

DESCRIPTION

Method for Producing Modified Conjugated Diene-Based Polymer,
Polymer Composition,
Crosslinked Polymer, and Tire

TECHNICAL FIELD

[0001]

The present disclosure relates to a method for a modified 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 good 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]

A pneumatic tire is required to achieve excellent low fuel consumption performance. In order to meet such a requirement, various modified conjugated diene-based polymers have been proposed, in which a functional group capable of interacting with silica is bonded to the polymerization initiation terminal or polymerization end terminal of a

conjugated diene-based polymer chain. Such a terminal-modified conjugated diene-based polymer exhibits higher affinity to a reinforcing filler (e.g., carbon black or silica), as compared with an unmodified conjugated diene-based polymer. Thus, such a modified conjugated diene-based polymer can achieve low-heat-generating property and improved low fuel consumption performance.

[0004]

Various compounds have been proposed as terminal-modifying agents of conjugated diene polymers. As one of them, conventionally, it has been proposed to use a polyorganosiloxane having two or more functional groups capable of reacting with the active terminal of a conjugated diene polymer (see, for example, Patent Documents 1 and 2).

RELATED-ART DOCUMENT

Patent Document

[0005]

Patent Document 1: Japanese Patent Application Laid-Open (*kokai*) No. H09-110904

Patent Document 2: International Patent Publication WO 2005/021637

SUMMARY OF THE INVENTION

Technical Problem

[0006]

In view of, for example, recent environmental

circumstances (e.g., global warming due to carbon dioxide emission), increasing awareness about resource saving and energy saving, and economic situations (e.g., an increase in the price of gasoline), rubber materials for automobile tires have been required to achieve low fuel consumption performance (low-heat-generating property) superior to that of conventional ones. In addition to low fuel consumption performance, such a rubber material is required to achieve well-balanced properties for tires, including tensile strength and wet grip property.

[0007]

In view of the foregoing, an object of the present disclosure is to provide a modified conjugated diene-based polymer capable of preparing a vulcanized rubber achieving excellent low fuel consumption performance, tensile strength and wet grip property.

Solution to Problem

[0008]

In order to solve the aforementioned problems, the present disclosure provides a modified conjugated diene-based polymer, a production method therefor, a polymer composition, a crosslinked polymer, and a tire, which are described below.

[0009]

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

polymerizing a monomer group X containing at least one

compound selected from the group consisting of a vinylsilane compound (A) and an aromatic vinyl compound (B) and a conjugated diene compound in the presence of a polymerization initiator, thereby preparing a polymer having an active terminal; and

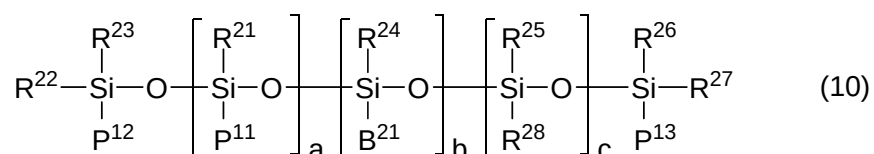
reacting the polymer having the active terminal with a polyorganosiloxane (C), wherein

the vinylsilane compound (A) is a vinylsilane compound having a group $-\text{SiR}^1\text{R}^2\text{R}^3$, wherein R^1 represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen;

the aromatic vinyl compound (B) is an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom; and

the polyorganosiloxane (C) is 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 is two or more.

[2] A modified conjugated diene-based polymer represented by formula (10):



wherein R^{21} to R^{28} each represent a hydrocarbyl group; P^{11} represents a group 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, or a conjugated diene-based polymer chain having a monomer unit derived from at least one compound selected from the group consisting of the aforementioned vinylsilane compound (A) and aromatic vinyl compound (B) and a monomer unit derived from a conjugated diene compound; P^{12} and P^{13} each represent the group having the specific functional group, the conjugated diene-based polymer chain, or a hydrocarbyl group; B^{21} 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; R^{21} to R^{28} , P^{11} , and B^{21} may be identical to or different from one another between structural units; and the number of the conjugated diene-based polymer chains present in the molecule is two or more.

[3] A modified conjugated diene-based polymer produced by polymerizing a monomer group X containing at least one compound selected from the group consisting of the aforementioned vinylsilane compound (A) and aromatic vinyl

compound (B) and a conjugated diene compound in the presence of a polymerization initiator to thereby prepare a polymer having an active terminal, and reacting the polymer having the active terminal with the aforementioned polyorganosiloxane (C).

