polymer. This mixture was stirred for 15 minutes.

The resulting polymer P5 and P6 compositions and several of its properties are summarized in Tables 4 and 5 below.

Table 4: Composition of Examples – amounts of reagents for polymerization

Polymer	Coupling agent type	Coupling agent (mmol)	Butadiene (mol)	Styrene (mol)	TMEDA (mol)	n-Butyl lithium (mmol)
P5	(C1) (C2)	2.023 16.94	52.8	7.03	36.52	19.73
P6	(C1) (C3)	1.316 16.65	55.4	7.63	37.9	18.57
P7	(C1) (C3)	0.298 16.91	55.4	7.71	37.85	18.91

Table5: Polymer P1 and P2 Characterizations

Polymer	Mw [kg/mol]	Mn [kg/mol]	Mp1 [kg/mol]	Mooney viscosity [MU]	Vinyl content[B] [wt%]	Styrene content[C] [wt%]
P5	414.0	290.0	258.0	48.7	63.3	20.1
P6	425.0	312.0	312.0	61.3	62.4	21.4
P7	488.0	328.0	313.0	68.7	62.4	21.5

A: determined by SEC
B: vinyl content is that of the 1,2-polybutadiene unit content of the final copolymer, and is determined by IR spectroscopy
C: styrene content of the final copolymer, and is determined by IR spectroscopy

Preparation of Polymer Compounds from Polymer Solution Glass Suspensions: Different amounts of the glass grades BK1 and BK3 were added to a vessel containing polymer P5 or P6 solution via a reactor inlet of 30 mm diameter. The addition of glass was performed gradually in equal portions within 30 minutes while the polymer solution was stirred (stirring speed: 100 rpm). The glass particles suspended in the polymer solution did not settle at the bottom of the storing vessel after 1 week storing period. Therefore the BK1 or BK3 in polymer P5 or P6 suspension was stable for at least one week. The chosen polymer solution as well as the added amount and type of glass particle grade are depicted in Table 6.

Polymer Solution & Polymer Solution Glass Suspension Work-Up Procedure: The resulting polymer suspension was than stripped with steam to remove solvent and other volatiles, and subsequently dried. The stripping device is depicted in FIG. 1.

Coagulation Procedure: 135 kg water containing 60 ppm Pluronic PE6400 from BASF AG surfactant were heated up using low pressure steam (central company supply, steam pressure: 4 bar, steam temperature: 130 °C) until a temperature of about 97-99 °C was reached in the coagulator vessel. The coagulator vessel (fabrication no. 09998256, year of construction: 2000, from SRI Holland/Veenwouden – Speciaal Roestvrijstaal Industrie Veenwouden) is of 206 L size. The coagulator is connected with a nozzle pipe. Steam (central company supply), Kondensat (water having a temperature of ~99 °C)) and the polymer suspension is fed through the nozzle pipe into the coagulator. The nozzle pipe contains a nozzle for transferring the polymer suspension in perpendicular direction and an outlet for Kondensat. In the right angle to the polymer suspension transfer nozzle and to the outlet for Kondensat, there is a steam transfer nozzle. After the coagulator temperature is reached steam was released via the steam nozzle into the coagulator vessel. The steam

pressure in the coagulator was adjusted to 4 bar. The steam velocity amounted to 15.0 kg/hr. In addition, Kondensat containing 60 ppm Pluoronic surfactant is fed continuously via the nozzle pipe into the coagulator. The Kondensat velocity amounted to 40 kg/hr. Then the polymer solution (solid polymer content 16.5%) was transferred into the coagulator vessel via the coagulation nozzle pipe. Two identical coagulation nozzle pipes (project number WO147-2, year of construction: 2000 and W0150-2, year of construction: 2002) of Weber Rohleitungsbau GmbH were applied to the experiments. The polymer solution velocity amounted to 8 kg/hr (pure polymer content 1.5 kg/hr). One of the nozzles, the steam transfer nozzle, has a nozzle exit surface of 22 mm2. The nozzle is of a trench shape. The other nozzle, the polymer solution transfer nozzle, has a nozzle exit surface of 15.2 mm2. The hole of the polymer solution transfer nozzle is of circular shape and has a diameter of 4.4 mm. Both nozzles only have only one hole. The coagulation process was performed for a period of 35 min. Afterwards the polymer solution and the Kondensat transfer into the coagulator vessel was stopped, while steam was fed for further 5 min into the coagulator vessel to remove residues of cyclohexane solvent. Then the steam feed stream into the coagulator was stopped as well, and the glass-polymer composite crumbs were removed from the coagulator. The glass-rubber crumbs were than dried for 12 hours at room temperature, further 30 min at a temperature of 70 °C and then another two days at room temperature.

The final glass-in-rubber concentration, calculated from the glass-rubber composite ash content and the glass-rubber composite Mooney value are listed in Table 6.

Table 6: Composition of Examples – amounts of reagents for polymerization and characteristics

Composite name	Polymer[b]	Glass grade type	Dosing amount of glass grade (wt% [phr])	Ash content of polymer composite [wt%]	Glass concentration in solvent-free polymer composite [wt%][a]	Mooney viscosity of solvent-free polymer composite [MU]
CN001	P5	G1	23.1 [30]	17.2 / 17.2	74	60.0
CN002	P5	G1	28.6 [40]	23.0 / 23.0	80	58.8
CN003	P6	G2	16.7 [20]	8.0 /8.0	48	65.9
CN004	P6	G1	16.7 [20]	15.0 / 14.9	90	69.8
CN005	P6	G2	28.6 [40]	20.7 / 20.6	72	73.3
CN006	P6	G1	28.6 [40]	22.9 / 23.3	81	73.5

[a] glass concentration in solvent-free polymer composite was calculated from the dosed amount of glass and the ash content of the rubber composite (The ash content of e.g. the glass free P6 rubber only amounts to 0.25 wt%. The ash content contribution of P5 and P6 was considered not significant and thus, was neglected.)

[b] The butadiene-styrene-copolymer in cyclohexane solution contained 16.5 wt% of the copolymer

(VI) Polymer Compound Preparation Recipes though Application of Mechanical Mixing Process

(VI-A) Compounds Based on Oil Free Rubber Grades (all individual components listed in Tables 7, 8 and 9 are added separately to the Brabender mixer)

Polymer Compositions: Polymer compositions were prepared by combining and compounding the constituents listed below in Table 7 and 9 in a N50 cc Banbury mixer, and vulcanized at 160 °C for T90. Vulcanization process data and physical properties for the each composition example are provided in Tables 20, 21 and 22.

Table 7: Polymer Compositions M1--M9 using Polymers P1, P2 and P3

Components		Amount (phr)[n]
Elastomeric polymer example (solution styrene butadiene copolymer)		80.0
High *cis*-1,4-polybutadiene	Buna cis 132-Schkopau[m]	20.0
Precipitated silica	Ultrasil 7000GR[f]	80.0[p]
Glass filler	G1, G2 or G3	
Silane	NXT Silane[i]	9.7
Stearic acid[j]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Antilux 110[h] Vulkanox HS[g]	 1.5 2.0
Zinc oxide[k]		2.5
Softener (Oil)	TDAE[e]	20.0
Sulfur[d,l]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Internal Banbury mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkazit D, Rhein Chemie Rheinau GmbH
d Second stage (curing system)
e VivaTec 500, Hansen & Rosenthal KG
f Evonik Industries AG
g 2.2.4-Trimethyl-1.2-dihydrochinolin (TMQ), Rhein Chemie Rheinau GmbH
h Light & ozone protective wax, Rhein Chemie Rheinau GmbH
i Momentive Performance Materials GmbH & Co. KG
j Cognis GmbH
k Grillo-Zinkoxid GmbH
l Solvay AG
m Dow Olefinverbund GmbH
n Based on sum weight of the styrene butadiene copolymer and high *cis*-1,4-polybutadiene
p Amount based on sum weight of precipitated silica and glass filler

Polymer compositions M10-M18 were prepared by combining and compounding the constituents listed below in Table 8 and 9 in a N50 Brabender mixer, and vulcanized at 160 °C for T90. Vulcanization process data and physical properties for the each composition example are provided in Tables 20, 21 and 22.

