

Method for Producing Hydrogenated Conjugated Diene Polymer, Hydrogenated Conjugated Diene Polymer, Polymer Composition, Crosslinked Polymer, and Tire

Technical Field

[0001]

The present disclosure relates to a method for producing a hydrogenated conjugated diene-based polymer, a hydrogenated conjugated diene-based polymer, a polymer composition, a crosslinked polymer, and a tire.

Background Art

[0002]

A conjugated diene-based polymer produced through polymerization of a conjugated diene compound exhibits favorable properties (e.g., thermal resistance, abrasion resistance, mechanical strength, and processability). Thus, the conjugated diene-based polymer has been used in various industrial products, including pneumatic tires, vibration-proof rubbers, and hoses.

[0003]

As has been known, a rubber composition used for, for example, the tread or sidewall of a pneumatic tire contains a conjugated diene-based polymer, and a reinforcing agent (e.g., carbon black or silica) for improving the durability and abrasion resistance of the tire. There has been provided a conventional rubber composition containing a modified

conjugated diene-based polymer prepared through modification of a terminal of a conjugated diene-based polymer with a silicon- or nitrogen-containing compound for enhancing the affinity of the conjugated diene-based polymer to, for example, silica (see, for example, Patent Documents 1 to 3). Patent Document 1 discloses modification of a terminal of a conjugated diene-based polymer with an aminosilane compound. Patent Documents 2 and 3 disclose modification of a terminal of a conjugated diene-based polymer with a polyorganosiloxane having a plurality of functional groups. A known technique involves reaction between a terminal of a conjugated diene-based polymer and a coupling agent for increasing the molecular weight of the conjugated diene-based polymer (see, for example, Patent Document 1).

[0004]

In recent years, there has been proposed a tire member which is prepared from a hydrogenated product of a modified conjugated diene-based polymer having a functional group (e.g., an amino group or an alkoxysilyl group) at one or both terminals of the polymer, and which achieves high tensile strength (fracture resistance) and high abrasion resistance (see Patent Document 4).

Prior Art Documents

Patent Documents

[0005]

Patent Document 1: Japanese Patent No. 4129619

Patent Document 2: Japanese Patent Application Laid-Open

(*kokai*) No. H09-110904

Patent Document 3: International Patent Publication WO
2005/021637

Patent Document 4: International Patent Publication WO
2014/133097

Summary of the Invention

Problems to be Solved by the Invention

[0006]

A conventional rubber composition containing a hydrogenated conjugated diene-based polymer exhibits insufficient processability and thus leaves room for further improvement. Thus, demand has arisen for a rubber material having high fracture strength and abrasion resistance and excellent processability.

[0007]

In view of the foregoing, an object of the present disclosure is to provide a hydrogenated conjugated diene-based polymer capable of preparing a rubber composition which exhibits excellent processability and which can produce a crosslinked product having high fracture resistance and abrasion resistance.

Solution to Problem

[0008]

The present disclosure provides a method for producing a hydrogenated conjugated diene-based polymer, a hydrogenated conjugated diene-based polymer, a polymer composition, a crosslinked polymer, and a tire, which are described below.

[0009]

[1] A method for producing a hydrogenated conjugated diene-based polymer, the method comprising:

reacting a conjugated diene-based polymer having an active terminal with a polyorganosiloxane having two or more specific functional groups each being at least one type selected from the group consisting of an epoxy group, an alkoxy group, a carbonyl group, a 2-pyrrolidonyl group, a vinyl group, and a halogen atom; and

hydrogenating a modified conjugated diene-based polymer prepared through the reaction.

[2] A hydrogenated conjugated diene-based polymer produced by a method of the aforementioned [1]

[3] A polymer composition comprising a hydrogenated conjugated diene-based polymer produced by the method of the aforementioned [1], silica, and a crosslinking agent.

[4] A crosslinked polymer produced through crosslinking of a polymer composition of the aforementioned [3].

[5] A tire obtained by employing a crosslinked polymer of the aforementioned [4] as a tread material, a sidewall material, or both.

Advantageous Effects of the Invention

[0010]

According to the present disclosure, there can be prepared a rubber composition exhibiting excellent processability. A crosslinked polymer produced through

crosslinking of the rubber composition has sufficiently high fracture resistance and abrasion resistance. Thus, the crosslinked polymer can be used for various applications.

Modes for Carrying Out the Invention

[0011]

The hydrogenated conjugated diene-based polymer of the present disclosure is a hydrogenated product of a conjugated diene-based polymer including structural units derived from a conjugated diene compound. The hydrogenated conjugated diene-based polymer is produced by the below-described method involving a polymerization step, a modification step, and a hydrogenation step. Embodiments of the present disclosure will now be described in detail.

[0012]

<Polymerization step>

This step involves polymerization of a monomer containing a conjugated diene compound to thereby prepare a conjugated diene-based polymer having an active terminal. The conjugated diene compound used for polymerization may be 1,3-butadiene alone, or a combination of 1,3-butadiene with a conjugated diene compound other than 1,3-butadiene (hereinafter may be referred to as an "additional conjugated diene compound"). Examples of the additional conjugated diene compound include isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 2-phenyl-1,3-butadiene, 3-methyl-1,3-pentadiene, and 2-chloro-1,3-butadiene. Of these, isoprene and 2,3-dimethyl-1,3-butadiene

are preferable.

[0013]

The conjugated diene-based polymer of the present disclosure may be a homopolymer of the conjugated diene compound, but is preferably a copolymer of the conjugated diene compound and an aromatic vinyl compound from the viewpoint of improving the strength of the rubber. Examples of the aromatic vinyl compound used in the polymerization include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, α -methylstyrene, 2,4-dimethylstyrene, 2,4-diisopropylstyrene, 4-*t*-butylstyrene, 5-*t*-butyl-2-methylstyrene, vinylethylbenzene, divinylbenzene, trivinylbenzene, divinylnaphthalene, *t*-butoxystyrene, vinylbenzyl dimethylamine, (4-vinylbenzyl) dimethylaminoethyl ether, *N,N*-dimethylaminoethylstyrene, *N,N*-dimethylaminomethylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 2-*t*-butylstyrene, 3-*t*-butylstyrene, 4-*t*-butylstyrene, vinylxylene, vinylnaphthalene, vinylpyridine, diphenylethylene, a tertiary amino group-containing diphenylethylene (e.g., 1-(4-*N,N*-dimethylaminophenyl)-1-phenylethylene). Among these, styrene and α -methylstyrene is preferable.