[4] A polymer composition comprising a modified conjugated diene-based polymer produced by a method of the aforementioned [1] or a modified conjugated diene-based polymer of the aforementioned [2] or [3], an inorganic filler, and a crosslinking agent.

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

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

EFFECTS OF THE INVENTION

[0010]

According to the present disclosure, it is possible to prepare a modified conjugated diene-based polymer preferable for obtaining a vulcanized rubber achieving excellent low fuel consumption performance, tensile strength, and wet grip property.

DESCRIPTION OF EMBODIMENTS

[0011]

The modified conjugated diene-based polymer of the

present disclosure may be produced using a method that includes a polymerization step and a modification step. The polymerization step involves polymerizing a monomer group X containing at least one compound selected from the group consisting of a vinylsilane compound (A) and an aromatic vinyl compound (B) and a conjugated diene compound in the presence of a polymerization initiator, thereby preparing a polymer having an active terminal. The modification step involves reacting the polymer having the active terminal with a polyorganosiloxane (C). Embodiments of the present disclosure will next be described in detail.

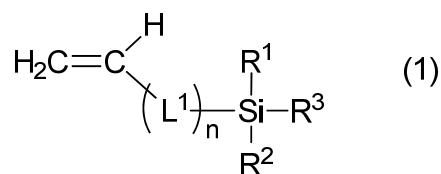
[0012]

[Polymerization step]

<Monomer group X>

Vinylsilane compound (A)

The vinylsilane compound (A) is a vinylsilane compound having a group "-SiR¹R²R³", and is preferably represented by the following formula (1):



wherein R¹ represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen; R² and R³ each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom,

an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen; L^1 represents a hydrocarbyl group; and n is 0 or 1.

[0013]

R^1 has at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom. Such a heteroatom is not bonded to active hydrogen, and may be protected with a protective group. As used herein, the term "active hydrogen" refers to a hydrogen atom bonded to an atom other than a carbon atom, preferably a hydrogen atom having a binding energy lower than that of a carbon-hydrogen bond of polymethylene. The term "protective group" refers to a functional group for transforming R^1 into an inactive functional group. Examples of the protective group include tri-substituted hydrocarbylsilyl groups.

[0014]

Specific examples of R^1 include a nitrogen-containing group in which two hydrogen atoms of a primary amino group are substituted by two protective groups, a nitrogen-containing group in which one hydrogen atom of a secondary amino group is substituted by one protective group, $-R^{33}-NR^{31}R^{32}$ (R^{31} and R^{32} each represent a hydrocarbyl group, or R^{31} and R^{32} taken together represent a ring together with the nitrogen atom to which R^{31} and R^{32} bond, and R^{33} represents a single bond or a hydrocarbylene group), an imino group, an oxygen-containing group in which one hydrogen atom of a

hydroxy group is substituted by one protective group, a phosphorus-containing group in which two hydrogen atoms of a primary phosphino group are substituted by two protective groups, a phosphorus-containing group in which one hydrogen atom of a secondary phosphino group is substituted by one protective group, a tertiary phosphino group, and a sulfur-containing group in which one hydrogen atom of a thiol group is substituted by one protective group. In view of high affinity of the modified conjugated diene-based polymer to silica, R^1 is preferably a group containing at least one of a nitrogen atom and an oxygen atom, more preferably a group containing a nitrogen atom.

[0015]

If R^1 is a group " $-R^{33}-NR^{31}R^{32}$ " (hereinafter, a group " $-NR^{31}R^{32}$ " may be referred to as a "substituted amino group"), the hydrocarbyl group represented by R^{31} or R^{32} is preferably a C1 to C10 alkyl group, more preferably a C1 to C5 alkyl group. R^{31} and R^{32} taken together may represent a ring together with the nitrogen atom to which R^{31} and R^{32} bond. Examples of the ring (cyclic amino group) include a 1-pyrrolidinyl group, a 1-piperidino group, a 1-hexamethyleneimino group, a 1-octamethyleneimino group, a pyridyl group, and a 1-imidazolyl group.

The hydrocarbylene group represented by R^{33} is preferably a C1 to C20 alkanediyl group, more preferably a C1 to C10 alkanediyl group.

[0016]

The aforementioned description regarding R^1 is applied to the case where R^2 or R^3 is a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen. The hydrocarbyl group represented by R^2 or R^3 is preferably a C1 to C20 alkyl group, a C3 to C20 cycloalkyl group, or a C6 to C20 aryl group. In view of the affinity of the modified conjugated diene-based polymer to a filler, at least two of R^1 to R^3 are preferably a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen.