Table 8: Polymer Composition using Polymers P2 and P3

Components		Amount (phr)[n]
Elastomeric polymer example (solution styrene butadiene copolymer)		100.0
Precipitated silica	Ultrasil 7000GR[f]	80.0[p]
Glass filler	G1, G2 or G3	
Silane	NXT Silane[i]	9.7
Stearic acid[j]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Antilux 110[h] Vulkanox HS[g]	 1.5 2.0
Zinc oxide[k]		2.5
Softener (Oil)	TDAE[e]	20.0
Sulfur[d,l]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Internal Banbury mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkazit D, Rhein Chemie Rheinau GmbH
d Second stage (curing system)
e VivaTec 500, Hansen & Rosenthal KG
f Evonik Industries AG
g 2,2,4-Trimethyl-1,2-dihydrochinolin (TMQ).
h Light & ozone protective wax, Rhein Chemie Rheinau GmbH
i Momentive Performance Materials GmbH & Co. KG
j Cognis GmbH
k Grillo-Zinkoxid GmbH
l Solvay AG
m Dow Olefinverbund GmbH
n Based on sum weight of the styrene butadiene copolymer
p Amount based on sum weight of precipitated silica and glass filler

Table 9: Silica/Glass Filler Ratio in Polymer Composition

Compound Name	Polymer Type	Precipitated Silica (phr)[g]	Glass filler type	Glass filler (phr)[g]	Compound Name	Polymer Type	Precipitated Silica (phr)[g]	Glass filler type	Glass Filler (phr)[g]
M1	P1/P2	80	-	0	M10	P2	80	-	0
M2	P1/P2	68	G1	12	M11	P2	68	G1	12
M3	P1/P2	68	G2	12	M12	P2	68	G2	12
M4	P1/P2	68	G3	12	M13	P2	68	G3	12
M5	P1/P3	80	-	0	M14	P3	80	-	0
M6	P1/P3	68	G1	12	M15	P3	68	G1	12
M7	P1/P3	76	G1	4	M16	P3	76	G1	4
M8	P1/P3	60	G1	20	M17	P3	60	G1	20
M9	P1/P3	68	G2	12	M18	P3	68	G2	12

g Based on sum weight of the styrene butadiene copolymer and high *cis*-1,4-polybutadiene

(VI-B) Compounds Based on Oil Free Rubber Grades (Compositions individually added to the Brabender mixer according to Tables 10 and 11 include a separately prepared glass filler containing SSBR composite component)

Additional polymer compositions were prepared by combining and compounding the constituents listed below in Table 10 and 11 in a N50 Brabender mixer, and vulcanized at

160 °C for T90. Vulcanization process data and physical properties for the each composition example are provided in Tables 23, 24 and 25.

Table 10: Polymer Composition M19–M21 using Composites CN4, CN5, CN6 and Polymer P1

Components		Amount (phr)[n]
High *cis*-1,4-polybutadiene	Buna cis 132-Schkopau[m]	20.0
Composite CN4, CN5 or CN6 example comprizing elastomeric polymer (solution styrene butadiene copolymer) P2 and glass filler G1 or G2	Rubber Content	80.0
	Glas Filler Content	80[p]
Precipitated silica	Ultrasil 7000GR[f]	
Silane	NXT Silane[i]	9.7
Stearic acid[j]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Antilux 110[h] Vulkanox HS[g]	 1.5 2.0
Zinc oxide[k]		2.5
Softener (Oil)	TDAE[e]	20.0
Sulfur[d,l]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Internal Banbury mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkazit D, Rhein Chemie Rheinau GmbH
d Second stage (curing system)
e VivaTec 500, Hansen & Rosenthal KG
f Evonik Industries AG
g 2,4-Trimethyl-1,2-dihydrochinolin (TMQ), Rhein Chemie Rheinau GmbH
h Light & ozone protective wax, Rhein Chemie Rheinau GmbH
i Momentive Performance Materials GmbH & Co. KG
j Cognis GmbH
k Grillo-Zinkoxid GmbH
l Solvay AG
m Dow Olefinverbund GmbH
n Based on sum weight of the styrene butadiene copolymer and high *cis*-1,4-polybutadiene
p Amount based on sum weight of precipitated silica and glass filler

Table 11: Silica/Glass Filler Ratio in Polymer Composition

Example	Polymer Composite Type	2nd Polymer Compound Component	Polymer Composite Glass Content (phr)[g]	Added Precipitated Silica (phr)[g]
M19	CN4	P1	12	68
M20	CN5	P1	17	63
M21	CN6	P1	18	62

g Based on sum weight of the styrene butadiene copolymer and high *cis*-1,4-polybutadiene

(VI-C) Compounds based on Oil extended Rubber Grades

Additional polymer compositions were prepared by combining and compounding the constituents listed below in Table 12 and 14 in a N50 Brabender mixer, and vulcanized at

160 °C for T90. Vulcanization process data and physical properties for the each composition example are provided in Tables 25, 26 and 27.

Table 12: Polymer Compositions M22-M25 using polymers P1 and P4

Components		Amount (phr)[g]
Elastomeric polymer example (solution styrene butadiene copolymer)		117.5
High *cis*-1.4-polybutadiene	Buna cis 132-Schkopau[f]	20.0
Precipitated silica	U7000GR[e]	80.0[p]
Glass filler	G1	
Silane	NXT Silane[e]	9.7
Stearic acid[e]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Vulkanox HS[e] Antilux 110[e]	 2.0 1.5
Zinc oxide[e]		2.5
Sulfur[d,e]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Banbury internal mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH)
c Diphenylguanidine, Vulkazit D, Rhein Chemie Rheinau GmbH
d Second stage (vulcanization)
e Evonik Industries AG
f Dow Olefinverbund GmbH
g Based on sum weight of the styrene butadiene copolymer and high *cis*-1.4-polybutadiene
p Amount based on sum weight of precipitated silica and glass filler

Additional polymer compositions were prepared by combining and compounding the constituents listed below in Table 13 and 14 in a N50 Brabender mixer, and vulcanized at 160 °C for T90. Vulcanization process data and physical properties for the each composition example are provided in Tables 25, 26 and 27.

Table 13: Polymer Compositions M26–M29 using Polymer P4

Components		Amount (phr)[g]
Elastomeric polymer example (solution styrene butadiene copolymer)		117.5
Precipitated silica	U7000GR[e]	80.0[p]
Glass filler	G1	
Silane	NXT Silane[e]	9.7
Stearic acid[e]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Vulkanox HS[e] Antilux 110[e]	 2.0 1.5
Zinc oxide[e]		2.5
Sulfur[d,e]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Banbury internal mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkazit D, Rhein Chemie Rheinau GmbH
d Second stage (vulcanization)
e Evonik Industries AG
f Dow Olefinverbund GmbH
g Based on sum weight of the styrene butadiene copolymer
p Amount based on sum weight of precipitated silica and glass filler

Table 14: Silica/Glass Filler Ratio in Polymer Composition

Compound Name	Polymer Type	Precipitated Silica (phr)[g]	Glass Filler type	Glass Filler (phr)[g]	Compound Name	Polymer Type	Precipitated Silica (phr)[g]	Glass Filler type	Glass Filler (phr)[g]
M22	P1/P4	80	-	0	M26	P4	80	-	0
M23	P1/P4	76	G1	4	M27	P4	76	G1	4
M24	P1/P4	68	G1	12	M28	P4	68	G1	12
M25	P1/P4	60	G1	20	M29	P4	60	G1	20

g Based on sum weight of the styrene butadiene copolymer and high *cis*-1,4-polybutadiene

(VI-D) Compounds Based on Oil Free Rubber Grades and on Zinc-Doped Glass Filler Component (compounds do not comprise Zinc oxide)

Polymer compositions were prepared by combining and compounding the constituents listed below in Table 15 and 17 in a N50 Brabender mixer, and vulcanized at 160 °C for T 90. Vulcanization process data and physical properties for the each composition example are provided in Tables 28, 29 and 30.

Table15: Polymer Compositions M30–M34 using polymers P1 and P3 and glass grades G4 and G5

Components		Amount (phr)[n]
Elastomeric polymer example (solution styrene butadiene copolymer)		80.0
High *cis*-1.4-polybutadiene	Buna cis 132-Schkopau[m]	20.0
Precipitated silica	Ultrasil 7000GR[i]	80.0[p]
Glass filler	G4 or G5	
Silane	NXT Silane[i]	9.7
Stearic acid[j]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Antilux 110[h] Vulkanox HS[g]	 1.5 2.0
Softener (Oil)	TDAE[e]	20.0
Sulfur[d,l]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, internal Banbury mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkazit D, Lanxess AG
d Second stage (curing system)
e VivaTec 500, Hansen & Rosenthal KG
f Evonik Industries AG
g 2,2,4-Trimethyl-1,2-dihydrochinolin (TMQ), Rhein Chemie Rheinau GmbH
h Light & ozone protective wax, Rhein Chemie Rheinau GmbH
i Momentive Performance Materials GmbH & Co. KG
j Cognis GmbH
l Solvay AG
m Dow Olefinverbund GmbH
n Based on sum weight of the styrene butadiene copolymer and high *cis*-1.4-polybutadiene
p Amount based on sum weight of precipitated silica and glass filler

Polymer compositions were prepared by combining and compounding the constituents listed below in Table 16 and 17 in a N50 Brabender mixer, and vulcanized at 160 °C for T90. Vulcanization process data and physical properties for the each composition example are provided in Tables 28, 29 and 30.