[0014]

When the conjugated diene-based polymer of the present disclosure is the copolymer of the conjugated diene compound and the aromatic vinyl compound, the copolymer is preferably a polymer formed of the monomer containing 1,3-butadiene and

styrene, in view of high living properties during anionic polymerization. The copolymer preferably contains a random copolymer moiety formed of the conjugated diene compound and the aromatic vinyl compound. The copolymer may contain a block moiety formed of the conjugated diene compound or the aromatic vinyl compound.

[0015]

When the conjugated diene-based polymer is the copolymer of the conjugated diene compound and the aromatic vinyl compound, the amount of the aromatic vinyl compound used for the polymerization is preferably 3 to 55 mass%, more preferably 5 to 50 mass%, relative to the total amount of the conjugated diene compound and aromatic vinyl compound used for the polymerization, from the viewpoint of a good balance between low hysteresis loss property and wet grip property of the resultant crosslinked polymer. The amount of the structural unit derived from the aromatic vinyl compound in the polymer is measured by means of ^1H -NMR. These conjugated diene compounds and aromatic vinyl compounds may be used singly or in combination of two or more species.

[0016]

The polymerization may involve the use of a compound other than the conjugated diene compound and the aromatic vinyl compound (hereinafter may referred to as "an additional monomer"). Examples of the additional monomer include acrylonitrile, methyl (meth)acrylate, ethyl (meth)acrylate. The amount of the additional monomer used is preferably 15

mass% or less, more preferably 10 mass% or less, relative to the total amount of the monomers used for the polymerization.

[0017]

The monomer may be polymerized using a solution polymerization method, a vapor-phase polymerization method, or a bulk polymerization method. Among these, the solution polymerization method is particularly preferable. The monomer may be polymerized in a batch-wise manner or a continuous manner. When using the solution polymerization method, the monomer that includes the conjugated diene compound may be polymerized in an organic solvent in the presence of an initiator and an optional randomizer, for example.

[0018]

At least one of an alkali metal compound and an alkaline-earth metal compound may be used as the initiator. Specific examples of these include alkylolithiums, such as methylolithium, ethylolithium, n-propylolithium, n-butylolithium, sec-butylolithium, and tert-butylolithium, 1,4-dilithiobutane, phenylolithium, stilbenelithium, naphthylolithium, 1,3-bis(1-lithio-1,3-dimethylpentyl)benzene, 1,3-phenylenebis(3-methyl-1-phenylpentylidene)dilithium, naphthylsodium, naphthylpotassium, di-n-butylmagnesium, di-n-hexylmagnesium, ethoxypotassium, calcium stearate, and a compound that is obtained by mixing at least one of the alkali metal compound and the alkaline-earth metal compound with a compound having a functional group that interacts with silica. Of these, the

initiator is preferably lithium compounds. The initiator is preferably used in an amount of 0.2 to 20 mmol based on 100 g of the monomer used for the polymerization.

[0019]

The monomer may be polymerized in the presence of a compound that is obtained by mixing at least one of the alkali metal compound and the alkaline-earth metal compound with a compound having a functional group that interacts with silica. The functional group that interacts with silica can be introduced into the polymerization-initiation terminal of the conjugated diene-based polymer by polymerizing the monomer in the presence of the compound. The term "interaction" used herein means that a covalent bond is formed between molecules, or an intermolecular force (intermolecular electromagnetic force such as ion-dipole interaction, dipole-dipole interaction, a hydrogen bond, or Van der Waals force) that is weaker than a covalent bond is formed.

[0020]

The compound having a functional group that interacts with silica, which is used to a modification of the polymerization-initiation terminal, is preferably a nitrogen-containing compound (e.g., a secondary amine compound). Specific examples of the nitrogen-containing compound include dimethylamine, diethylamine, dipropylamine, dibutylamine, dodecamethyleneimine, N,N'-dimethyl-N'-trimethylsilyl-1,6-diaminohexane, piperidine, pyrrolidine, hexamethyleneimine,

heptamethyleneimine, dicyclohexylamine, N-methylbenzylamine, di-(2-ethylhexyl)amine, diallylamine, morpholine, N-(trimethylsilyl)piperazine, N-(tert-butyltrimethylsilyl)piperazine, and 1,3,5-triazinane.

[0021]

In the modification of the polymerization-initiation terminal, a mixture may be prepared by mixing at least one of the alkali metal compound and the alkaline-earth metal compound with the compound having a functional group that interacts with silica, and added to the polymerization system. Alternatively, at least one of the alkali metal compound and the alkaline-earth metal compound, and the compound having a functional group that interacts with silica may be added to the polymerization system, and mixed in the polymerization system.

[0022]

The randomizer may be used to adjust vinyl bond content that represents the content of vinyl bonds in the polymer. Examples of the randomizer include dimethoxybenzene, tetrahydrofuran, dimethoxyethane, diethylene glycol dibutyl ether, diethylene glycol dimethyl ether, 2,2-di(tetrahydrofuryl)propane, 2-(2-ethoxyethoxy)-2-methylpropane, triethylamine, pyridine, N-methylmorpholine, and tetramethylethylenediamine. These compounds may be used singly or in combination of two or more species.

[0023]

The organic solvent used for polymerization may be an organic solvent that is inert to the reaction. Examples of the organic solvent used for polymerization include aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic hydrocarbons. It is preferable to use a hydrocarbon having 3 to 8 carbon atoms. Specific examples of the hydrocarbon having 3 to 8 carbon atoms include propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, cyclohexane, propene, 1-butene, isobutene, trans-2-butene, cis-2-butene, 1-pentyne, 2-pentyne, 1-hexene, 2-hexene, benzene, toluene, xylene, ethylbenzene, heptane, cyclopentane, methylcyclopentane, methylcyclohexane, 1-pentene, 2-pentene, and cyclohexene. These organic solvents may be used singly or in combination of two or more species.

