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(54) Title: RUBBER COMPOSITIONS REINFORCED WITH IRON OXIDE

(57) Abstract: Articles including tire components made of rubber compositions having an epoxidized rubber component and iron oxide as a reinforcement filler. The iron oxide may be ferric oxide, iron (II, III) oxide and combinations thereof and may in some embodiments be limited to ferric oxide and may be limited to iron oxides having a particle size no more than 500 nm. Examples of suitable epoxidized rubber components in embodiments of the rubber compositions having an epoxidized rubber component having a content of units of conjugated diene origin that is great than 50 mol% include, but are not limited to, epoxidized polybutadiene, epoxidized natural rubber, epoxidized polyisoprene rubber, epoxidized styrene-butadiene rubber and combinations thereof.



RUBBER COMPOSITIONS REINFORCED WITH IRON OXIDE

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to rubber compositions and more particularly, to epoxidized rubber compositions reinforced with an iron oxide.

Description of the Related Art

[0002] Rubber is a well-known polymer that is used in many products ranging from tires and other automobile applications to playground equipment, shoes, clothing, flooring and household supplies. Rubber comes in many forms and sources including, for example, natural production as from the rubber tree and synthetic production as from petrochemical sources.

[0003] Rubber is typically compounded with other materials in a rubber composition to provide the desired physical attributes of the cured rubber composition. Since rubber by itself is not particularly strong, reinforcement fillers may be added to improve its strength and, for example, to provide increased wear properties, rigidity and longevity for products made from the rubber compositions. Examples of well-known reinforcement fillers include carbon blacks and silica, both of which are extensively used in the tire industry to reinforce the rubber compositions that are used in tires.

[0004] Research continues in the field of reinforcement fillers in rubber compositions in the search for new reinforcement fillers that are useful in rubber compositions to improve the physical properties of the resulting rubber compositions and/or to improve the mixing, handling and processing of the rubber compositions that will be used to form useful products.

SUMMARY OF THE INVENTION

[0005] Particular embodiments of the present invention include rubber compositions having an epoxidized rubber component and iron oxide as a reinforcement filler. Also provided are articles made of such rubber compositions including tires and tire components such as treads.

[0006] Such embodiments include rubber compositions that are based upon cross-linkable rubber compositions comprising, in parts by weight per 100 parts by weight of rubber (phr) an epoxidized rubber and between 30 phr and 800 phr of an iron oxide reinforcement filler having an average particle diameter of no more than 500 nm. Such rubber compositions further include a curing system.

[0007] The iron oxide may be ferric oxide, iron (II, III) oxide and combinations thereof. Some embodiments may be limited to just ferric oxide. Examples of suitable epoxidized rubber components in embodiments of the rubber compositions having an epoxidized rubber component with a content of units of conjugated diene origin that is great than 50 mol% include, but are not limited to, epoxidized polybutadiene, an epoxidized natural rubber, an epoxidized polyisoprene rubber, an epoxidized styrene-butadiene rubber and combinations thereof.

[0008] The foregoing and other objects, features and advantages of the invention will be apparent from the following more detailed descriptions of particular embodiments of the invention.

DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

[0009] Particular embodiments of the present invention include rubber compositions and articles made from such rubber compositions including, for example, tires made at least in part from the rubber compositions disclosed herein. Surprisingly it has been found that very small particles, *i.e.*, of nanosized or approaching nanosized particles, of an iron oxide such as ferric oxide (Fe_2O_3) can be useful in an epoxidized rubber composition as a rubber reinforcement filler.

[0010] The rubber compositions disclosed herein include an epoxidized rubber component and an iron oxide reinforcement filler having an average particle diameter of no more than 500 nm. The rubber compositions will further include a curing system. It is believed, but not limiting to the invention, that the iron oxide is useful as a reinforcement filler because it reacts or interacts with the epoxy function of the elastomer to reinforce it. The usefulness of the iron oxide in such rubber compositions is limited to fillers having an average particle diameter that is no more than 500 nanometers in size.

[0011] In particular embodiments, the disclosed rubber compositions are useful for the manufacture of tire treads. The tire treads may be included on passenger or light truck tires as well as, for example, on heavy truck, aircraft tires and agricultural tires.

[0012] As used herein, “phr” is “parts per hundred parts of rubber by weight” and is a common measurement in the art wherein components of a rubber composition are measured relative to the total weight of rubber in the composition, *i.e.*, parts by weight of the component per 100 parts by weight of the total rubber(s) in the composition.

[0013] As used herein, elastomer and rubber are synonymous terms.

[0014] As used herein, “based upon” is a term recognizing that embodiments of the present invention are made of vulcanized or cured rubber compositions that were, at the time of their assembly, uncured. The cured rubber composition is therefore “based upon” the uncured rubber composition. In other words, the cross-linked rubber composition is based upon or comprises the constituents of the cross-linkable rubber composition.

[0015] As is generally known, a tire tread includes the road-contacting portion of a vehicle tire that extends circumferentially about the tire. It is designed to provide the handling characteristics required by the vehicle; *e.g.*, traction, dry braking, wet braking, cornering and so forth – all preferably being provided with a minimum amount of generated noise and at low rolling resistance.

[0016] Treads of the type disclosed herein include tread elements, the structural features of the tread that contact the ground. Such structural features may be of any type or shape, examples of which include tread blocks and tread ribs. Tread blocks have a perimeter defined by one or more grooves that create an isolated structure in the tread while a rib runs substantially in the longitudinal (circumferential) direction and is not interrupted by grooves that run in the substantially lateral (axial) direction or any other grooves that are oblique thereto. The radial (depth) direction is perpendicular to the lateral direction.