Table 16: Polymer Composition M35-M39 using polymers P2 and glass grades G4 and G5

Components		Amount (phr)[n]
Elastomeric polymer example (solution styrene butadiene copolymer)		100.0
Precipitated silica	Ultrasil 7000GR[f]	80.0[p]
Glass filler	G4 or G5	
Silane	NXT Silane[f]	9.7
Stearic acid[f]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Antilux 110[h] Vulkanox HS[g]	 1.5 2.0
Softener (Oil)	TDAE[e]	20.0
Sulfur[d,l]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Internal Banbury mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkacit D, Lanxess AG
d Second stage (curing system)
e VivaTec 500, Hansen & Rosenthal KG
f Evonik Industries AG
g 2.2.4-Trimethyl-1.2-dihydrochinolin (TMQ), Rhein Chemie Rheinau GmbH
h Light & ozone protective wax, Rhein Chemie Rheinau GmbH
i Momentive Performance Materials GmbH & Co. KGj Cognis GmbH
l Solvay AG
m Dow Olefinverbund GmbH
n Based on sum weight of the styrene butadiene copolymer
p Amount based on sum weight of precipitated silica and glass filler

Table 17: Silica/Glass Filler Ratio in Polymer Composition

Compound Name	Polymer Type	Precipitated Silica (phr)[g]	Glass filler type	Glass filler (phr)[g]	Compound Name	Polymer Type	Precipitated Silica (phr)[g]	Glass filler type	Glass Filler (phr)[g]
M30	P1/P3	80	-	0	M35	P2	80	-	0
M31	P1/P3	80	G4	5	M36	P2	68	G4	12
M32	P1/P3	80	G4	10	M37	P2	68	G5	12
M33	P1/P3	80	G5	5	M38	P2	76	G4	4
M34	P1/P3	80	G5	10	M39	P2	76	G5	4

g Based on sum weight of the styrene butadiene copolymer and high *cis*-1.4-polybutadiene

(VI-E) Compounds Based on Oil Free Rubber Grades Prepared With a Reduced Silane Coupling Agent Content

Polymer compositions were prepared by combining and compounding the constituents listed below in Table 18 and 19 in a 350 cc Banbury mixer, and vulcanized at 160 °C for T 90. Vulcanization process data and physical properties for the each composition example are provided in Tables 31, 32 and 33.

Table 18: Polymer Composition M40–M53 using polymers P1 and P7 and glass grades G1 and G2

Components		Amount (phr)[n]
Elastomeric polymer example (solution styrene butadiene copolymer)		80.0
High *cis*-1.4-polybutadiene	Buna cis 132-Schkopau[m]	20.0
Precipitated silica	Ultrasil 7000GR[f]	80.0[p]
Glass filler	G1 or G2	
Silane	NXT Silane[f]	6.9-9.7[q]
Stearic acid[j]		1.0
Stabilizer system Ozone protecting wax Antiozonant	 Antilux 110[h] Dusantox[g] 6PPD	 1.5 2.0
Zinc oxide[k]		2.5
Softener (Oil)	TDAE[e]	20.0
Sulfur[d,l]		1.4
CBS[b,d]		1.5
DPG[c,d]		1.5

a 2 stage mixing, Brabender N50, Internal Banbury mixer
b N-cyclohexyl-2-benzothiazylsulfenamide, Vulkazit CZ/EG, Rhein Chemie Rheinau GmbH
c Diphenylguanidine, Vulkazit D, Rhein Chemie Rheinau GmbH
d Second stage (curing system)
e VivaTec 500, Hansen & Rosenthal KG
f Evonik Industries AG
g N-(1,3-dimethylbutyl)-N'-phenyl-1,4-benzenediamine, Duslo a.s.
h Light & ozone protective wax, Rhein Chemie Rheinau GmbH
i Momentive Performance Materials GmbH & Co. KG
j Cognis GmbH
k Grillo-Zinkoxid GmbH
l Solvay AG
m Dow Olefinverbund GmbH
n Based on sum weight of the styrene butadiene copolymer and high *cis*-1.4-polybutadiene
p Amount based on sum weight of precipitated silica and glass filler
q Detailed amount see Table 19 below

Table 19: Silica/Glass Filler Ratio in Polymer Composition

Compound Name	Silane (phr)[g]	Precipitated Silica (phr)[g]	Glass filler type	Glass filler (phr)[g]	Compound Name	Silane (phr)[g]	Precipitated Silica (phr)[g]	Glass filler type	Glass Filler (phr)[g]
M40	9.70	80	-	0	M47	9.70	80	-	0
M41	9.09	75	G2	5	M48	9.14	75	G2	5
M42	7.88	65	G2	15	M49	8.02	65	G2	15
M43	6.67	55	G2	25	M50	6.90	55	G2	25
M44	9.09	75	G1	5	M51	9.11	75	G1	5
M45	7.88	65	G1	15	M52	7.92	65	G1	15
M46	6.67	55	G1	25	M53	6.74	55	G1	25

g Based on sum weight of the styrene butadiene copolymer and high *cis*-1.4-polybutadiene

(VII) Polymer Compound Vulcanizate Properties

(VII-A) Compound Vulcanisates Based on Oil Free Rubber Grades (vulcanizates made from polymer compounds in a Brabender mixer through separate addition of all individual components listed in Tables 7, 8 and 9)

Table 20: Silica/Glass Containing Polymer Vulcanizate Composition Process Data

Example	W5 [kJ]	ML [Nm]	MH [Nm]	MH-ML [Nm]	TS 2 [min]	TC 90 [min]
MV1	105.6	0.26	0.98	0.72	2.2	8.7
MV2	86.2	0.21	0.97	0.76	3.2	7.9
MV3	82.3	0.11	1.08	0.97	2.4	9.9
MV4	88.9	0.18	0.96	0.78	2.0	5.7
MV5	104.9	0.20	1.25	1.05	2.3	21.5
MV6	86.7	0.13	1.17	1.04	2.9	12.9
MV7	96.3	0.16	1.21	1.05	1.5	17.3
MV8	78.7	0.11	1.06	0.95	2.9	9.3
MV9	91.6	0.15	1.03	0.88	2.8	10.9
MV10	101.6	0.28	1.08	0.80	2.0	9.9
MV11	87.8	0.17	0.99	0.82	2.7	9.7
MV12	78.9	0.11	1.03	0.92	2.3	19.1
MV13	85.8	0.15	0.99	0.84	1.9	7.4
MV14	117.6	0.29	1.21	0.92	3.2	14.8
MV15	84.1	0.14	1.18	1.04	3.6	21.0
MV16	100.0	0.17	1.22	1.05	2.8	17.4
MV17	74.5	0.11	1.03	0.92	3.4	14.5
MV18	81.7	0.10	1.06	0.96	1.6	19.1

Table 21: Silica/Glass Containing Polymer Vulcanizate Composition Properties (second values in each cell in parenthesize are values of the standard deviation)

Example	σ_M [MPa]	σ_{100} [MPa]	σ_{300} [MPa]	Elongation at Break [%]	Shore A	T_S [N/mm]	J_d [N/mm]
MV1	16.6 (0.85)	2.96 (0.07)	11.00 (0.25)	408 (14.5)	68.8 (0.3)	n.d.[1]	315 (85.0)
MV2	17.7 (1.7)	2.73 (0.04)	9.61 (0.09)	474 (30)	65.4 (1.1)	n.d.[1]	283 (30.0)
MV3	18.7 (1.6)	2.59 (0.03)	10.09 (0.08)	482 (30.3)	64.6 (0.4)	16.16 (1.11)	220 (13.4)
MV4	16.64 (3.4)	2.70 (0.03)	9.83 (0.18)	444 (65)	65.3 (0.5)	n.d.[1]	277 (42.0)
MV5	19.65 (1.8)	2.59 (0.07)	10.74 (0.28)	453.01 (28.1)	66 (0.6)	16.08 (2.06)	318.29 (14.4)
MV6	18.9 (1.1)	2.55 (0.10)	9.8 (0.20)	482 (18)	61.7 (0.2)	10.7 (1.10)	312.5 (12.5)
MV7	20 (1.4)	2.80 (0.05)	11.1 (0.20)	461 (23)	65.5 (0.9)	23.0 (0.50)	282.3 (22.5)
MV8	15.9 (3.0)	2.40 (0.04)	8.9 (0.10)	461 (68)	59.3 (0.4)	11.7 (6.70)	274.9 (28.1)
MV9	19.8 (1.64)	2.25 (0.02)	9.86 (0.06)	496 (27.6)	58.4 (0.6)	26.12 (3.8)	225 (8.4)
MV10	14.9 (0.61)	3.55 (0.09)	14.1 (0.48)	312 (5.2)	73.1 (0.6)	n.d.[1]	322 (40.0)
MV11	18.6 (1.30)	3.22 (0.09)	11.5 (0.13)	430 (20.0)	66.2 (0.3)	n.d.[1]	291 (28.0)
MV12	15.37 (1.18)	5.44 (0.20)	n.d.[1]	229.54 (18.07)	73.0 (2.1)	2.89 (0.19)	139.36 (6.6)
MV13	15.6 (3.1)	3.07 (0.05)	11.5 (0.20)	373 (55)	65.4 (2.9)	n.d.[1]	264 (12.0)
MV14	16.6 (2.37)	3.35 (0.17)	15.22 (0.43)	319.43 (29.3)	66.8 (0.5)	13.18 (1.69)	294.62 (15.9)
MV15	18.03 (0.67)	2.71 (0.03)	10.56 (0.06)	442 (12)	62.5 (0.5)	6.5 (0.30)	375.3 (24.5)
MV16	14.46 (1.45)	2.57 (0.06)	11.05 (0.16)	360 (24.9)	64.9 (0.6)	8.97 (0.20)	304.5 (48.4)
MV17	14.9 (2.88)	2.36 (0.01)	9.19 (0.06)	419 (54)	59.9 (0.4)	6.2 (0.23)	317.5 (39.6)
MV18	16.66 (1.01)	4,71 (0.27)	n.d.[1]	252.15 (11.8)	73.2 (1.6)	3.17 (0.38)	155.1 (8.6)