[0024]

When using the solution polymerization method, the monomer concentration in the reaction solvent is preferably 5 to 50 mass%, and more preferably 10 to 30 mass%, from the viewpoint of maintaining the balance between productivity and polymerization controllability. The polymerization reaction temperature is preferably -20 to 150°C, more preferably 0 to 120°C. It is preferable to effect the polymerization reaction under a pressure sufficient to substantially maintain the monomer to be in a liquid phase. Such a pressure may be achieved by pressurizing the reactor using gas that is inert to the polymerization reaction.

[0025]

The polymerization reaction can produce a conjugated diene-based polymer having an active terminal. The resultant conjugated diene-based polymer preferably has a weight average molecular weight (Mw) (in terms of polystyrene) of 1.0×10^4 to 2.0×10^6 as measured by means of gel permeation chromatography (GPC). The Mw of less than 1.0×10^4 may lead to deterioration of tensile strength, low fuel consumption performance, and abrasion resistance of the resultant crosslinked polymer, whereas the Mw exceeding 2.0×10^6 may lead to poor processability of the polymer composition. The Mw is more preferably 1.2×10^4 to 1.5×10^6 , still more preferably 1.5×10^4 to 1.0×10^6 .

[0026]

In the conjugated diene-based polymer having the active terminal, the vinyl bond content of a butadiene unit is preferably 30 to 70 mol%, more preferably 33 to 68 mol%, still more preferably 35 to 65 mol%. The vinyl bond content of less than 30 mol% may lead to poor grip property, whereas the vinyl bond content exceeding 70 mol% may lead to a reduction in the abrasion resistance of the resultant vulcanized rubber. The term "vinyl bond content" refers to the percentage of the structural unit having a 1,2-bond with respect to all the butadiene units in the conjugated diene-based polymer. The vinyl bond content is measured by means of ^1H -NMR.

[0027]

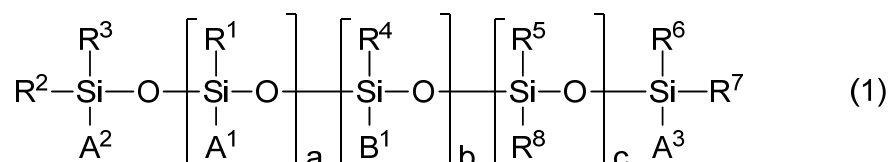
<Modification step>

In the modification step, the active terminal of the conjugated diene-based polymer obtained by the polymerization step is reacted with a polyorganosiloxane having at least one specific functional group selected from the group consisting of an epoxy group, an alkoxy group, a carbonyl group, a 2-pyrrolidonyl group, a vinyl group, and a halogen atom, wherein the total number of the specific functional groups in a molecule is two or more (hereinafter the polyorganosiloxane may be referred to as a "specific polyorganosiloxane").

[0028]

The specific polyorganosiloxane is a linear, cyclic, or branched compound having a siloxane bond. Specific examples of preferred specific polyorganosiloxanes include compounds represented by the following formula (1):

[F1]



(where R^1 to R^8 each represent a hydrocarbyl group; A^1 represents a group having the specific functional group; A^2 and A^3 each represent a hydrocarbyl group or a group having the specific functional group; B^1 represents a group having a polyether structure; a is an integer of 3 to 200; b is an integer of 0 to 200; c is an integer of 0 to 200; and R^1 , R^4 , R^5 , R^8 , A^1 , and B^1 may be identical to or different from one another between structural units).

[0029]

Examples of the hydrocarbyl group represented by R^1 to R^8 , A^2 , or A^3 in the formula (1) include a C1 to C20 linear or branched alkyl group, a C3 to C20 cycloalkyl group, and a C6 to C20 aryl group. Of these, an alkyl group or a phenyl group is preferred.

Examples of the group having the specific functional group represented by A^1 to A^3 include a C4 to C12 group having an epoxy group, a C4 to C20 group having a 2-pyrrolidonyl group, a C1 to C5 alkoxy group, a C1 to C5 halogenated alkyl group, a C2 to C5 alkenyl group, a styryl group, a vinyl phenyl group, and an ester group. Preferred is a C4 to C12 group having an epoxy group, a C4 to C20 group having a 2-pyrrolidonyl group, or a C1 to C5 alkoxy group.

[0030]

Examples of the polyether structure represented by B^1 include a structure having a C2 to C20 alkylene glycol repeating unit. Specific examples of the structure include a polyethylene glycol structure and a polypropylene glycol structure.

In the formula (1), a is preferably an integer of 20 to 150, more preferably an integer of 30 to 120, in order to sufficiently secure an improvement in the processability of the polymer composition, and to prevent an excessive increase in the viscosity of the specific polyorganosiloxane. In the formula (1), b is preferably 0 to 150, more preferably 0 to 120, and c is preferably 0 to 180, more preferably 10 to 150.

The total number of a , b , and c is preferably 400 or

less, more preferably 300 or less, from the viewpoint of ease of handling of the specific polyorganosiloxane. The specific polyorganosiloxane can be prepared by any known synthetic method. The specific polyorganosiloxane may be a commercially available product.

[0031]

The reaction between the conjugated diene-based polymer having the active terminal and the specific polyorganosiloxane may be, for example, a solution reaction. The amount of the specific polyorganosiloxane (or the total amount of two or more the specific polyorganosiloxane) is adjusted such that the amount of the specific functional group is preferably 0.001 mol or more, more preferably 0.005 mol or more, relative to 1 mol of the metal atom (responsible for the polymerization) of the polymerization initiator, from the viewpoint of the compatibility between the processability of the polymer composition and the fracture resistance and viscoelasticity of the resultant crosslinked polymer. The maximum amount of the specific polyorganosiloxane is adjusted such that the amount of the specific functional group is preferably less than 0.1 mol, more preferably less than 0.05 mol, relative to 1 mol of the metal atom (responsible for the polymerization) of the polymerization initiator.