[0017] It is recognized that treads may be formed from only one rubber composition or in two or more layers of differing rubber compositions, *e.g.*, a cap and base construction. In a cap and base construction, the cap portion of the tread is made of one rubber composition that is designed for contact with the road. The cap is supported on the base portion of the tread, the base portion made of different rubber composition. In particular embodiments of

the present invention the entire tread may be made from the rubber compositions disclosed herein while in other embodiments only the cap portions of the tread may be made from such rubber compositions or only the base may be made from such rubber compositions.

[0018] In other embodiments it is recognized that the contact surface of the tread elements, *i.e.*, that portion of the tread element that contacts the road, may be formed totally and/or only partially from the rubber compositions disclosed herein. In particular embodiments the tread block, for example, may be formed as a composite of laterally layered rubber compositions such that at least one lateral layer of a tread block is of the rubber compositions disclosed herein and another lateral layer of a tread block is of an alternative rubber composition. For example, at least 80 % of the total contact surface area of the tread may be formed solely from the rubber compositions disclosed herein. The total contact surface area of the tread is the total surface area of all the radially outermost faces of the tread elements that are adapted for making contact with the road.

[0019] Embodiments of the rubber compositions that are disclosed herein include an epoxidized rubber component that results at least in part from conjugated diene monomers and typically having (in some embodiments required to have) a content of units of diene origin (conjugated diene) that is greater than 50 mol%. Such epoxidized rubber components may include, for example, an epoxidized polybutadiene rubber (eBR), an epoxidized styrene-butadiene rubber (eSBR), an epoxidized natural rubber (eNR), an epoxidized polyisoprene rubber (eIR), epoxidized butadiene copolymers, epoxidized isoprene copolymers and mixtures of these elastomers including, for example, epoxidized isoprene/butadiene copolymers (eBIR), epoxidized isoprene/styrene copolymers (eSIR) and epoxidized isoprene/butadiene/styrene copolymers (eSBIR). The rubber compositions may include, for example, any one of these rubber components or combinations of any of them.

[0020] Particular embodiments may have the epoxidized rubber component selected from an epoxidized polybutadiene, an epoxidized natural rubber, an epoxidized polyisoprene rubber, an epoxidized styrene-butadiene rubber or combinations thereof. Alternatively the epoxidized rubber component may be limited to eBR, eSBR or combinations thereof. Alternatively the epoxidized rubber component may be limited to just eNR or alternatively just eNR, eSBR, eBR and combinations thereof.

[0021] Epoxidized rubber components are well-known in the art and may be obtained, as is known to those skilled in the art, by processes based on chlorohydrin or bromohydrin or processes based on hydrogen peroxides, alkyl hydroperoxides or peracids (such as peracetic acid or performic acid).

[0022] As noted above, not all of the epoxidized rubber components must be highly unsaturated rubber components, *i.e.*, having a content of conjugated diene origin that is greater than 50 mol%. While some embodiments only include highly unsaturated rubber components as the epoxidized rubber component, other embodiments may include rubber components having a content of conjugated diene origin that is at least 15 mol% but no more than 50 mol% (essentially unsaturated) or even less (essentially saturated diene elastomers). Examples of such epoxidized essentially saturated diene elastomers include an epoxidized butyl rubber (eIIR) and epoxidized copolymers of dienes and of alpha-olefins of the EPDM type (eEPDM). These are known to those skilled in the art and as examples, description of the epoxidation of eIIR is available in WO2014/089674 and a description of the epoxidation of eEPDM is available in EP0149192, both fully incorporated herein by reference for all that they disclose.

[0023] To obtain the targeted technical effect, the epoxidized rubber includes between 1 mol% and 25 mol% of the epoxy functionality or alternatively between 2 mol% and 25 mol%, between 2 mol% and 18 mol%, between 5 mol% and 25 mol%, between 5 mol% and 18 mol%, between 8 mol% and 15 mol%, between 3 mol% and 10 mol% or between 8 mol% and 20 mol%. Since the Tg of the rubber increases with increasing epoxy functionality, in particular embodiments greater than 25 mol% impacts the desired properties of the rubber compositions disclosed herein and less than the 1 mol% impacts the reactivity with the iron oxide reinforcement filler. The epoxy functionality by mole percent can be determined in known way through NMR analysis.

[0024] While particular embodiments of the disclosed rubber compositions include only one or more epoxidized rubber components, others may additionally include a capped amount of up to 25 phr of one or more second diene elastomers that are not epoxidized or alternatively, up to 5 phr, up to 10 phr, up to 20 phr, up to 35 phr, up to 55 phr, up to 60 phr, up to 75 phr or up to 90 phr of such second diene elastomers. As is mentioned above, such

diene elastomers are understood to be those elastomers resulting at least in part, *i.e.*, a homopolymer or a copolymer, from diene monomers, *i.e.*, monomers having two double carbon-carbon bonds, whether conjugated or not. Particular embodiments of such rubber compositions may include a lower limit for each of these caps of 0 phr and others may include a lower limit of 5 phr or alternatively a lower limit of 10 phr; *e.g.*, between 0 phr and 25 phr or between 5 phr and 25 phr of such second rubber component.

[0025] These second rubber component diene elastomers may be classified as either “essentially unsaturated” diene elastomers or “essentially saturated” diene elastomers. As used herein, essentially unsaturated diene elastomers are diene elastomers resulting at least in part from conjugated diene monomers, the essentially unsaturated diene elastomers having a content of such members or units of diene origin (conjugated dienes) that is at least 15 mol%. Within the category of essentially unsaturated diene elastomers are highly unsaturated diene elastomers, which are diene elastomers having a content of units of diene origin (conjugated diene) that is greater than 50 mol%.