1) n.d. means not determined

Table 22: Dynamic Silica/Glass Containing Polymer Vulcanizate Composition Properties

Example	Tan δ at	Tan δ at	Temp. at Tan δ max [°C]

	0 °C	60 °C	
MV1	0.4249	0.1417	n.d.[1]
MV2	0.4594	0.1482	n.d.[1]
MV3	0.4301	0.1373	n.d.[1]
MV4	0.4602	0.1398	n.d.[1]
MV5	0.4458	0.1488	n.d.[1]
MV6	0.4452	0.1251	n.d.[1]
MV7	0.4338	0.1347	n.d.[1]
MV8	0.4418	0.1191	n.d.[1]
MV9	0.4437	0.1109	n.d.[1]
MV10	0.7466	0.1417	n.d.[1]
MV11	0.7844	0.1343	n.d.[1]
MV12	0.5777	0.1031	n.d.[1]
MV13	0.7911	0.1330	n.d.[1]
MV14	0.8016	0.1230	-10.0
MV15	0.8260	0.1202	-10.0
MV16	0.8143	0.1336	-10.0
MV17	0.8403	0.1156	-9.9
MV18	0.6641	0.0876	n.d.[1]

(VII-B) Compound Vulcanizates Based on Oil Free Rubber Grades (vulcanizates made from polymer compounds in a Brabender mixer through separate addition of all individual components comprising a glass filler containing SSBR composite component as listed in Tables 10 and 11)

Table 23: Silica/Glass Containing Polymer Vulcanizate Composition Process Data

Example	W5 [kJ]	ML [Nm]	MH [Nm]	TS 2 [min]	TC 90 [min]
MV19	86.9	0.15	1.21	2.9	14.9
MV20	82.1	0.13	1.25	2.2	11.3
M21	80.0	0.13	1.22	3.0	7.1

Table 24: Silica/Glass Containing Polymer Vulcanizate Composition Properties (second values in each cell in parenthesize are values of the standard deviation)

Example	σ_M [MPa]	σ_{100} [MPa]	σ_{300} [MPa]	Elongation at Break [%]	Shore A	T_S [N/mm]	J_d [N/mm]
MV19	15.8 (1.72)	3.04 (0.03)	12.37 (0.07)	360.19 (30.40)	65.9 (0.4)	12.11 (1.68)	195.18 (11.20)
MV20	16.32 (0.62)	3.23 (0.06)	13.09 (0.13)	362.06 (13.12)	65.6 (0.5)	16.16 (5.95)	217.21 (5.95)
M21	16.53 (0.85)	3.44 (0.04)	12.44 (0.06)	382.56 (15.17)	65.8 (0.5)	19.36 (11.39)	221.49 (12.77)

(VII-C) Compound Vulcanizates based on Oil extended Rubber Grades (vulcanizates made from polymer compounds in a Brabender mixer through separate addition of all individual components listed in Tables 12, 13 and 14)

Table 25: Silica/Glass Containing Polymer Vulcanizate Composition Process Data

Example	W5 [kJ]	ML [Nm]	MH [Nm]	MH-ML [Nm]	TS 2 [min]	TC 90 [min]
MV22	107.2	0.30	1.07	0.77	1.3	11.8
MV23	99.4	0.22	0.98	0.76	1.0	18.2
MV24	90.5	0.15	0.81	0.66	1.0	15.1
MV25	82.4	0.14	0.86	0.72	1.7	11.8
MV26	97.5	0.33	1.03	0.70	2.0	12.2
MV27	91.6	0.20	0.98	0.78	3.2	19.5
MV28	83.5	0.18	0.89	0.71	3.7	16.8
MV29	76.9	0.15	0.82	0.67	3.5	16.7

Table 26: Silica/Glass Containing Polymer Vulcanizate Composition Properties (second values in each cell in parenthesize are values of the standard deviation)

Example	σ_M [MPa]	σ_{100} [MPa]	σ_{300} [MPa]	Elongation at Break [%]	Shore A	T_S [N/mm]	J_d [N/mm]
MV22	20 (1.35)	2.22 (0.08)	9.24 (0.20)	503 (20)	64.1 (0.5)	n.d.[1]	325 (27.0)
MV23	20.4 (1.50)	1.86 (0.03)	7.6 (0.08)	583 (30)	58.2 (0.4)	25.6 (2.2)	414.6 (53.0)
MV24	20.5 (2.00)	1.75 (0.04)	7 (0.05)	609 (34)	55.5 (0.4)	9.3 (0.2)	376.6 (17.2)
MV25	17.2 (1.00)	1.97 (0.06)	7.5 (0.10)	538 (18)	55.7 (0.4)	11.7 (1.7)	287.9 (12.9)
MV26	18.5 (3.90)	2.05 (0.15)	9.05 (0.54)	477 (58)	63 (1.4)	n.d.[1]	(n.d.[1])
MV27	16.43 (3.43)	1.86 (0.04)	8.43 (0.06)	464 (63)	58.1 (0.7)	12.1 (2.0)	472.7 (29.4)
MV28	17.38 (3.46)	1.72 (0.02)	7.39 (0.06)	525 (65)	56.8 (0.6)	8 (1.2)	402.5 (54.5)
MV29	15.92 (2.79)	1.61 (0.03)	6.54 (0.07)	488 (145)	52.8 (0.4)	6.2 (0.4)	367.7 (26.0)

1) n.d. means not determined

Table 27: Dynamic Silica/Glass Containing Polymer Vulcanizate Composition Properties

Example	Tan δ at 0 °C	Tan δ at 60 °C	Temp. at Tan δ max [°C]
MV22	0.4870	0.1375	n.d.[1]
MV23	0.4915	0.1414	n.d.[1]
MV24	0.4871	0.1323	n.d.[1]
MV25	0.4883	0.1077	n.d.[1]
MV26	0.7991	0.1383	-12.9
MV27	0.8530	0.1267	-9.9
MV28	0.8907	0.1117	-10.0
MV29	0.9345	0.1056	-10.0

(VII-D) Compound Vulcanizates Based on Oil Free Rubber Grades and on Zinc-Doped Glass Filler Component (compounds do not comprise Zinc oxide; vulcanizates made

from polymer compounds in a Brabender mixer through separate addition of all individual components listed in Tables 15, 16 and 17)

Table 28: Silica/Glass Containing Polymer Vulcanizate Composition Process Data

Example	W5 [kJ]	ML [Nm]	MH [Nm]	MH-ML [Nm]	TS 2 [min]	TC 90 [min]
MV30	n.d.[1]	0.18	1.25	1.07	1.1	20.2
MV31	n.d.[1]	0.29	1.48	1.19	1.5	16.5
MV32	n.d.[1]	0.29	1.21	0.92	1.1	13.7
MV33	n.d.[1]	0.29	1.31	1.02	0.6	18.4
MV34	n.d.[1]	0.30	1.28	0.98	0.5	17.6
MV35	101.6	0.28	1.08	80	2.0	9.9
MV36	86.8	0.11	1.24	1.13	2.4	18.0
MV37	n.d.[1]	0.16	1.02	0.86	1.8	18.8
MV38	94.1	0.15	1.21	1.06	3.5	11.8
MV39	99.8	0.16	1.28	1.12	3.9	14.1

1) n.d. means not determined

Table 29: Silica/Glass Containing Polymer Vulcanizate Composition Properties (second values in each cell in parenthesize are values of the standard deviation)