The modification reaction temperature is generally equal to the polymerization reaction temperature, and is preferably -20°C to 150°C, more preferably 0 to 120°C. A low reaction temperature may lead to an increase in the viscosity

of the modified polymer, whereas a high reaction temperature facilitates the inactivation of the active terminal of the polymer. The reaction time is preferably 1 minute to 5 hours, more preferably 2 minutes to 1 hour.

[0032]

The reaction between the conjugated diene-based polymer having the active terminal and the specific polyorganosiloxane may involve the use of an additional modifying agent together with the specific polyorganosiloxane. No particular limitation is imposed on the additional modifying agent, so long as the modifying agent is any known compound that has a functional group capable of interactive with silica and can react with the active terminal of the polymer. If the additional modifying agent is used, the amount thereof is preferably 10 mol% or less, more preferably 5 mol% or less, relative to the total amount of the specific polyorganosiloxane and the additional modifying agent, for sufficient progress of the reaction between the conjugated diene-based polymer having the active terminal and the specific polyorganosiloxane.

[0033]

The modified conjugated diene-based polymer produced through reaction between the conjugated diene-based polymer having the active terminal and the specific polyorganosiloxane is preferably a specific polyorganosiloxane having a plurality of conjugated diene-based polymer chains bonded thereto. The incorporation of a

hydrogenated product of the modified conjugated diene-based polymer having a structure in which the conjugated diene-based polymer chains are bonded via the specific polyorganosiloxane into the polymer composition together with silica is preferred, since the polymer composition exhibits sufficient processability and the resultant crosslinked polymer exhibits sufficiently improvement in fracture resistance and viscoelasticity. The number of conjugated diene-based polymer chains included in the modified conjugated diene-based polymer is preferably three or more, more preferably four or more.

The resultant modified conjugated diene-based polymer preferably has a weight average molecular weight (M_w) (in terms of polystyrene) of 1.0×10^5 to 3.0×10^6 as measured by means of GPC, from the viewpoint of achieving well-balanced improvements in fracture strength, abrasion resistance, and processability. The M_w is more preferably 1.2×10^5 to 2.0×10^6 , still more preferably 1.5×10^5 to 1.2×10^6 .

[0034]

<Hydrogenation step>

In the hydrogenation step, the modified conjugated diene-based polymer obtained by the modification step is hydrogenated. The hydrogenation may be performed by any method under any conditions, so long as the resultant polymer exhibits a desired hydrogenation rate. Examples of the hydrogenation method include a method involving the use of a

hydrogenation catalyst containing an organic titanium compound as a main component; a method involving the use of a catalyst containing an organic compound of iron, nickel, or cobalt and an organic metal compound (e.g., an alkylaluminum); a method involving the use of an organic complex of an organic metal compound of, for example, ruthenium or rhodium; and a method involving the use of a catalyst including a carrier (e.g., carbon, silica, or alumina) on which a metal (e.g., palladium, platinum, ruthenium, cobalt, or nickel) is supported. Of these methods, industrially preferred is a method involving hydrogenation under mild conditions (low pressure and low temperature) by use of a homogeneous catalyst containing an organic titanium compound only, or containing an organic titanium compound and an organic compound of a metal (lithium, magnesium, or aluminum) (Japanese *Kokoku* Patent Publication Nos. S63-4841 and H01-37970). Such a hydrogenation method achieves high hydrogenation selectivity to a double bond derived from butadiene, and is suitable for the object of the present disclosure.

[0035]

The hydrogenation may be performed in a solvent that is inert to the catalyst and can dissolve the conjugated diene-based polymer. An aliphatic hydrocarbon such as n-pentane, n-hexane, and n-octane, an alicyclic hydrocarbon such as cyclohexane and cyclohexane, an aromatic hydrocarbon such as benzene and toluene, an ether such as diethyl ether and

tetrahydrofuran, and a mixture that includes them as the main component are preferable as the solvent.

[0036]

The hydrogenation reaction is normally effected by holding a polymer at a given temperature in a hydrogen atmosphere or an inert atmosphere, adding the hydrogenation catalyst to the conjugated diene-based polymer with or without stirring, and introducing hydrogen gas to pressurize the system to a given pressure. The term "inert atmosphere" used herein refers to an atmosphere that does not react with the materials that are subjected to the hydrogenation reaction. Examples of the inert atmosphere include helium, neon, and argon. It is not desirable to be present air or oxygen since inactivation of the catalyst may occur due to oxidation. It is not desirable to be present nitrogen since nitrogen may act as a catalyst poison during the hydrogenation reaction, and decrease the hydrogenation activity. Especially, it is preferable to fill the hydrogenation reactor with hydrogen gas. The hydrogenation reaction process for obtaining the hydrogenated conjugated diene-based polymer may be effected using a batch process, a continuous process, or a combination thereof. The hydrogenation catalyst is preferably added in an amount of 0.02 to 20 mmol per 100 g of the unhydrogenated conjugated diene-based polymer.

[0037]

In the hydrogenated conjugated diene-based polymer, the

hydrogenation rate of a butadiene unit is preferably 70 to 99%, but is not particularly. A hydrogenation rate of 70% or more can achieve a rubber exhibiting sufficiently improved mechanical strength by crosslinking. The hydrogenation rate is more preferably 80% or more, still more preferably 90% or more, particularly preferably 92% or more. The maximum hydrogenation rate is preferably 99% or less in order to prevent production efficiency decrease. The hydrogenation rate is more preferably 98% or less, still more preferably 97% or less. The hydrogenation rate is determined through $^1\text{H-NMR}$. The hydrogenation rate may be appropriately adjusted by modifying the amount of a hydrogenation catalyst, the hydrogen pressure during hydrogenation reaction, or the reaction time.