[0026] Those diene elastomers that do not fall into the definition of being essentially unsaturated are, therefore, the essentially saturated diene elastomers. Such elastomers include, for example, butyl rubbers and copolymers of dienes and of alpha-olefins of the EPDM type. These diene elastomers have low or very low content of units of diene origin (conjugated dienes), such content being less than 15 mol. %. Particular embodiments of the present invention exclude any additional diene elastomers that are essentially saturated.

[0027] Particular embodiments of the rubber compositions disclosed herein may include, as the second diene elastomer, highly unsaturated diene elastomers such as polybutadienes (BR), polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers and mixtures of these elastomers. The polyisoprenes may include synthetic *cis*-1,4 polyisoprene, which in particular embodiments may be characterized as possessing *cis*-1,4 bonds of more than 90 mol% or alternatively, of more than 98 mol%.

[0028] In addition to these examples, other examples of copolymers that may be useful include, for example, butadiene-styrene copolymers (SBR), butadiene-isoprene copolymers (BIR), isoprene-styrene copolymers (SIR) and isoprene-butadiene-styrene copolymers (SBIR) and mixtures thereof.

[0029] Any of these examples may be used singly or in any combination as the second rubber component in particular embodiments of the disclosed rubber compositions. Optionally they may also be used in any combination with essentially unsaturated diene elastomers.

[0030] Of course as is known to those skilled in the art, the elastomers useful as the second rubber component may also be functionalized with a suitable functionalizing agent. These elastomers can be functionalized by reacting them with suitable functionalizing agents prior to or in lieu of terminating the elastomer. Exemplary functionalizing agents include, but are not limited to, metal halides, metalloid halides, alkoxysilanes, imine-containing compounds, esters, ester-carboxylate metal complexes, alkyl ester carboxylate metal complexes, aldehydes or ketones, amides, isocyanates, isothiocyanates and imines. These types of functionalized elastomers are known to those of ordinary skill in the art. While particular embodiments may include one or more of these functionalized elastomers, other embodiments may include one or more of these functionalized elastomers mixed with one or more of the non-functionalized as the second elastomer component.

[0031] In addition to the epoxidized rubber component and optionally a second rubber component as described above, the rubber composition disclosed herein further includes an iron oxide reinforcement filler. Iron oxides are well-known materials and are used in such industries as the iron industry in the production of alloys, in the polishing industry in the fine polishing of metallic jewelry and lenses, in the cosmetics industry, in the paint industry as a pigment and in the magnetic recording industry as a recording medium. Iron (II,III) oxide is also used in making the catalyst for the industrial synthesis of ammonia.

[0032] Large particles of iron oxide are not useful as a reinforcement filler in an epoxidized rubber composition. Therefore, particular embodiments of the rubber compositions disclosed herein include iron oxide particles having an average particle diameter capped at no more than 500 nm or alternatively, no more than 450 nm, no more than 400 nm, no more than 300 nm, no more than 250 nm, no more than 150 nm or no more than 100 nm. Particular embodiments of such rubber compositions may include a lower limit for each of these average diameter caps of 1 nm or alternatively 5 nm, 10 nm, 15 nm or 30 nm as the lower limit of a range of the average diameter of the iron oxide reinforcement filler. For

example, the iron oxide may have an average diameter of between 5 nm and 150 nm or of between 30 nm and 150 nm. More particularly the iron oxide filler particles of particular embodiments may have an average particle diameter of between 5 nm and 500 nm or alternatively between 10 nm and 400 nm, between 15 nm and 300 nm, between 30 and 100 nm or between 30 nm and 65 nm.

[0033] Iron oxides are available in many forms. For example, ferrous oxide (FeO) is fairly rare and not readily available. The more common forms include iron (II, III) oxide (for example Fe_3O_4), which is naturally occurring as the mineral magnetite and iron (III) oxide (Fe_2O_3), which is also known as ferric oxide and as the mineral hematite and is a source of iron for the steel industry.

[0034] In particular embodiments of the rubber compositions disclosed herein, the iron oxide reinforcement filler may be selected from the group consisting of ferric oxide, iron (II, III) oxide and combinations thereof. In other embodiments the iron oxide reinforcement filler may be just ferric oxide or alternatively, just iron (II,III) oxide. In particular embodiments, including those listed above, the iron (II,III) oxide may be limited to Fe_3O_4 .

[0035] The amount of iron oxide reinforcement filler is determined by the degree of reinforcement desired in the resulting cured rubber composition and in those cases the amount of iron oxide is not particularly limited. In particular embodiments, however, the amount of iron oxide added to the epoxidized rubber composition may be between 30 phr and 800 phr or alternatively between 50 phr and 800 phr, between 50 phr and 500 phr, between 50 phr and 400 phr, between 30 phr and 500 phr, between 100 phr and 800 phr, between 100 phr and 600 or between 100 phr and 500 phr.

[0036] Iron oxides may be obtained from different sources. For example US Research Nanomaterials of Houston Texas provides iron oxides such as Fe_2O_3 with an average particle size of 30 nm and in a different product, with an average particle size of between 20 nm and 40 nm. The also provide Fe_3O_4 iron oxide with an average particle size of between 15 nm to 20 nm. Iron oxides are also available from Sigma-Aldrich with offices in St. Louis MO as ferric oxide with an average particle size less than 50 nm.

[0037] Average particle size may be determined by several different methods as known to those skilled in the art including dynamic light scattering (DLS), microscopy (SEM

or TEM) and calculating the particle size based on the BET surface area measurement. Methods that include the TEM determination and BET measurement provide suitable results.