Example	σ_M [MPa]	σ_{100} [MPa]	σ_{300} [MPa]	Elongation at Break [%]	Shore A	T_S [N/mm]	J_d [N/mm]	DIN Abrasion 1.25 kg load [mm3]
MV30	19.65 (1.77)	2.59 (0.07)	10.74 (0.28)	453.01 (28.1)	66 (0.6)	16.08 (2.06)	318.29 (14.4)	111.4
MV31	15.34 (0.88)	5.36 (0.06)	n.d.[1]	217.23 (8.87)	71.7 (0.4)	19.27 (1.25)	123.64 (10.33)	106.0
MV32	18.79 (1.54)	4.25 (0.24)	18.05 (0.27)	308.14 (21.44)	68.6 (0.4)	11.95 (2.62)	195.18 (10.56)	n.d.[1]
MV33	18.63 (2.48)	3.8 (0.09)	19.43 (0.32)	293.16 (26.37)	67.1 (0.4)	n.d.[1]	175.33 (13.81)	n.d.[1]
MV34	18.07 (1.54)	4.09 (0.13)	18.11 (0.06)	299.82 (19.28)	68.1 (0.3)	22.08 (4.14)	182.43 (9.76)	n.d.[1]
MV35	14.9 (0.61)	3.55 (0.09)	14.1 (0.48)	312 (5.2)	73.1 (0.6)	n.d.[1]	322 (40)	n.d.[1]
MV36	17.4 (2.07)	3.02 (0.13)	12.08 (0.28)	392 (34.0)	64.9 (0.8)	4.3 (0.50)	279 (29.0)	n.d.[1]
MV37	16.05 (1.91)	2.97 (0.19)	12.63 (0.34)	356 (36.0)	63.4 (0.4)	6.75 (0.65)	291.8 (9.8)	n.d.[1]
MV38	14.4 (1.27)	2.95 (0.12)	11.43 (0.35	354 (25.6)	67.1 (1.1)	8.8 (1.2)	n.d.[1]	n.d.[1]
MV39	14.8 (1.72)	2.61 (0.25)	10.12 (0.89)	394 (44.4)	66.4 (0.9)	8.75 (0.63)	n.d.[1]	n.d.[1]

1) n.d. means not determined

Table 30: Dynamic Silica/Glass Containing Polymer Vulcanizate Composition Properties

Example	Tan δ at 0 °C	Tan δ at 60 °C
MV30	0.4458	0.1488
MV31	0.4463	0.1064
MV32	0.4535	0.1230
MV33	0.4784	0.1302
MV34	0.4472	0.1383
MV35	0.7466	0.1417
MV36	0.7559	0.1273
MV37	0.8424	0.1443
MV38	0.6744	0.1451
MV39	0.7479	0.1550

(VII-E) Compound Vulcanizates Based on Oil Free Rubber Grades, Prepared With a Reduce Silane Coupling Agent Content (vulcanizates made from polymer compounds in a 350 cc Banbury mixer through separate addition of all individual components listed in Tables 18 and 19)

Table 31: Vulcanization Process Data & Silica Containing Polymer Vulcanizate Composition

	Property						
Example	TS 1 [min]	TS 2 [min]	TC 50 [min]	TC 90 [min]	TC 95 [min]	Compound Mooney [Mu]	Compound Mooney – Polymer Mooney [Mu]
MV40	4.2	5.1	6.9	14.8	19.5	74.7	6
MV41	4.0	4.8	6.1	10.8	14.3	66.4	-2.3
MV42	3.9	4.7	6.2	11.9	16.0	73.7	5
MV43	4.0	4.5	5.4	8.3	10.3	53.5	-15.2
MV44	4.0	4.8	6.3	12.7	17.0	77.0	8.3
MV45	4.3	5.0	6.1	10.2	12.8	68.7	0
MV46	4.4	5.2	6.3	10.0	12.3	62.0	-6.7
MV47	3.8	4.6	6.4	14.5	19.3	73.2	4.5
MV48	3.7	4.4	5.7	12.2	16.9	73.5	4.8
MV49	3.9	4.7	5.9	10.2	13.7	66.1	-2.6
MV50	3.7	4.3	5.2	8.3	10.5	56.4	-12.3
MV51	4.2	5.0	6.3	11.4	15.4	76.8	8.1
MV52	4.3	5.1	6.4	10.7	13.8	70.8	2.1
MV53	4.3	5.1	6.2	9.8	12.2	64.0	-4.7

Table 32: Silica Containing Polymer Vulcanizate Composition Properties

Example	Elongation at Break [%]	σ_M [MPa]	σ_{300} [MPa]	Tan δ at 0 °C	Tan δ at 60 °C	Temp. at Tan δ max [°C]
MV40	461	20.4	10.3	0.241	0.085	-20
MV41	498	20.0	9.8	0.226	0.077	-22
MV42	363	13.1	10.1	0.210	0.067	-22
MV43	521	17.4	8.9	0.185	0.047	-22
MV44	464	19.9	10.4	0.230	0.079	-22
MV45	503	18.2	9.2	0.197	0.058	-22
MV46	543	18.7	8.2	0.188	0.050	-22
MV47	469	20.7	10.2	0.237	0.090	-22
MV48	453	20.0	11.1	0.234	0.082	-22
MV49	470	18.5	10.0	0.215	0.070	-22
MV50	481	16.6	9.2	0.197	0.052	-22
MV51	393	16.2	10.8	0.226	0.071	-22
MV52	487	20.0	10.0	0.214	0.063	-22
MV53	493	16.2	8.3	0.188	0.054	-22

Table 33: Silica Containing Polymer Vulcanizate Composition Properties

Example	DIN Abrasion 0.5 kg load [mm3]	Example	DIN Abrasion 0.5 kg load [mm3]
MV40	91	MV47	58
MV41	n.d.[1]	MV48	54
MV42	n.d.[1]	MV49	53
MV43	n.d.[1]	MV50	59
MV44	95	MV51	n.d.[1]
MV45	115	MV52	n.d.[1]
MV46	79	MV53	n.d.[1]

One important application of the present teachings is the production of first polymer compositions (non-crosslinked elastomeric polymer compositions) comprising at least one primary filler, at least one secondary glass powder filler, and at least one polymer having lower first polymer composition Mooney values and lower energy input during first polymer composition processing when compared with first polymer compositions not comprising secondary glass powder filler. The lower Mooney values and the lower energy input of the first polymer composition in accordance with the present teachings enables use of the first polymer composition in mixing steps of reduced mixing periods and/or a reduced number of mixing steps and, therefore, in less energy consuming mixing steps and in higher throughput rubber compound extrusion processes.

It has been furthermore discovered that the combination of at least one primary filler, at least one secondary glass powder filler, and at least one polymer, each described herein, form first polymer compositions having improved polymer processing characteristics as evidenced in reduced Mooney viscosity and reduced energy input (or reduced energy

consumption) W5 during two mixing steps for a speed of the rotor blades in the mixer of 60 rpm during the first mixing step and 50 rpm during the second mixing step in the process of formation of the first polymer composition, when compared with polymer compositions not comprising secondary glass powder fillers. The use of the first polymer composition in accordance with the present teachings leads to decreased mixing periods and/or to a reduced number of mixing steps and, consequently, less energy is consumed and/or a higher throughput in the course of the rubber compound extrusion process is achieved.

An additional important application of the present teachings is the production of second polymer compositions (vulcanized or crosslinked elastomeric polymer compositions) made from first polymer compositions (non-crosslinked elastomeric polymer compositions) in accordance with the present teachings and at least one vulcanization agent having lower "Tan δ at 60 °C" values and/or higher "Tan δ at 0 °C" values. If one of the-two values, which relate to tire rolling resistance or to tire wet grip performance, is improved, the other value as well as other physical properties, such as abrasion resistance and processability should not be negatively impacted to improve the key tire performance properties. Tire treads made from polymer compositions having lower "Tan δ at 60 °C" values have corresponding lower rolling resistance, while those with higher "Tan δ at 0 °C" values have corresponding better wet skid properties.

It has been discovered that the combination of at least one primary filler, at least one secondary glass powder filler, and at least one polymer, described herein as a first polymer composition, and at least one vulcanization agent, each described herein, form vulcanized second polymer compositions in accordance with the present teachings with lower hysteresis energy loss, as measured at low value of the Tan delta at 60 °C and excellent grip properties on a wet surface, as measured at Tan delta at 0 °C upon mechanical stress, when compared with (vulcanized) second polymer compositions not comprising secondary glass powder fillers. The use of (vulcanized) second polymer compositions in accordance with the present teachings in tire treads leads to an improved low rolling resistance (high wet grip balance of a tire when compared with tires based on vulcanized second polymer compositions not comprising secondary glass powder fillers0.

It has also been discovered that vulcanized second polymer compositions in accordance with the present teachings having an improved low rolling resistance-high wet grip balance as discussed above can be prepared from first polymer compositions comprising

at least one polymer, at least one silica filler selected from the group consisting of primary fillers and at least one secondary glass powder filler and from at least one vulcanization agent comprising a relatively reduced silane coupling agent concentration, when compared with second polymer compositions made from first polymer compositions comprising silica filler, but not comprising a secondary glass powder filler, which have a relatively higher silane coupling agent concentration.