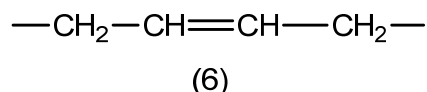
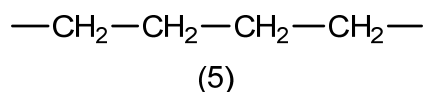
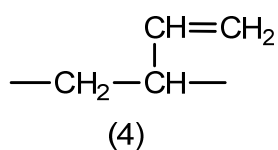
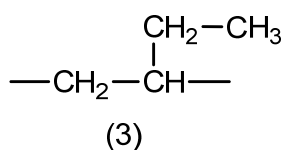
[0038]

The hydrogenated conjugated diene-based polymer of the present disclosure preferably includes a butadiene-derived structural unit satisfying the following formula (A):

$$0.70 \leq (p+r)/(p+q+r+s) \leq 0.99 \dots (A)$$

where p represents the ratio of a structural unit represented by the following formula (3) in the polymer, q represents the ratio of a structural unit represented by the following formula (4) in the polymer, r represents the ratio of a structural unit represented by the following formula (5) in the polymer, and s represents the ratio of a structural unit represented by the following formula (6) in the polymer:

[F2]



The formula (A) corresponds to the following description "the hydrogenation rate of butadiene-derived structural units is 70 to 99%." The vinyl bond content of the hydrogenated conjugated diene-based polymer is represented the following description

"[(p+q)/(p+q+r+s)]*100."

[0039]

The hydrogenated conjugated diene-based polymer is preferably produced by a method involving solution polymerization of monomers including a butadiene in the presence of an alkali metal compound, modification reaction of the resultant polymer solution, and then hydrogenation reaction of the polymer solution. Such a method is industrially useful. The hydrogenated conjugated diene-based polymer of the present disclosure is isolated from the above-prepared solution through removal of the solvent therefrom. The polymer can be isolated by, for example, a known solvent removal method (e.g., steam stripping) and a drying operation (e.g., thermal treatment).

[0040]

<Polymer composition>

The polymer composition of the present disclosure

contains the aforementioned hydrogenated conjugated diene-based polymer, silica, and a crosslinking agent. The amount of the hydrogenated conjugated diene-based polymer contained in the polymer composition is preferably 20 mass% or more, more preferably 30 mass% or more, still more preferably 40 mass% or more, relative to the total amount of the polymer composition.

[0041]

Examples of the silica include wet silica (hydrated silica), dry silica (silicic anhydride), colloidal silica, precipitated silica, calcium silicate, and aluminum silicate. Of these, wet silica is particularly preferred from the viewpoints of an improvement in fracture resistance, and the compatibility between wet grip property and low rolling resistance. The use of high dispersible-type silica is preferred for achieving effective dispersion of the silica in the polymer composition and improvements in physical properties and processability. These silica materials may be used singly or in combination of two or more species.

[0042]

The polymer composition may optionally include any reinforcing filler (e.g., carbon black, clay or calcium carbonate) in addition to the silica. Silica singly or a combination of carbon black and silica is preferably used as the filler. The total amount of silica and carbon black contained in the polymer composition is preferably 20 to 130 parts by mass, more preferably 25 to 110 parts by mass,

relative to 100 parts by mass of the total amount of polymer components contained in the polymer composition.

[0043]

Examples of the crosslinking agent include sulfur, sulfur halides, organic peroxides, quinone dioximes, organic polyamine compounds, and alkyl phenolic resins having a methylol group. Sulfur is generally used. The amount of sulfur is preferably 0.1 to 5 parts by mass, more preferably 0.5 to 3 parts by mass, relative to 100 parts by mass of the total amount of polymer components contained in the polymer composition.

[0044]

The polymer composition of the present disclosure, which contains the hydrogenated conjugated diene-based polymer produced above, may contain an additional rubber component. Examples of the type of the additional rubber component include, but are not particularly limited to, butadiene rubber (BR, such as high cis BR having a cis-1,4 bond content of 90% or more, or BR containing syndiotactic-1,2-polybutadiene (SPB)), styrene butadiene rubber (SBR), natural rubber (NR), isoprene rubber (IR), styrene-isoprene copolymer rubber, and butadiene-isoprene copolymer rubber. The additional rubber component is more preferably BR or SBR.

[0045]

The polymer composition may contain, as an extender oil, a process oil commonly used for oil extension of an elastomer. The process oil is incorporated into the polymer composition

through, for example, direct addition of the oil during incorporation of a rubber component. The process oil used may be an extender oil present in the elastomer, or may be added during preparation of the polymer composition. Examples of preferred process oils include various oils known in the art. Examples of the process oils include aromatic oils, paraffinic oils, naphthenic oils, vegetable oils, and oils having a low polycyclic aromatic compound content (low PCA oils), such as mild extraction solvate (MES), treated distillate aromatic extract (TDAE), special residual aromatic extract (SRAE), and heavy naphthenic oil. Examples of commercially available MES include Catenex SNR (heavy paraffin prepared through dewaxing of distillate oil with a solvent) (manufactured by Shell). Examples of commercially available TDAE include Vivatec 500 (manufactured by H&R Wasag AG). Examples of commercially available SRAE include NC140 (manufactured by Japan Energy Corp.). The amount of the process oil incorporated is preferably 10 to 100 parts by mass relative to the total amount (100 parts by mass) of the polymer components contained in the polymer composition.

[0046]

The polymer composition may contain, in addition to the aforementioned components, any additive that is commonly used in a rubber composition for tire. Examples of the additive include an antioxidant, zinc oxide, stearic acid, a softener, sulfur, a vulcanization accelerator, a silane coupling agent, a compatibilizer, a vulcanization aid, a processing aid, and

an anti-scorching agent. The amount of such additives incorporated into the polymer composition may be appropriately determined, so long as the advantageous effects of the present disclosure are not impaired.

[0047]

The polymer composition of the present disclosure can be prepared through kneading of the polymer component, silica, the crosslinking agent, and an optional component by means of, an open-type kneader (e.g., a roll) or a closed-type kneader (e.g., a Banbury mixer). The polymer composition is prepared into a crosslinked polymer through molding and subsequent crosslinking (vulcanization). The resultant crosslinked polymer can be applied to various rubber products. For example, the crosslinked polymer can be applied to tires (e.g., tire tread, undertread, carcass, sidewall, and bead); sealing materials, such as packing, gasket, weather strip, and O-ring; interior and exterior surface materials for various vehicles, such as automobile, ship, aircraft, and train; building materials; vibration-proof rubbers for industrial machines and facilities; hoses and hose covers, such as diaphragm, roll, radiator hose, and air hose; belts, such as belts for power transmission; linings; dust boots; materials for medical devices; fenders; insulating materials for electric wires; and other industrial products. In particular, the crosslinked polymer obtained by using the hydrogenated conjugated diene-based polymer of the present disclosure achieves excellent wet skid resistance, low

hysteresis loss property, and abrasion resistance. Thus, the crosslinked polymer is suitable for use as a material of a tire tread or sidewall.