[0038] For example, determination of the average particle diameter may be determined based on the following equation: $d = 6000 / (\text{BET} * \text{Density})$, wherein d is the average particle diameter of the iron oxide in nanometers, BET is the BET surface area in m^2/g and density is the density of the particles in g/cc . An explanation of this test method may be found in the article A Case Study in Sizing Nanoparticles by F. Thiele, M. Poston and R. Brown and published by Micromeritics Analytical Services of Norcross GA, which article is hereby fully incorporated herein by reference. A suitable procedure for determining BET and density are provided below.

[0039] The BET measurement may be obtained in accordance with ASTM method D6556 to determine the nitrogen surface area SSA. For example, such measurements may be made on a TriStar II surface area and porosity instrument manufactured by Micromeritics. Samples may be treated with nitrogen gas to remove adsorbed contaminants, then cooled under vacuum using liquid nitrogen. Controlled increments of nitrogen gas are given to the sample at a constant temperature and a specified pressure. The gas volume adsorbed is calculated by the instrument software and the SSA (BET) is determined.

[0040] The density measurement may be obtained in accordance with ASTM C604-02 by gas comparison pycnometer. This technique uses the gas displacement method to measure volume accurately. For example, using a Micromeritics AccuPyc II 1340 pycnometer, an inert gas such as helium is used as the displacement medium. The sample is sealed in the instrument compartment of known volume, the helium is admitted, and then expanded into another precision internal volume. The pressures observed upon filling the sample chamber and then discharging it into a second empty chamber allow computation of the sample solid phase volume. Helium molecules rapidly fill pores as small as one angstrom in diameter; only the solid phase of the sample displaces the gas. Dividing this volume into the sample weight gives the gas displacement density.

[0041] In addition to the epoxidized rubber component, the optional second rubber component and the iron oxide reinforcement filler, particular embodiments may further include an amount of a secondary reinforcement filler. It may be especially desired to add

such secondary reinforcement filler for those embodiments that include the second rubber composition because the iron oxide will provide little if any reinforcement for those rubbers. Optionally such secondary reinforcement fillers may be included in embodiments that include just the epoxidized rubber component. Particular embodiments include only the iron oxide reinforcement filler with no secondary reinforcement fillers.

[0042] Reinforcing fillers useful as the secondary reinforcement filler are well known in the art and include, for example, carbon blacks and silica though any additional reinforcing filler known to those skilled in the art may also be useful. In particular embodiments of the rubber composition, the secondary filler may be selected from carbon black, silica or combinations thereof. Other embodiments may be limited to just carbon black or limited to just silica as the secondary reinforcement filler.

[0043] Carbon black, which is an organic filler, is well known to those having ordinary skill in the rubber compounding field. Suitable carbon blacks are any carbon blacks known in the art and suitable for the given purpose. Suitable carbon blacks of the type HAF, ISAF and SAF, for example, are conventionally used in tire treads. Non-limitative examples of carbon blacks include, for example, the N115, N134, N234, N299, N326, N330, N339, N343, N347, N375 and the 600 series of carbon blacks, including, but not limited to N630, N650 and N660 carbon blacks.

[0044] As noted above, silica may also be useful as reinforcement filler. The silica may be any reinforcing silica known to one having ordinary skill in the art including, for example, any precipitated or pyrogenic silica having a BET surface area and a specific CTAB surface area both of which are less than 450 m²/g or alternatively, between 30 and 400 m²/g may be suitable for particular embodiments based on the desired properties of the cured rubber composition. Particular embodiments of rubber compositions disclosed herein may include a silica having a CTAB of between 80 and 200 m²/g, between 100 and 190 m²/g, between 120 and 190 m²/g or between 140 and 180 m²/g. The CTAB specific surface area is the external surface area determined in accordance with Standard AFNOR-NFT-45007 of November 1987.

[0045] Highly dispersible precipitated silicas (referred to as "HDS") may be useful in particular embodiments of such rubber compositions disclosed herein, wherein "highly

dispersible silica" is understood to mean any silica having a substantial ability to disagglomerate and to disperse in an elastomeric matrix. Such determinations may be observed in known manner by electron or optical microscopy on thin sections. Examples of known highly dispersible silicas include, for example, Perkasil KS 430 from Akzo, the silica BV3380 from Degussa, the silicas Zeosil 1165 MP and 1115 MP from Rhodia, the silica Hi-Sil 2000 from PPG and the silicas Zeopol 8741 or 8745 from Huber.

[0046] When silica is added to the rubber composition, a proportional amount of a silane coupling agent is also added to the rubber composition. The silane coupling agent is a sulfur-containing organosilicon compound that reacts with the silanol groups of the silica during mixing and with the elastomers during vulcanization to provide improved properties of the cured rubber composition. A suitable coupling agent is one that is capable of establishing a sufficient chemical and/or physical bond between the inorganic filler and the diene elastomer; which is at least bifunctional, having, for example, the simplified general formula "Y-T-X", in which: Y represents a functional group ("Y" function) which is capable of bonding physically and/or chemically with the inorganic filler, such a bond being able to be established, for example, between a silicon atom of the coupling agent and the surface hydroxyl (OH) groups of the inorganic filler (for example, surface silanols in the case of silica); X represents a functional group ("X" function) which is capable of bonding physically and/or chemically with the diene elastomer, for example by means of a sulfur atom; T represents a divalent organic group making it possible to link Y and X.