As previously stated, an additional significant application of the present teachings is the production of specific first polymer compositions (non-crosslinked and thus non-vulcanized elastomeric polymer compositions), which are made from at least one (elastomeric) polymer, at least one primary filler and at least one zinc-doped secondary glass powder filler, selected from the group consisting of secondary glass powder fillers having a reduced total concentration of the heavy metal zinc and a reduced (or eliminated) concentration of zinc oxide. The reduced concentration of zinc, partly or completely located in the pores or on the surface of zinc-doped secondary glass powder fillers comprised in the first polymer compositions reduces or eliminates the amount of powdery zinc oxide, which is classified as environmentally dangerous according to EG 67/548/EEC, and which is handled in the process of preparing first polymer compositions. Furthermore, the reduced total concentration of zinc in second polymer compositions in accordance with the present teachings reduces the total amount of zinc released into the environment through abrasion of vulcanizates, including but not limited to the abrasion of tire treads, in comparison with zinc oxide-containing second polymer compositions, without affecting typical (vulcanized) second polymer composition performance properties. Therefore, the preparation of specific first polymer compositions and second polymer compositions in accordance with the present teachings and articles made therefrom is considered to be more environmentally friendly.

It has been also discovered that the combination of at least one primary filler, at least one secondary glass powder filler comprising at least one zinc-doped secondary glass powder filler and at least one polymer, each described herein, form first polymer compositions and second polymer compositions in accordance with the present teachings additionally comprising at least one vulcanization agent, having a decreased total zinc concentration and having a decreased or eliminated zinc oxide concentration compared with first polymer compositions and second polymer compositions not comprising zinc-doped secondary glass powder filler. The reduced zinc oxide concentration and the reduced total

zinc concentration in first polymer compositions in accordance with the present teachings does not negatively impact parameters, such as for example scorch time (TS2), vulcanization conversion (TC90) or crosslinking (MH-ML), describing the vulcanization kinetic of the first polymer compositions or processing characteristics of the first polymer compositions. In addition, the reduced zinc oxide concentration and the reduced total zinc concentration in second polymer compositions in accordance with the present teachings does not negatively impact typical (vulcanized) second polymer composition performance properties such as for example, polymer hysteresis properties, such as determined by tan δ @ 60 °C and by tan δ @ 0 °C measurements, heat buildup, elongation at break or abrasion resistance performance values.

As previously stated, one significant application for the (non-vulcanized elastomeric) first polymer compositions in accordance with the present teachings, which are made from at least one (elastomeric) polymer, at least one primary filler and at least one secondary glass powder filler, is their use in preparing (vulcanized elastomeric) second polymer compositions in accordance with the present teachings, and which have one or more of the following three key characteristics: reduced rolling resistance and/or increased wet skid performance, as represented by compositions having relatively lower (or reduced) values of Tan δ at 60 °C; improved wet skid resistance, as represented by compositions having relatively higher values of Tan δ at 0 °C; improved processing characteristics and, in the case of silica-containing compositions, relatively decreased silane coupling agent concentration.

Depending on the nature of the at least one elastomeric polymer, the at least one primary filler, and the at least one secondary glass powder filler on the (non-vulcanized) first polymer composition and on the (vulcanized) second polymer composition, one, two, three or four of the aforementioned property values can be improved, without any of the above Tan δ values or processing characteristics being significantly deteriorated. The polymer preparation and the polymer characteristics of those polymers used for the preparation of compositions containing the primary filler silica and secondary glass powder filler as well as vulcanizates formed from the same, are stated in Table 3, Table 4 and Table 5. The composition of the secondary glass powder filler grades used for the preparation of compositions containing the primary filler silica and vulcanizates formed from the same, are stated in Table 2. The polymer-secondary glass powder filler compositions made by adding the secondary glass powder filler into the polymer solution following low pressure solvent

removal used for the preparation of compositions containing the primary filler silica and vulcanizates formed from the same, are stated in Table 6. The compounding and vulcanization formulations are stated in Table 7 to Table 19. The corresponding vulcanizate composition process data and vulcanizate composition performance properties are stated in Table 20 to Table 33.

As illustrated in Tables 7, 8 and 9, "silica-containing" polymer compositions are prepared from oil-free modified polymers, silica primary filler, zinc oxide, and secondary glass powder filler. The corresponding vulcanizate composition process data are stated in Table 20 and the corresponding vulcanizate composition performance properties are stated in Table 21 and Table 22.

As already stated, first polymer compositions in accordance with the present teachings are easier to process than comparable polymer compositions not comprising secondary glass powder filler. Exemplary polymer compositions M5, M7, M6 and M8 each contain polymer P1, modified polymer P3, and silica primary filler. The polymer compositions furthermore contain an increasing amount of the secondary glass powder filler grade G1 of 0 phr (M5, reference without G1), 4 phr (M7), 12 phr (M6) or 20 phr (M8) as stated in Table 9. Table 20 shows the decreasing energy uptake W5 during mixing of the first and second polymer compositions of 104.9 kJ (composition MV5 made from M5 composition ingredients), 96.3 kJ (MV7 made from M7), 86.7 kJ (MV6 made from M6), and 78.7 kJ (MV8 made from M8). The examples demonstrate the possibility of saving energy in the process of preparing the compositions in accordance with the present teachings.

The vulcanized compositions MV5, MV7, MV6, and MV8 also indicate, as already stated above, an improved rolling resistance performance as represented by improved data of Tan δ @ 60 °C, when the concentration of the secondary glass powder filler grade is increased. For example, Tan δ @ 60 °C values decrease for MV5, MV7, MV6 and MV8 in the order 0.1488, 0.1347, 0.1251, and 0.1191, while the corresponding Tan δ @ 0 °C values do not or do not significantly change with increasing G1 concentration.

As illustrated in Tables 10 and 11, "silica-containing" polymer compositions are prepared from secondary glass powder filler containing oil-free modified polymers, silica primary filler, zinc oxide, and secondary glass powder filler. The corresponding vulcanizate composition process data are stated in Table 23 and the corresponding vulcanizate composition performance properties are stated in Table 24.

As illustrated in Tables 18 and 19, "silica-containing" polymer compositions are prepared from oil-free modified polymers, silica primary filler, zinc oxide and secondary glass powder filler and a reduced silane coupling agent concentration. The corresponding vulcanizate composition process data are stated in Table 31 and the corresponding vulcanizate composition performance properties are stated in Table 32 and Table 33.

As already stated, the first polymer compositions in accordance with the present teachings are easier to process than comparable polymer compositions not comprising secondary glass powder filler. Exemplary polymer compositions M48, M49 and M50 each contain polymer P1, modified polymer P7 and silica primary filler. The polymer compositions furthermore contain an increasing amount of the secondary glass powder filler grade G2 of 5 phr (M48), 15 phr (M49) or 25 phr (M50) (see Table 19). Table 31 shows decreasing compound Mooney viscosities of the polymer composition with increasing secondary glass powder filler grade G2 of 73.5 MU (MV48 made from M48 ingredients), 66.1 MU (MV49 made from M49 ingredients), and 56.4 MU (MV50 made from M50 ingredients). The examples demonstrate the reduction of the polymer composition viscosity in case an increased secondary glass powder filler concentration is applied to the composition manufacturing process.

The vulcanized compositions MV47 (reference without G2), MV48, MV49, and MV50 also indicate an improved rolling resistance-wet grip performance balance as indicated by improved data of Tan δ @ 60 °C at only slightly decreased Tan δ @ 0 °C values, when the concentration of the secondary glass powder filler grade G2 is increased and the silane coupling agent concentration is decreased. The Tan δ @ 60 °C values clearly overcompensate the impaired Tan δ @ 0 °C values. For example, the Tan δ @ 60 °C values decrease for MV47, MV48, MV49, and MV50 in the order 0.090 (MV47 reference value), 0.082 (MV48, 9% improvement vs. MV47), 0.070 (MV49, 22% improvement vs. MV47) and 0.052 (MV50, 42% improvement vs. MV47), while the corresponding Tan δ @ 0 °C are only impaired by 1% (MV48), 9% (MV49) and 17% (MV50) with increasing G2 concentration. As already stated, the increasing secondary glass powder filler grad concentration is accompanied with a decreasing silane coupling agent concentration. For example, the reference composition M47 comprised 9.70 phr silane coupling agent while only 6.90 phr silane coupling agent were added to composition M50 containing the highest concentration of G2.

As illustrated in Tables 12, 13 and 14, "silica-containing" polymer compositions are prepared from oil-containing polymers, silica primary filler, zinc oxide, and secondary glass powder filler. The corresponding vulcanizate composition process data are stated in Table 25 and the corresponding vulcanizate composition performance properties are stated in Table 26 and Table 27.

As already stated, the first polymer compositions in accordance with the present teachings are easier to process than comparable polymer compositions not comprising secondary glass powder filler. Exemplary polymer compositions M22, M23, M24 and M25 each contain polymer P1, oil-extended polymer P7, and silica primary filler. The polymer compositions furthermore contain an increasing amount of the secondary glass powder filler grade G1 of 0 phr (M22), 4 phr (M23), 12 phr (M24), and 20 phr (M25) (see Table 14).

Table 25 shows the decreasing energy uptake W5 during mixing of the first and second polymer compositions of 107.2 kJ (reference, composition MV22 made from M22 ingredients), 99.4 kJ (MV23 made from M23), 90.5 kJ (MV24 made from M24), and 82.4 kJ (MV25 made from M25). The examples demonstrate the possibility of saving energy in the process of preparing the compositions in accordance with the present teachings.