[0048]

The tire can be produced by a customary method. For example, the polymer composition is mixed by means of a kneader to form a sheet, and the sheet is disposed at a predetermined position and vulcanized by a customary method, to thereby form a tread rubber or a sidewall rubber. A pneumatic tire is thereby produced.

Examples

[0049]

The present disclosure will next be described in detail by way of examples, which should not be construed as limiting the disclosure thereto. Unless otherwise specified, the units "part(s)" and "%" described in Examples and Comparative Examples refer to "part(s) by mass" and "mass%," respectively. Physical properties are determined as described below.

[0050]

[Bonded styrene content (%)] : the bonded styrene content was determined by means of ^1H -NMR (500 MHz).

[Vinyl bond content (%)] : the 1,2-vinyl bond content of an unhydrogenated polymer was determined by means of ^1H -NMR (500 MHz).

[Glass-transition temperature ($^{\circ}\text{C}$)] : the glass-transition temperature was measured in accordance with ASTM D3418.

[Molecular weight before modification] : the molecular weight

(in terms of polystyrene) was determined from the retention time corresponding to the vertex of the maximum peak of a gel permeation chromatography (GPC) curve obtained by means of GPC (HLC-8120GPC (trade name, manufactured by Tosoh Corporation)).

(GPC conditions)

Column: trade name "GMHXL" (manufactured by Tosoh Corporation) (two columns)

Column temperature: 40°C

Mobile phase: tetrahydrofuran

Flow rate: 1.0 mL/min

Sample concentration: 10 mg/20 mL

[Mooney viscosity (ML1+4, 100°C)]: the Mooney viscosity was measured in accordance with JIS K 6300 using an L rotor (preheating time: 1 minute, rotor operation time: 4 minutes, temperature: 100°C).

[Hydrogenation rate (%)]: the hydrogenation rate of a butadiene unit was determined by ¹H-NMR (500 MHz).

[0051]

[Example 1]

<Synthesis of hydrogenated conjugated diene-based polymer A>

Cyclohexane (25,600 g), tetrahydrofuran (384 g), styrene (800 g), and 1,3-butadiene (2,336 g) were added to an autoclave reactor (inner volume: 50 L) purged with nitrogen. The internal temperature of the reactor was adjusted to 45°C, and then a solution of n-butyllithium (60.0 mmol) in cyclohexane was added to thereby initiate polymerization.

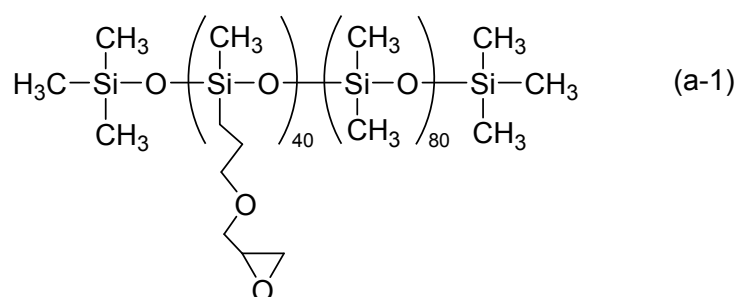
The polymerization was performed under adiabatic conditions, and the maximum temperature reached 85°C. After the polymerization conversion had reached 99%, 1,3-butadiene (64 g) was added for further polymerization for one minute, to thereby prepare a polymer-containing reaction mixture. Thereafter, the reaction mixture was mixed with a compound represented by the formula (a-1) described below (0.4 mmol), and then reaction was allowed to proceed for 15 minutes.

Subsequently, the resultant reaction mixture was heated to 80°C or higher, and hydrogen was introduced into the reaction system. Thereafter, [bis(η 5-cyclopentadienyl)titanium(furfuryloxy) chloride] (2.34 g), diethylaluminum chloride (3.72 g), and n-butyllithium (1.28 g) were added, and then reaction was allowed to proceed so as to maintain a hydrogen pressure of 0.7 MPa or more. After the cumulative hydrogen amount had reached a predetermined level, the reaction mixture was removed from the reactor at ambient temperature and ambient pressure. Thus, a polymer solution was prepared.

Subsequently, 2,6-di-tert-butyl-p-cresol (14.1 g) was added to the polymer solution. An aqueous solution (temperature: 80°C) having a pH (measured at 80°C by the glass electrode method, the same shall apply hereinafter) of 8.5 (adjusted with ammonia) was added to a solvent removing vessel, and the polymer solution was added thereto so that the amount of the aqueous solution was 200 parts by mass relative to 100 parts by mass of the polymer solution. The

solvent was removed through steam stripping (steam temperature: 190°C) for two hours (temperature of the liquid phase of the solvent removing vessel: 95°C), followed by drying by means of a heat roller at 110°C, to thereby produce a hydrogenated conjugated diene-based polymer A. Table 1 shows the polymerization formulation of the hydrogenated conjugated diene-based polymer A, and Table 2 shows the properties of the hydrogenated conjugated diene-based polymer A.

[F3]



[0052]

<Production of polymer composition and crosslinked polymer, and evaluation of properties>

The hydrogenated conjugated diene-based polymer A produced above was mixed with other components according to the formulation shown below in Table 3, and the mixture was kneaded to produce a polymer composition. The kneading was performed as follows. In a first kneading step, the hydrogenated conjugated diene-based polymer A, silica, carbon black, a silane coupling agent, an extender oil, stearic acid, an antioxidant, and zinc oxide were mixed and kneaded by means of a plastomill (inner volume: 250 mL) equipped with a

temperature controller (charging rate: 72%, rotation speed: 60 rpm). In a second kneading step, the above-kneaded product was cooled to room temperature, and then mixed with sulfur and a vulcanization accelerator, followed by kneading. The resultant product was molded and vulcanized by means of a vulcanizing press at 160°C for a specific period of time, to thereby produce a crosslinked polymer. The crosslinked polymer was evaluated for the properties (1) to (4) described below. A non-vulcanized polymer composition was evaluated for the property (5) described below. The results are shown in Table 4.