[0047] Any of the organosilicon compounds that contain sulfur and are known to one having ordinary skill in the art are useful for practicing embodiments of the present invention. Examples of suitable silane coupling agents having two atoms of silicon in the silane molecule include 3,3'-bis(triethoxysilylpropyl) disulfide and 3,3'-bis(triethoxysilylpropyl) tetrasulfide (known as Si69). Both of these are available commercially from Degussa as X75-S and X50-S respectively, though not in pure form. Degussa reports the molecular weight of the X50-S to be 532 g/mole and the X75-S to be 486 g/mole. Both of these commercially available products include the active component mixed 50-50 by weight with a N330 carbon black. Other examples of suitable silane coupling agents having two atoms of silicon in the silane molecule include 2,2'-bis(triethoxysilylethyl) tetrasulfide, 3,3'-

bis(tri-t-butoxy-silylpropyl) disulfide and 3,3'-bis(di t-butylmethoxysilylpropyl) tetrasulfide. Examples of silane coupling agents having just one silicon atom in the silane molecule include, for example, 3,3'(triethoxysilylpropyl) disulfide and 3,3' (triethoxy-silylpropyl) tetrasulfide. The amount of silane coupling agent can vary over a suitable range as known to one having ordinary skill in the art. Typically the amount added is between 7 wt. % and 15 wt. % or alternatively between 8 wt. % and 12 wt. % or between 9 wt. % and 11 wt. % of the total weight of silica added to the rubber composition.

[0048] The disclosed rubber compositions may include an amount of secondary filler as deemed necessary for those skilled in the art to acquire the desired properties of the final cured product. The amounts added to the rubber compositions are not particularly limited since the amounts will be determined in known way by those skilled in the art to provide the desired properties. Examples of suitable amounts may include none or for reinforcement, between 0 phr and 150 phr, between 0 phr and 100 phr, between 3 phr and 120 phr, between 3 phr and 30 phr, between 3 phr and 80 phr. As is well-known, carbon black may be added in small amounts, *e.g.*, between 3 phr and 8 phr or between 3 phr and 5 phr, to make the article black, such as for a tire component. In particular embodiments, such amounts are not included in the disclosed amounts that are suitable for reinforcement of the rubber compositions.

[0049] In addition to the epoxidized rubber component, the optional second rubber component, the iron oxide reinforcement filler and the secondary reinforcement filler, particular embodiments may further include a plasticizing system. Plasticizing systems are well known in the art and are used for adjusting the processability of the rubber composition as well as adjusting the final cured properties of the rubber composition including the glass transition temperature (T_g).

[0050] For example, a plasticizing system is described in patent application publication WO2016/106408 that is useful for rubber compositions, including those having a functionalized rubber component, such publication being hereby fully incorporated by reference for all that it teaches.

[0051] Suitable plasticizing systems may include, for example, high T_g resins (T_g greater than 23° C), low T_g resins and/or liquid plasticizers such as oil. Although any of the known resins may be useful for particular embodiments, and the rubber compositions

disclosed herein are not particularly limited to any one plasticizing system, terpene-phenol resins and hydrocarbon resins derived from petroleum products are useful examples of a suitable high Tg resin.

[0052] Terpene phenolic resins are available on the market from, for example, Arizona Chemical having offices in Savannah, GA. Arizona Chemical markets a range of terpene phenolic resins under the name SYLVARES with varying softening points (SP), glass transition temperatures (Tg) hydroxyl numbers (HN), number-average molecular masses (Mn) and polydispersity indices (Ip), examples of which include: SYLVARES TP105 (SP: 105 °C; Tg: 55 °C; HN: 40; Mn: 540; Ip:1.5); SYLVARES TP115 (SP: 115 °C; Tg: 55 °C; HN: 50; Mn: 530; Ip:1.3); and SYLVARES TP2040 (SP: 125 °C; Tg: 80 °C; HN: 135-150; Mn: 600; Ip:1.3).

[0053] Other useful resins include the OPPERA resins available from ExxonMobil, these resins being modified aliphatic hydrocarbon resins, and SYLVARES 600 resin (M_n 850 g/mol; Ip 1.4; T_g 47° C.; HN of 31 mg KOH/g) that is an octyl phenol-modified copolymer of styrene and alpha methyl styrene as well as the coumarone-indene resins.

[0054] It may be noted that the glass transition temperatures of plasticizing resins may be measured by Differential Scanning Calorimetry (DCS) in accordance with ASTM D3418 (1999).

[0055] As noted, if the Tg of the rubber composition is too high with the addition of the high Tg resin, then the Tg can be adjusted downward by adding a plasticizing oil or a low Tg resin. Suitable plasticizing liquids may include any liquid known for its plasticizing properties with diene elastomers. At room temperature (23 °C), these liquid plasticizers or these oils of varying viscosity are liquid as opposed to the resins that are solid. Examples include those derived from petroleum stocks, those having a vegetable base and combinations thereof. Examples of oils that are petroleum based include aromatic oils, paraffinic oils, naphthenic oils, MES oils, TDAE oils and so forth as known in the industry. Also known are liquid diene polymers, the polyolefin oils, ether plasticizers, ester plasticizers, phosphate plasticizers, sulfonate plasticizers and combinations of liquid plasticizers.

[0056] Examples of suitable vegetable oils include sunflower oil, soybean oil, safflower oil, corn oil, linseed oil and cotton seed oil. These oils and other such vegetable oils

may be used singularly or in combination. In some embodiments, sunflower oil having a high oleic acid content (at least 70 weight percent or alternatively, at least 80 weight percent) is useful, an example being AGRI-PURE 80, available from Cargill with offices in Minneapolis, MN. In particular embodiments of the present invention, the selection of a suitable plasticizing oil is limited to a vegetable oil having a high oleic acid content.

[0057] The amounts of high Tg resin, low Tg resin and liquid plasticizer useful in any particular embodiment depends upon the particular circumstances and the desired results. Some embodiments may include no plasticizing system at all. Others may include just a high Tg resin or just a plasticizing oil. Such determinations are well within the skill of those having ordinary skill in the art. Examples of useful amounts of plasticizing oil for some embodiments may be zero or alternatively between 0 or 10 phr and 60 phr or alternatively, between 0 or 10 phr and 55 phr, between 0 or 10 phr and 50 phr, between 0 or 5 phr and 40 phr or between 0 or 10 phr and 35 phr. Examples of useful amounts of high Tg resin for some embodiments may be zero or alternatively between 0 phr and 150 phr, between 5 phr and 150 phr or between 10 phr and 100 phr of the high Tg resin.