The vulcanized compositions MV23, MV24, and MV25 also indicate, as already stated above, an improved rolling resistance performance as indicated by improved data of Tan δ @ 60 °C, when the concentration of the secondary glass powder filler grade is increased. For example, Tan δ @ 60 °C value decreases for MV23, MV24, and MV25 in the order 0.1414, 0.1323, and 0.1077, while the corresponding Tan δ @ 0 °C values do not or do not significantly change with increasing G1 concentration (see Table 27).

As illustrated in Tables 15, 16, and 17, "silica-containing" polymer compositions are prepared from oil-free modified polymers, silica primary filler, and secondary zinc-doped glass powder filler. The corresponding vulcanizate composition process data are stated in Table 28 and the corresponding vulcanizate composition performance properties are stated in Table 29 and Table 30.

Exemplary compounds M30 (reference), M31, and M32 comprise silica primary filler, modified polymer P3, and polymer P1. M36 and M37 additionally contain 5 phr and 10 phr zinc-doped secondary glass powder fillers G4 and G5, respectively (see Table 17). The crosslinking density (MH-ML) of the corresponding vulcanized compositions MV30, MV31, and MV32 of 1.07, 1.19, and 0.92 are in a comparable order. Furthermore, the

scorch time TS2 is similar (1.1 min for MV30, 1.5 min for MV31 and 1.1 min for MV32). The period to achieve 90% vulcanization conversion represented by the TC90 value somewhat decreases with increasing zinc concentration of the secondary glass powder fillers (zinc pore/surface concentration, G4: 2.1 wt% zinc and G5: 4.5 wt% zinc) in the order 20 min (MV30), 16.5 min (MV31), and 14 min (MV32). The reduced TC90 value is, however, still acceptable for a technical vulcanization process. Overall, the application of zinc-doped secondary glass powder fillers does not significantly influence the composition vulcanization kinetic.

The vulcanized compositions MV30, MV31, and MV32 also indicate, as already stated above, an improved rolling resistance performance as indicated by improved data for Tan δ @ 60 °C, when the concentration of the secondary glass powder filler grade is increased. For example, the Tan δ @ 60 °C value decreases for MV30, MV31, and MV32 in the order 0.1488, 0.1064, and 0.1230 with increasing G1 concentration (see Table 30). The corresponding Tan δ @ 0 °C value is in the range of the MV30 reference value for MV31 or is improved in case of MV32.

It is particularly advantageous that the aforementioned benefits were found, when in accordance with the present teachings, "oil free" polymers and "oil extended" polymers were used as a polymer source in "silica-containing" polymer compositions.

In addition, it is advantageous that the aforementioned benefits with respect to the improved rolling resistance-wet grip balance were found as well, when in accordance with the present teachings, second (vulcanized) polymer compositions comprising a zinc-doped secondary glass powder filler were used as secondary filler source. Accordingly, the benefits of the improved rolling resistance-wet grip balance and the decreased total zinc and zinc oxide concentration can be beneficially combined.

Modified polymers are reported, when used as components of vulcanized compositions, to improve the rolling resistance-wet grip performance balance in compounds only comprising silica or carbon black as filler. Secondary glass powder fillers and zinc-doped secondary glass powder fillers are demonstrated, when contained in vulcanized polymer-filler compositions in accordance with the present teachings, also to improve the rolling resistance-wet grip performance balance. Therefore, it is furthermore advantageous that the application of second polymer compositions in accordance with the present teachings comprising both modified polymers and secondary glass powder fillers or zinc-

doped secondary glass powder fillers leads to vulcanizates with especially low hysteretic energy loss.

The foregoing detailed description and examples have been provided solely by way of explanation and illustration, and are not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments illustrated herein will be apparent to one of ordinary skill in the art, and remain within the scope of the appended claims and their equivalents.

CLAIMS

1. A first composition comprising:

i) a polymer;

ii) a primary filler; and

iii) a secondary filler;

wherein the secondary filler comprises a material selected from the group consisting of a secondary glass powder filler, a zinc-doped secondary glass powder filler, and a combination thereof.

2. The first composition of claim 1, wherein the secondary filler comprises soda-lime-glass, borosilicate glass or a combination thereof.

3. The first composition of claim 1, wherein the secondary filler comprises borosilicate glass.

4. The first composition of claim 1, wherein the secondary filler comprises zinc-doped secondary glass powder filler.

5. The first composition of claim 4, wherein the zinc-doped secondary glass powder filler comprises soda-lime-glass, borosilicate glass or a combination thereof.

6. The first composition of claim 1, wherein the polymer is selected from the group consisting of polybutadiene, butadiene/C1-C4-alkyl, butadiene/acrylate copolymers, polyisoprene, styrene/butadiene copolymers, styrene/isoprene copolymers, isobutylene/isoprene copolymers, isoprene/butadiene copolymers, butadiene-styrene-isoprene terpolymers, butadiene/acrylonitrile copolymers, NBR, partially hydrogenated NBR, fully hydrogenated NBR, polyisobutylene, EPDM, modified polybutadiene, modified butadiene/C1-C4-alkyl, modified butadiene/acrylate copolymers, modified polyisoprene, modified styrene/butadiene copolymers, modified styrene/isoprene copolymers, modified butadiene-styrene-isoprene terpolymers, modified isobutylene/isoprene copolymers, modified isoprene/butadiene copolymers, modified butadiene/acrylonitrile copolymers, modified NBR, modified partially hydrogenated NBR, modified fully hydrogenated NBR, modified polyisobutylene, modified EPDM, and combinations thereof.

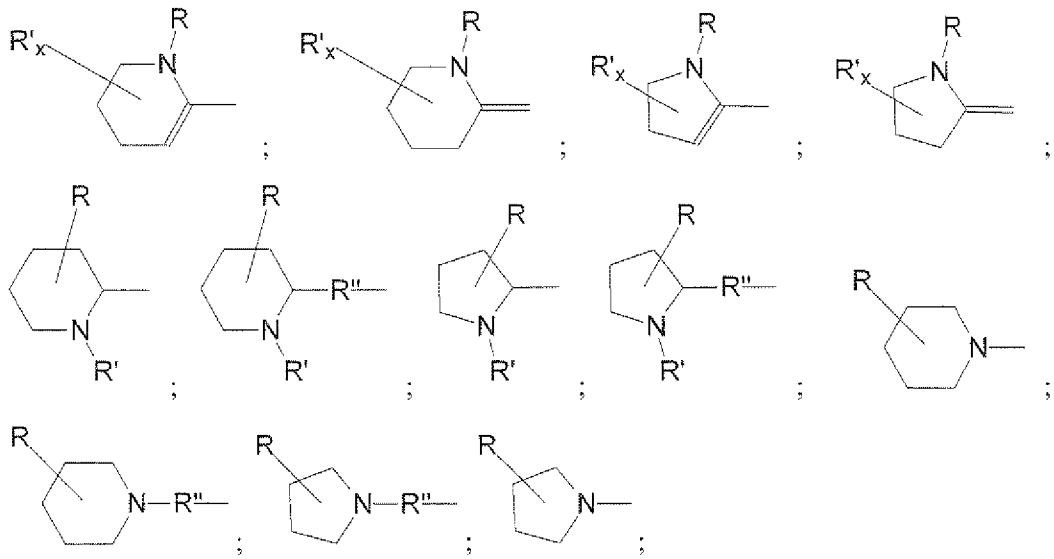
7. The first composition of claim 1, wherein the polymer is selected from the group consisting of modified polybutadiene, modified butadiene/C1-C4-alkyl, modified butadiene/acrylate copolymers, modified polyisoprene, modified styrene/butadiene copolymers, modified styrene/isoprene copolymers, modified isobutylene/isoprene copolymers, modified isoprene/butadiene copolymers, modified butadiene-styrene-isoprene terpolymers, modified butadiene/acrylonitrile copolymers, modified NBR, modified partially hydrogenated NBR, modified fully hydrogenated NBR, modified polyisobutylene, modified EPDM, and combinations thereof.