[0053]

(1) Tensile strength

100% modulus (M100), 300% modulus (M300), tensile strength at break (TB), and elongation at break (EB) were determined according to JIS K6251:2010. A determined value is represented by an index relative to that (taken as 100) of the crosslinked polymer of Comparative Example 1. A higher index indicates a higher tensile strength at break and a higher elongation at break (viscoelasticity); i.e., superior properties.

(2) 0°C tanδ

0°C tanδ was determined by means of ARES-RDA (manufactured by TA Instruments) under the following conditions: shear strain 1.0%, angular velocity: 100 radians/second, temperature: 0°C. A determined value is represented by an index relative to that (taken as 100) of

the crosslinked polymer of Comparative Example 1. A higher index indicates superior wet grip property.

(3) 50°C $\tan\delta$

50°C $\tan\delta$ was determined by means of ARES-RDA (manufactured by TA Instruments) under the following conditions: shear strain 1.0%, angular velocity: 100 radians/second, temperature: 50°C. A determined value is represented by an index relative to that (taken as 100) of the crosslinked polymer of Comparative Example 1. A higher index indicates a smaller energy loss and superior low hysteresis loss property.

(4) Abrasion resistance

Abrasion resistance was determined by means of a DIN abrasion tester (manufactured by Toyo Seiki) according to JIS K6264 at a load of 10 N and 25°C. A determined value is indicated by an index relative to that (taken as 100) of the crosslinked polymer of Comparative Example 1. A higher index indicates superior abrasion resistance.

(5) Processability

The non-vulcanized polymer composition was wound around a 6-inch open roll at 60°C. The state of winding of the polymer composition around the roll was visually observed for evaluation of roll processability on the basis of the following four criteria (I to IV):

I: the polymer composition adheres to and winds around the roll at initial application of the composition to the roll; i.e., excellent roll processability;

II: the polymer composition winds around the roll to some extent at initial application of the composition to the roll; i.e., no considerable problem in roll processability;

III: the polymer composition does not wind around the roll at initial application of the composition to the roll, but gradually winds around the roll; i.e., acceptable roll processability; and

IV: the polymer composition neither adheres to nor winds around the roll; i.e., encounters difficulty in roll processing (the sample is in a powdery or granular form).

[0054]

[Comparative Example 1 [synthesis and evaluation of hydrogenated conjugated diene-based polymer Q]]

The procedure of Example 1 was repeated, except that the compound represented by the formula (a-1) was replaced with silicon tetrachloride (13.2 mmol) for polymerization, to thereby produce a hydrogenated conjugated diene-based polymer Q (Table 1). Table 2 shows the properties of the hydrogenated conjugated diene-based polymer Q. In the same manner as in Example 1, the hydrogenated conjugated diene-based polymer Q was mixed with other components according to the formulation shown below in Table 3, to thereby produce a polymer composition. The polymer composition was vulcanized to produce a crosslinked polymer, and the crosslinked polymer was evaluated for the aforementioned properties. The results are shown in Table 4.

[Example 2 [synthesis and evaluation of hydrogenated

conjugated diene-based polymer B]]

The procedure of Example 1 was repeated, except that piperidine (42.3 mmol) was added to the autoclave reactor during addition of cyclohexane, tetrahydrofuran, styrene, and 1,3-butadiene for polymerization, to thereby produce a hydrogenated conjugated diene-based polymer B (Table 1). Table 2 shows the properties of the hydrogenated conjugated diene-based polymer B. In the same manner as in Example 1, the hydrogenated conjugated diene-based polymer B was mixed with other components according to the formulation shown below in Table 3, to thereby produce a polymer composition. The polymer composition was vulcanized to produce a crosslinked polymer, and the crosslinked polymer was evaluated for the aforementioned properties. The results are shown in Table 4.

[Comparative Example 2 [synthesis and evaluation of hydrogenated conjugated diene-based polymer R]]

The procedure of Comparative Example 1 was repeated, except that piperidine (42.3 mmol) was added to the autoclave reactor during addition of cyclohexane, tetrahydrofuran, styrene, and 1,3-butadiene for polymerization, to thereby produce a hydrogenated conjugated diene-based polymer R (Table 1). Table 2 shows the properties of the hydrogenated conjugated diene-based polymer R. In the same manner as in Example 1, the hydrogenated conjugated diene-based polymer R was mixed with other components according to the formulation shown below in Table 3, to thereby produce a polymer

composition. The polymer composition was vulcanized to produce a crosslinked polymer, and the crosslinked polymer was evaluated for the aforementioned properties. The results are shown in Table 4.

[0055]

[Table 1]

	Example 1	Comparative Example 1	Example 2	Comparative Example 2
Type of hydrogenated conjugated diene-based polymer	A	Q	B	R
Polymerization formulation				
Cyclohexane (g)	25,600	25,600	25,600	25,600
Tetrahydrofuran (g)	384	384	384	384
Styrene (g)	800	800	800	800
Butadiene (g)	2,336	2,336	2,336	2,336
Supplemental butadiene (g)	64	64	64	64
n-Butyllithium (mmol)	60.0	60.0	60.0	60.0
Piperidine (mmol)	—	—	42.3	42.3
Specific polyorganosiloxane A (mmol)	0.4	—	0.4	—
Compound B (mmol)	—	13.2	—	13.2

[0056]

The abbreviations of compounds shown in Table 1 are as follows.