[0058] For embodiments of the rubber compositions disclosed herein that may be useful for tire treads, the amounts of the plasticizing system may be adjusted to provide, for example, glass transition temperatures of between -35° C and -25° C and/or alternatively, between -28° C and -14° C, between -30° C and -16° C and/or between -16° C and 10° C.

[0059] The rubber compositions disclosed herein may be cured with any suitable curing system including a peroxide curing system or a sulfur curing system. Particular embodiments are cured with a sulfur curing system that includes free sulfur and may further include, for example, one or more of accelerators, stearic acid and zinc oxide. Suitable free sulfur includes, for example, pulverized sulfur, rubber maker's sulfur, commercial sulfur, and insoluble sulfur. The amount of free sulfur included in the rubber composition is not limited and may range, for example, between 0.5 phr and 10 phr or alternatively between 0.5 phr and 5 phr or between 0.5 phr and 3 phr. Particular embodiments may include no free sulfur added in the curing system but instead include sulfur donors.

[0060] Accelerators are used to control the time and/or temperature required for vulcanization and to improve the properties of the cured rubber composition. Particular

embodiments of the present invention include one or more accelerators. One example of a suitable primary accelerator useful in the present invention is a sulfenamide. Examples of suitable sulfenamide accelerators include n-cyclohexyl -2-benzothiazole sulfenamide (CBS), N-tert-butyl-2-benzothiazole Sulfenamide (TBBS), N-Oxydiethyl-2-benzthiazolsulfenamid (MBS) and N'-dicyclohexyl-2-benzothiazolesulfenamide (DCBS). Combinations of accelerators are often useful to improve the properties of the cured rubber composition and the particular embodiments include the addition of secondary accelerators.

[0061] Particular embodiments may include as a secondary accelerant the use of a moderately fast accelerator such as, for example, diphenylguanidine (DPG), triphenyl guanidine (TPG), diorthotolyl guanidine (DOTG), o-tolylbigaunide (OTBG) or hexamethylene tetramine (HMTA). Such accelerators may be added in an amount of up to 4 phr, between 0.5 and 3 phr, between 0.5 and 2.5 phr or between 1 and 2 phr. Particular embodiments may exclude the use of fast accelerators and/or ultra-fast accelerators such as, for example, the fast accelerators: disulfides and benzothiazoles; and the ultra-accelerators: thiurams, xanthates, dithiocarbamates and dithiophosphates.

[0062] Other additives can be added to the rubber compositions disclosed herein as known in the art. Such additives may include, for example, some or all of the following: antidegradants, antioxidants, fatty acids, waxes, stearic acid and zinc oxide. Examples of antidegradants and antioxidants include 6PPD, 77PD, IPPD and TMQ and may be added to rubber compositions in an amount, for example, of from 0.5 phr and 5 phr. Zinc oxide may be added in an amount, for example, of between 1 phr and 6 phr or alternatively, of between 1.5 phr and 4 phr. Waxes may be added in an amount, for example, of between 1 phr and 5 phr.

[0063] The rubber compositions that are embodiments of the present invention may be produced in suitable mixers, in a manner known to those having ordinary skill in the art, typically using two successive preparation phases, a first phase of thermo-mechanical working at high temperature, followed by a second phase of mechanical working at lower temperature.

[0064] The first phase of thermo-mechanical working (sometimes referred to as "non-productive" phase) is intended to mix thoroughly, by kneading, the various ingredients

of the composition, with the exception of the vulcanization system. It is carried out in a suitable kneading device, such as an internal mixer or an extruder, until, under the action of the mechanical working and the high shearing imposed on the mixture, a maximum temperature generally between 120° C and 190° C, more narrowly between 130° C and 170° C, is reached.

[0065] After cooling of the mixture, a second phase of mechanical working is implemented at a lower temperature. Sometimes referred to as "productive" phase, this finishing phase consists of incorporating by mixing the vulcanization (or cross-linking) system (sulfur or other vulcanizing agent and accelerator(s)), in a suitable device, for example an open mill. It is performed for an appropriate time (typically between 1 and 30 minutes, for example between 2 and 10 minutes) and at a sufficiently low temperature lower than the vulcanization temperature of the mixture, so as to protect against premature vulcanization.

[0066] The rubber composition can be formed into useful articles, including treads for use on vehicle tires. The treads may be formed as tread bands and then later made a part of a tire or they be formed directly onto a tire carcass by, for example, extrusion and then cured in a mold. As such, tread bands may be cured before being disposed on a tire carcass or they may be cured after being disposed on the tire carcass. Typically a tire tread is cured in a known manner in a mold that molds the tread elements into the tread, including, *e.g.*, the sipes molded into the tread blocks.

[0067] The invention is further illustrated by the following examples, which are to be regarded only as illustrations and not delimitative of the invention in any way. The properties of the compositions disclosed in the examples were evaluated as described below and these utilized methods are suitable for measurement of the claimed properties of the claimed invention.

[0068] Modulus of elongation (MPa) was measured at 10% (MA10), 100% (MA100) and 300% (MA300) at a temperature of 23 °C based on ASTM Standard D412 on dumb bell test pieces. The measurements were taken in the second elongation; *i.e.*, after an accommodation cycle. These measurements are secant moduli in MPa, based on the original cross section of the test piece.