8. The first composition of claim 7, wherein the polymer comprises one or a plurality of functionalities each of which is independently selected from the group consisting of:

thiol groups, protected thiol groups, hydrocarbyl thioethers, trihydrocarbylsilyl-thioethers, trihydrocarbylstannyl-thioethers, primary amine groups, protected primary amino groups, bis-trihydrocarbylsilyl-amino groups, bis-trihydrocarbylstannyl-amino groups, trihydrocarbylsilyl-amino groups, trihydrocarbylstannyl-amino groups, hydrocarbyl amino groups, protected hydrocarbyl amino groups, trihydrocarbylsilyl-hydrocarbyl-amino groups, trihydrocarbylstannyl-hydrocarbyl-amino groups, cyclic amine groups, dihydrocarbylamino groups, primary phosphane groups, protected primary phosphane groups, bis-trihydrocarbylsilyl-phosphane groups, bis-trihydrocarbylstannyl-phosphane groups, trihydrocarbylsilyl-phosphane groups, bis-trihydrocarbylstannyl-phosphane groups, hydrocarbyl phosphane groups, protected hydrocarbyl phosphane groups, trihydrocarbylsilyl-hydrocarbyl-phosphane groups, trihydrocarbylstannyl-hydrocarbyl-phosphane groups, alcohol groups, protected alcohol groups, trihydrocarbylsilyl-ethers, trihydrocarbylstannyl-ethers, carboxyl groups, protected carboxy groups, carbon acid hydrocarbylesters, carboxy amide-anhydride groups, carboxy hydrocarbyl amides, hydrocarboxysilyl groups, trihydrocarboxysilyl groups, hydrocarbyl-dihydrocarboxysilyl groups, dihydrocarbyl-hydrocarboxysilyl groups, dihydrocarbylsilanol groups, hydrocarbyldisilanol groups, trichlorosilyl groups, dichloro-hydrocarbylsilyl groups, chloro-dihydrocarbylsilyl groups, hydrocarbylcarbylolegosiloxane, dihydrocarbylolegosiloxane, and combinations thereof.

9. The first composition of claim 8, wherein the functionalities are independently selected from the group consisting of:

HS-; HS-R''-; RS-; RS-R''-; $(R_3Si)S$-; $(R_3Si)S$-R''-; H_2N-; H_2N-R''-; $(R_3Si)_2N$-; $(R_3Si)_2N$-R''-; $(R_3Sn)_2N$-; $(R_3Sn)_2N$-R''; $R_3Si(H)N$-; $R_3Si(H)N$-R''-; $R_3Sn(H)N$-; $R_3Sn(H)N$-R''-; R(H)N- or R(H)N-R''-; $(R(R'_3Si)N$-; $(R(R'_3Si)N$-R''-; $(R(R'_3Sn)N$-; $(R(R'_3Sn)N$-R''; R_2N-; R_2N-R''-; H_2P-; H_2P-R''-; $(R_3Si)_2P$-; $(R_3Si)_2P$-R''-; $(R_3Sn)_2P$- or $(R_3Sn)_2P$-R''-; $(R_3Si)(H)P$-; $(R_3Si)(H)P$-R''-; $(R_3Sn)(H)P$-; $(R_3Sn)(H)P$-R''-; R(H)P-; R(H)P-R''-; (R(R'3Si)P- or (R(R'3Si)P-R''-; $(R(R'_3Sn)P$-; $(R(R'_3Sn)P$-R''-; HO-; HO-R''-; R_3Si-O-; R_3Si-O-R''-; R_3Sn-O-; R_3Sn-O-R''-; ROOC-; ROOC-R''-; HOOC-; HOOC-R''-; H_2NOC; H_2NOC-R''-; ((R)(H)N)OC-; ((R)(H)N)OC-R''-; $(RO)_3Si$-; $(RO)_3Si$-R''-; $R'(RO)_2Si$-; R'(RO)2Si-R''-; $R'_2(RO)Si$-R''-; $(HO)(R_2)Si$-; $(HO)(R_2)Si$-R''-; $(HO)_2(R)Si$-; $(HO)_2(R)Si$-R''-; Cl_3Si-; Cl_3Si-R''-; $R(Cl)_2Si$-; $R(Cl)_2Si$-R''-; $R_2(Cl)Si$-; $R_2(Cl)Si$-R''-;



dihydrocarbylolegosiloxanes; and combinations thereof;

wherein the dihydrocarbylolegosiloxanes are formed through reaction of tris-dimethylsiloxane with living anionic polymer chains;

wherein x is 0, 1, 2 or 3;

wherein R and R' are independently selected hydrocarbyl groups; and

wherein R'' is a divalent hydrocarbon group.

10. The first composition of claim 1, wherein the polymer is selected from the group

consisting of polyisoprene, styrene/butadiene copolymers, styrene/isoprene copolymers, isoprene/butadiene copolymers, modified polybutadiene, modified polyisoprene, modified styrene/butadiene copolymers, modified styrene/isoprene copolymers, modified isoprene/butadiene copolymers, polybutadiene, modified butadiene-styrene-isoprene terpolymers, and combinations thereof.

11. The first composition of claim 1, wherein the primary filler is selected from the group consisting of carbon black, silica, carbon-silica dual-phase-filler, clay, calcium carbonate, magnesium carbonate, lignin, magadiite, and combinations thereof.

12. The first composition of claim 1, wherein the primary filler comprises silica.

13. The first composition of any one of claims 1-12, further comprising an oil.

14. The first composition of any one of claims 1-12, further comprising a silane coupling agent.

15. The first composition of any one of claims 1-12, further comprising a vulcanization agent.

16. An article comprising a component formed from the first composition of one of claims 1-12.

17. The article of claim 16, wherein the article is selected from the group consisting of a tire, a tire tread, a tire side wall, a tire carcass, a belt, a hose, a vibration damper, a footwear component, and combinations thereof.

18. A vulcanized composition comprising a reaction product of a vulcanizing agent and the first composition of any of claims 1-12.

19. An article comprising a component formed from the vulcanized composition of claim 18.

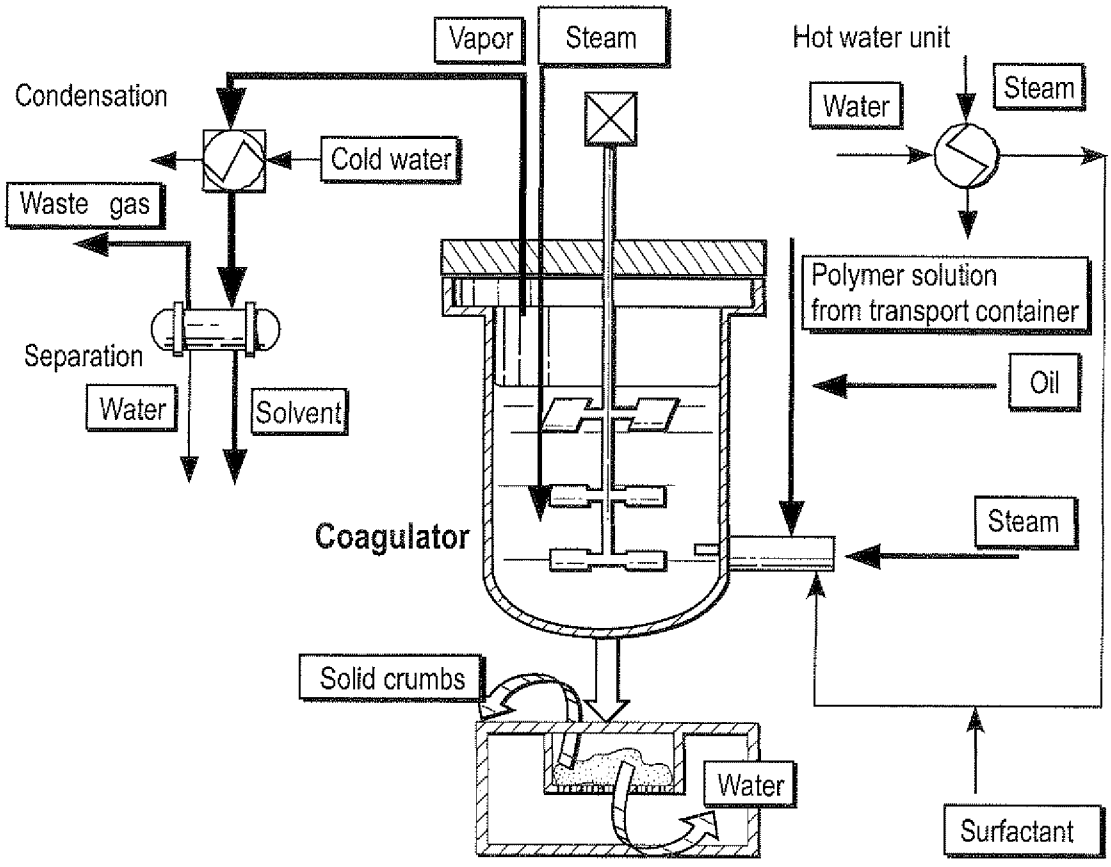
20. The article of claim 19, wherein the article is selected from the group consisting of a tire, a tire tread, a tire side wall, a tire carcass, a belt, a hose, a vibration damper, a footwear component, and combinations thereof.

21. A method of making the first composition of any of claims 1-12, comprising reacting i) a polymer, ii) a primary filler, and iii) a secondary filler.

22. A method of making a vulcanized composition, comprising reacting a vulcanization agent with the first composition of any of claims 1-12.

23. The composition of claim 1 wherein the secondary glass powder filer, the zinc-doped secondary glass powder filler, or both are produced by a high-temperature extrusion process.

FIG. 1


Vapor
Steam
Hot water unit
Condensation
Water
Steam
Cold water
Waste gas
Polymer solution
from transport container
Separation
Oil
Water
Solvent
Steam
Coagulator
Solid crumbs
Water
Surfactant