Specific polyorganosiloxane A: a compound represented by the aforementioned formula (a-1)

Compound B: silicon tetrachloride

[0057]

[Table 2]

	Example 1	Comparative Example 1	Example 2	Comparative Example 2
Type of hydrogenated conjugated diene-based polymer	A	Q	B	R
Properties of hydrogenated conjugated diene-based polymer				
Bonded styrene content (wt%)	25	25	25	25
Vinyl bond content (%)	56	55	56	56
Glass-transition temperature (°C)	-36	-35	-36	-36
Weight average molecular weight ($\times 10^4$)	34	30	33	32
Mooney viscosity (ML1+4, 100°C)	85	95	110	120
Hydrogenation rate (%)	95	96	95	96

[0058]

[Table 3]

Compounding formulation	(phr)
Hydrogenated conjugated diene-based polymer	100
Silica *1	70
Carbon black *2	5.6
Silane coupling agent *3	5.6
Extender oil *4	37.5
Stearic acid	2
Antioxidant *5	1
Zinc oxide	3
Vulcanization accelerator CZ *6	1.8
Vulcanization accelerator DPG *7	1.5
Sulfur	1.5

[0059]

The details of each component in Table 3 are shown below.

*1: Zeosil 1165MP manufactured by Rhodia, *2: DIABLACK N339 manufactured by Mitsubishi Chemical Corporation, *3: Si75 manufactured by Evonik, *4: JOMO Process NC-140 manufactured by Japan Energy Corporation, *5: OZONONE 6C manufactured by Seiko Chemical Co., Ltd., *6: NOCCERL CZ manufactured by Ouchi Shinko Chemical Industrial Co., Ltd., *7: NOCCERL D manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

[0060]

[Table 4]

	Example 1	Comparative Example 1	Example 2	Comparative Example 2
Type of hydrogenated conjugated diene-based polymer	A	Q	B	R
Physical properties of crosslinked polymer				
100% modulus (M100) (INDEX)	102	100	105	106
300% modulus (M300) (INDEX)	104	100	112	110
Tensile strength at break (TB) (INDEX)	110	100	111	101
Elongation at break (EB) (INDEX)	98	100	94	90
0°C tanδ (INDEX)	112	100	116	106
50°C tanδ (INDEX)	110	100	121	110
Abrasion resistance (INDEX)	110	100	115	105
Physical property of polymer composition				
Processability	I	II	II	III

[0061]

As shown in Table 4, the hydrogenated conjugated diene-based polymer of Example 1 or 2, which is a hydrogenated product of a polymer prepared through reaction between a specific polyorganosiloxane and a conjugated diene-based polymer having an active terminal, exhibited processability superior to that of the hydrogenated conjugated diene-based polymer of Comparative Example 1 or 2. The crosslinked polymer of Example 1 or 2 exhibited well-balanced properties in terms of tensile strength at break, viscoelasticity, abrasion resistance, wet grip property, and low hysteresis loss property.

Claims

1. A method for producing a hydrogenated conjugated diene-based polymer, the method comprising:

reacting a conjugated diene-based polymer having an active terminal with a polyorganosiloxane having two or more specific functional groups each being at least one type selected from the group consisting of an epoxy group, an alkoxy group, a carbonyl group, a 2-pyrrolidonyl group, a vinyl group, and a halogen atom; and

hydrogenating a modified conjugated diene-based polymer prepared through the reaction.

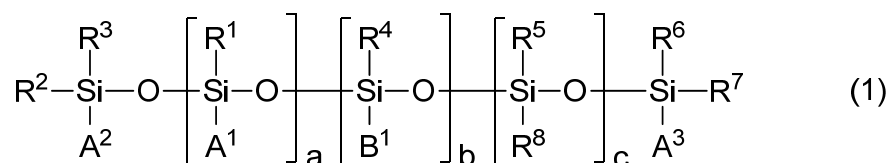
2. The method for producing a hydrogenated conjugated diene-based polymer according to claim 1, wherein the modified conjugated diene-based polymer is prepared through bonding of a plurality of conjugated diene-based polymer chains to the polyorganosiloxane having two or more specific functional groups.

3. The method for producing a hydrogenated conjugated diene-based polymer according to claim 1 or 2, wherein the conjugated diene-based polymer having an active terminal comprises a butadiene unit, and the modified conjugated diene-based polymer is hydrogenated so as to achieve a hydrogenation rate of 70 to 99% in the butadiene unit.

4. The method for producing a hydrogenated conjugated diene-based polymer according to any one of claims 1 to 3, wherein the polyorganosiloxane is a compound represented by

the following formula (1):

[F1]



(where R¹ to R⁸ each represent a hydrocarbyl group; A¹ represents a group having the specific functional group; A² and A³ each represent a hydrocarbyl group or a group having the specific functional group; B¹ represents a group having a polyether structure; a is an integer of 3 to 200; b is an integer of 0 to 200; c is an integer of 0 to 200; and R¹, R⁴, R⁵, R⁸, A¹, and B¹ may be identical to or different from one another between structural units).

5. The method for producing a hydrogenated conjugated diene-based polymer according to any one of claims 1 to 4, wherein the conjugated diene-based polymer having an active terminal is prepared through polymerization of a monomer containing a conjugated diene compound in the presence of at least one of an alkali metal compound and an alkaline earth metal compound.

6. The method for producing a hydrogenated conjugated diene-based polymer according to claim 5, wherein the monomer is polymerized in the presence of a mixture of at least one of an alkali metal compound and an alkaline earth metal compound and a compound having a functional group capable of interacting with silica.

7. A hydrogenated conjugated diene-based polymer

produced by hydrogenation of a product prepared through reaction between a conjugated diene-based polymer having an active terminal and a polyorganosiloxane having two or more specific functional groups each being at least one type selected from the group consisting of an epoxy group, an alkoxy group, a carbonyl group, a 2-pyrrolidonyl group, a vinyl group, and a halogen atom.

8. A polymer composition comprising a hydrogenated conjugated diene-based polymer produced by a method as recited in any one of claims 1 to 6 or a hydrogenated conjugated diene-based polymer as recited in claim 7, silica, and a crosslinking agent.

9. A crosslinked polymer produced through crosslinking of a polymer composition as recited in claim 8.

10. A tire obtained by employing a crosslinked polymer as recited in claim 9 as a tread material, a sidewall material, or both.