[0069] The elongation property was measured as elongation at break (%) and the corresponding elongation stress (MPa), which is measured at 23 °C in accordance with ASTM Standard D412 on ASTM C test pieces.

[0070] Dynamic properties (T_g and G^*) for the rubber compositions were measured on a Metravib Model VA400 ViscoAnalyzer Test System in accordance with ASTM D5992-96. The response of a sample of vulcanized material (double shear geometry with each of the two 10 mm diameter cylindrical samples being 2 mm thick) was recorded as it was being subjected to an alternating single sinusoidal shearing stress of a constant 0.7 MPa and at a frequency of 10 Hz over a temperature sweep from -80° C to 100° C with the temperature increasing at a rate of 1.5° C/min. The shear modulus G^* was captured at 60 °C and the temperature at which the max tan delta occurred was recorded as the glass transition temperature, T_g .

[0071] The maximum tan delta dynamic properties for the rubber compositions were measured at 23° C on a Metravib Model VA400 ViscoAnalyzer Test System in accordance with ASTM D5992-96. The response of a sample of vulcanized material (double shear geometry with each of the two 10 mm diameter cylindrical samples being 2 mm thick) was recorded as it was being subjected to an alternating single sinusoidal shearing stress at a frequency of 10 Hz under a controlled temperature of 23° C. Scanning was effected at an amplitude of deformation of 0.05 to 50 % (outward cycle) and then of 50 % to 0.05% (return cycle). The maximum value of the tangent of the loss angle tan delta (max tan δ) was determined during the return cycle. The complex shear modulus G^* was determined at 10% strain during the return cycle.

[0072] The mole percent of the epoxide functional group was determined by NMR characterization. First a 25 mg sample of the epoxidized elastomer is dissolved in 1 mL of deuterated chloroform ($CDCl_3$). The NMR analyses were performed on a 500MHz Bruker Spectrometer equipped with a 5mm Broad Band Cryoprobe. The sequence used was a quantitative 30 degrees 1H simple impulsion with a recycle delay of 5 seconds. The spectral width was 12 ppm and the number of scans was 64. Calibration was carried out at 7.20 ppm on the $CHCl_3$ signal. Acquisition parameters were adjusted to obtain a full spectrum without FID truncation.

[0073] The ^1H NMR Spectrum shows the characteristic signal of the $\text{CH}=\text{CH}$ of BR1-4 ($\delta=5.32$ ppm) and the $\text{CH}-\text{CH}$ of epoxidized BR1-4 ($\delta=2.86$ ppm). A small signal at 2.63 ppm is also attributed to epoxidized BR. These attributions were confirmed by 2D NMR ^1H - ^{13}C HSQC and HMBC.

[0074] The ^1H NMR spectrum makes it possible to quantify the functional group by integration of the signal characteristic of the protons of the epoxidized group situated in the vicinity of $\delta = 2.86$ ppm. The ^1H NMR technique was used to determine the microstructure of the elastomers obtained.

[0075] The molar ratio was estimated with the ratio of each pattern on the total according to the following calculation:

$$\%Epoxy = \frac{1H(Epoxy)}{1H(BR1-4)+1H(Epoxy)}.$$

Example 1

[0076] Rubber compositions were prepared using the components shown in Table 1. The amount of each component making up the rubber compositions are provided in parts per hundred parts of rubber by weight (phr). The percent epoxidation of the epoxidized rubber component was 5 mol%.

[0077] The silica was Zeosil 165G from Rhodia. The resin was a combination of three resins in quantities that were adjusted, *inter alia*, to provide the desired Tg of the cured rubber composition: Oppera 373N available from ExxonMobil and having a z-average molecular weight greater than 20,000, a weight average molecular weight of about 2500 Da, a softening point of about 89 ° C and a glass transition temperature of about 39 ° C, Dertopene T115 available from DRT of France, a terpene phenolic resin having a molecular weight of about 700 Da, a hydroxyl value of 20-100 and glass transition temperature of 66 ° C and LP9800, available from Kolon Industries, Inc. in South Korea, a low Tg methyl styrene/styrene/C9 monomer blend resin type, with a Tg of -27°C and a M_n of approximately 250 Da.

[0078] The iron oxide was ferric oxide and was obtained from US Research Nanomaterials, Inc. and had an average particle diameter of less than 50 nm. The cure package included sulfur and accelerators as well as zinc oxide and stearic acid.

Table 1 – Rubber Formulations

Formulations	W1	W2	W3	F1	F2	F3	F4	F5	F6	F7	F8
BR	100		100					50	50	50	50
eBR 8 mol%		100		100	100	100	100	50	50	50	50
N234	4	4	4	4	4		52			52	26
Silica	104	104				52			52		26
Ferric Oxide			265	265	454	133	133	265	133	133	133
Resins	73	73	73	73	73	73	73	73	73	73	73
Si69	10	10				5			5		2.6
Wax	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
6PPD	2	2	2	2	2	2	2	2	2	2	2
DPG	1.7	1.7	1	1	1	1.8	1	1	1.8	1	1.4
Cure Package	8.2	8.2	9.5	9.5	9.5	8.9	9.5	9.5	8.9	9.5	9.2
Phys. Properties											
MA10, MPa	5.4	5.25	2.55	2.58	5.76	3.26	3.68	3	3.78	3.86	3.34
MA100, MPa	4.07	4.55	2	3.59	4.8	3.46	4.12	3.76	3.96	4.05	3.75
MA300, MPa	8.37	10.37	3.02	8.13	9.68	7.63	9.83	7.59	7.91	9.02	8.37
MA300/MA100	2.06	2.28	1.51	2.26	2.02	2.21	2.39	2.02	2.00	2.23	2.23
% Elong at Break	772	586	1354	507	432	668	574	415	633	670	646
Break Force, MPa	22.1	20.67	16.93	12.4	14.19	17.76	17.86	9.93	15.95	18.76	18
Tg, ° C	-32	-29	-41	-28	-25	-30	-27	-32	-27	-26	-28
Max TanD, 23° C	0.38	0.31	0.22	0.18	0.27	0.24	0.27	0.21	0.30	0.32	0.28

[0079] The rubber formulations were prepared by mixing the components given in Table 1, except for the accelerators and sulfur, in a Banbury mixer until a temperature of between 110 °C and 170 °C was reached. The accelerators and sulfur were added in the second phase on a mill. Vulcanization was effected at 150 °C for 40 minutes. The formulations were then tested to measure their properties, the results of which are shown in Table 1.