Examples of L^1 include a C1 to C20 alkanediyl group, a C3 to C20 cycloalkylene group, and a C6 to C20 arylene group. In the formula (1), n is preferably 0.

[0017]

The vinylsilane compound (A) is preferably at least one species selected from the group consisting of a substituted-amino-group-containing vinylsilane compound and a hydrocarbyloxy-group-containing vinylsilane compound.

Specific examples of the substituted-amino-group-containing vinylsilane compound include

(dialkylamino)dialkylvinylsilane,

[bis(trialkylsilyl)amino]dialkylvinylsilane,

(dialkylamino)di(alkoxyalkyl)vinylsilane, a cyclic aminodialkylvinylsilane compound,

(dialkylamino)dialkylvinylphenylsilane,
 bis(dialkylamino)alkylvinylsilane,
 bis[bis(trialkylsilyl)amino]alkylvinylsilane,
 bis(dialkylamino)alkoxyalkylvinylsilane, bis(cyclic
 amino)alkylvinylsilane,
 bis(dialkylamino)alkylvinylphenylsilane,
 tris(dialkylamino)vinylsilane, and
 tris(dialkylamino)vinylphenylsilane. Specific examples of
 the hydrocarbyloxy-group-containing vinylsilane compound
 include trihydrocarbyloxyvinylsilane,
 dialkoxyalkylvinylsilane, dialkoxyarylvinylsilane,
 monoalkoxydialkylvinylsilane, monoalkoxydiarylvinylsilane,
 and monoalkoxyalkylarylvinylsilane.

[0018]

The substituted-amino-group-containing vinylsilane
 compound is preferably a compound of the formula (1) in which
 one or two of R^1 to R^3 have a substituted amino group and n
 is 0. Specific examples of the
 (dialkylamino)dialkylvinylsilane include
 (dimethylamino)dimethylvinylsilane,
 (ethylmethylamino)dimethylvinylsilane, and (di- n -
 propylamino)dimethylvinylsilane. Specific examples of the
 bis(dialkylamino)alkylvinylsilane include
 bis(dimethylamino)methylvinylsilane,
 bis(diethylamino)methylvinylsilane, bis(di- n -
 propylamino)methylvinylsilane, bis(di- n -
 butylamino)methylvinylsilane, and

bis(dimethylamino)ethylvinylsilane. Specific examples of the bis[bis(trialkylsilyl)amino]alkylvinylsilane include bis[bis(trimethylsilyl)amino]methylvinylsilane and bis[bis(trimethylsilyl)amino]ethylvinylsilane. Specific examples of the bis(dialkylamino)alkoxyalkylvinylsilane include bis(dimethylamino)methoxymethylvinylsilane and bis(dimethylamino)(2-methoxyethyl)vinylsilane. Specific examples of the cyclic aminodialkylvinylsilane include 1-pyrrolidinyl dimethylvinylsilane, 1-piperidinyl dimethylvinylsilane, 1-hexamethyleneiminodimethylvinylsilane, and 4,5-dihydro-1-imidazolyl dimethylvinylsilane. Specific examples of the bis(cyclic amino)alkylvinylsilane include bis(1-pyrrolidinyl)methylvinylsilane and bis(1-piperidinyl)methylvinylsilane.

[0019]

Specific examples of the hydrocarbyloxy-group-containing vinylsilane compound include trimethoxyvinylsilane, triethoxyvinylsilane, tripropoxyvinylsilane, methyldimethoxyvinylsilane, di(tert-butoxy)phenylvinylsilane, dimethylmethoxyvinylsilane, tert-butoxydiphenylvinylsilane, tert-butoxymethylphenylvinylsilane, and tert-butoxyethylphenylvinylsilane. These vinylsilane compounds (A) may be used singly or in combination of two or more species.

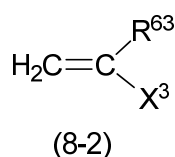
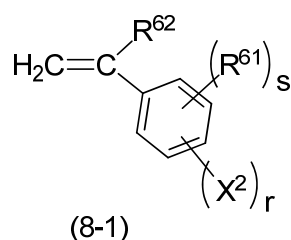
[0020]

Aromatic vinyl compound (B)

In the aromatic vinyl compound (B), none of the nitrogen, phosphorus, and sulfur atoms is bonded to active hydrogen, and each of these atoms may be protected with, for example, a tri-substituted hydrocarbylsilyl group. In view of the dispersibility of a filler, the aromatic vinyl compound (B) is particularly preferably a nitrogen-containing aromatic vinyl compound.