[0080] As may be seen from the properties shown in Table 1, the witness W3 that included the iron oxide without an epoxidized rubber component did not provide reinforcement to the rubber composition. The inventive mixes, F1- F8 demonstrate that the rubber composition was reinforced with the iron oxide with the epoxidized rubber component in the composition.

[0081] The terms “comprising,” “including,” and “having,” as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term “consisting essentially of,” as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic

and novel characteristics of the claimed invention. The terms “a,” “an,” and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. The terms “at least one” and “one or more” are used interchangeably. The term “one” or “single” shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as “two,” are used when a specific number of things is intended. The terms “preferably,” “preferred,” “prefer,” “optionally,” “may,” and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention. Ranges that are described as being “between a and b” are inclusive of the values for “a” and “b.”

[0082] It should be understood from the foregoing description that various modifications and changes may be made to the embodiments of the present invention without departing from its true spirit. The foregoing description is provided for the purpose of illustration only and should not be construed in a limiting sense. Only the language of the following claims should limit the scope of this invention.

CLAIMS

What is claimed is:

1. A rubber composition that is based upon a cross-linkable rubber composition, the cross-linkable rubber composition comprising, parts by weight per 100 parts by weight of rubber (phr):
an epoxidized rubber;
between 30 phr and 800 phr of an iron oxide reinforcement filler having an average particle diameter of no more than 500 nm; and
a curing system.
2. The rubber composition of claim 1, wherein the iron oxide reinforcement filler is selected from the group consisting of ferric oxide, iron (II, III) oxide and combinations thereof.
3. The rubber composition of claim 2, wherein the iron oxide reinforcement filler is ferric oxide.
4. The rubber composition of claim 2, wherein the iron (II, III) oxide is Fe_3O_4 .
5. The rubber composition of any of the preceding claims, wherein the epoxidized rubber has a content of units of conjugated diene origin that is great than 50 mol%.
6. The rubber composition of claim 5, wherein the epoxidized rubber is selected from the group consisting of an epoxidized polybutadiene, an epoxidized natural rubber, an epoxidized polyisoprene rubber, an epoxidized styrene-butadiene rubber and combinations thereof.
7. The rubber composition of claim of any of the preceding claims, wherein an epoxy-function content of the epoxidized rubber is between 2 mol% and 25 mol%.
8. The rubber composition of claim 7, wherein the epoxy-function content is between 5 mol% and 10 mol%.

9. The rubber composition of any of the preceding claims, wherein the cross-linkable rubber composition comprises between 25 phr and 100 phr of the epoxidized rubber and further comprises between 0 phr and 25 phr of a second rubber component that is not epoxidized.
10. The rubber composition of any of claims 1 through 8, wherein the cross-linkable rubber composition comprises between 45 phr and 100 phr of the epoxidized rubber and further comprises between 0 phr and 55 phr of a second rubber component that is not epoxidized.
11. The rubber composition of claim 9 or 10, wherein the second rubber component is selected from the group consisting of natural rubber, polybutadiene rubber, styrene-butadiene rubber, polyisoprene rubber and combinations thereof.
12. The rubber composition of any of the preceding claims, wherein the iron oxide reinforcement filler has an average particle diameter of no more than 250 nm.
13. The rubber composition of claim 12, wherein the iron oxide reinforcement filler has an average particle diameter of no more than 100 nm.
14. The rubber composition of claim 12, wherein the iron oxide reinforcement filler has an average particle diameter of between 30 nm and 65 nm.
15. The rubber composition of any of the preceding claims, wherein the cross-linkable rubber composition comprises between 50 phr and 800 phr of the iron oxide reinforcing filler.
16. The rubber composition of claim 15, wherein the cross-linkable rubber composition comprises between 50 phr and 600 phr of the iron oxide reinforcing filler.
17. The rubber composition of claim 15, wherein the cross-linkable rubber composition comprises between 100 phr and 500 phr of the iron oxide reinforcing filler.
18. The rubber composition of any of the preceding claims, where the cross-linkable rubber composition further comprises a secondary reinforcement filler selected from the group consisting of carbon black, silica and combinations thereof.

19. A tire, formed at least in part with the rubber composition of any of the preceding claims.
20. The tire of claim 19, wherein the tire comprises a tread formed at least in part by the rubber composition.
21. The tire of claim 20, wherein the tread is of a cap and base construction and wherein the cap is formed by the rubber composition.
22. The tire of claim 20, wherein the base is formed by the rubber composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/063404

A. CLASSIFICATION OF SUBJECT MATTER
INV. B60C1/00 C08K3/22
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B60C C08K C08L

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2006/183840 A1 (HIRAYAMA TOMOAKI [JP] ET AL) 17 August 2006 (2006-08-17) paragraph [0018] example 11	1-22
A	----- EP 2 161 300 A1 (SUMITOMO RUBBER IND [JP]) 10 March 2010 (2010-03-10) paragraph [0021] -----	1-22

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Further documents are listed in the continuation of Box C.

☒

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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