[0021]

Specific examples of preferred nitrogen-containing aromatic vinyl compounds include compounds represented by the following formulae (8-1) and (8-2):



wherein X^2 represents a nitrogen-containing group having no active hydrogen, R^{61} represents a substituent, R^{62} represents a hydrogen atom, a methyl group, or a phenyl group, r is an integer of 1 to 5, s is an integer of 0 to 4, and $r + s \leq 5$; and,

X^3 represents a nitrogen-containing aromatic heterocyclic group (which may have a substituent on the ring moiety), and R^{63} represents a hydrogen atom or a methyl group.

The aromatic vinyl compound (B) is preferably at least one compound selected from the group consisting of the compounds represented by the aforementioned formulae (8-1)

and (8-2).

[0022]

In the formula (8-1), X^2 may be in a chain or cyclic form, and X^2 is, for example, the aforementioned group " $-R^{33}-NR^{31}R^{32}$." Examples of the substituent represented by R^{61} include a C1 to C10 hydrocarbyl group and a C1 to C10 hydrocarbyloxy group. In the formula (8-1), r is preferably 1 or 2, more preferably 1, and s is preferably 0 to 2, more preferably 0 or 1.

In the formula (8-2), X^3 is, for example, a group prepared through removal of one hydrogen atom from the ring moiety of a pyridine ring, a pyrimidine ring, a pyrazine ring, or a quinoline ring. The description regarding R^{61} can be applied to the substituent that may be possessed by the ring moiety.

[0023]

Specific examples of the nitrogen-containing aromatic vinyl compound represented by the formula (8-1) include dihydrocarbylstyrenes, such as 3-dimethylaminostyrene and 4-dimethylaminostyrene; dihydrocarbylaminoalkylstyrenes, such as 4-(diethylaminomethyl)styrene and 4-[2-(dimethylamino)ethyl]styrene; cyclic-amino-group-containing styrenes, such as 3-(1-pyrrolidinyl)styrene, 4-(1-pyrrolidinyl)styrene, 4-piperidinostyrene, 3-(1-pyrrolidinyl)methylstyrene, 3-(1-pyrrolidinyl)ethylstyrene, 4-(1-pyrrolidinyl)methylstyrene, and 4-(1-pyrrolidinyl)ethylstyrene; and tertiary-amino-group-

containing diphenylethylenes, such as 1-(4-dimethylaminophenyl)-1-phenylethylene. Specific examples of the nitrogen-containing aromatic vinyl compound represented by the formula (8-2) include vinylpyridines, such as 3-vinylpyridine and 4-vinylpyridine. These aromatic vinyl compounds (B) may be used singly or in combination of two or more species.

[0024]

(Conjugated diene compound)

Examples of the conjugated diene compound used for polymerization include 1,3-butadiene, 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, 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene are preferred. Particularly preferred is 1,3-butadiene, from the viewpoint of well-balanced improvements in processability and low hysteresis loss property. These conjugated diene compounds may be used singly or in combination of two or more species.

[0025]

In the aforementioned polymerization, it is preferable that the monomer group X further contains an aromatic vinyl compound having none of a nitrogen atom, a phosphorus atom and a sulfur atom (hereinafter the aromatic vinyl compound may be referred to as "additional aromatic vinyl compound), from the viewpoint of improving the strength of the resultant rubber. Examples of the additional aromatic vinyl compound

include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, α -methylstyrene, 2,4-dimethylstyrene, 2,4-diisopropylstyrene, 4-t-butylstyrene, 5-t-butyl-2-methylstyrene, vinyl ethylbenzene, divinylbenzene, trivinylbenzene, divinyl naphthalene, t-butoxystyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 2-t-butylstyrene, 3-t-butylstyrene, vinyl xylene, vinyl naphthalene, vinyl pyridine, and diphenylethylene. Among these, the additional aromatic vinyl compound is preferably styrene and α -methylstyrene.

[0026]

In particular, the modified conjugated diene-based polymer of the present disclosure is preferably a copolymer formed of the monomer group X containing 1,3-butadiene and styrene, in view of high a living property during anionic polymerization. The copolymer preferably contains a random copolymer moiety formed of the conjugated diene compound and the aromatic vinyl compound (including the aromatic vinyl compound (B) and the additional aromatic vinyl compound). The aforementioned copolymer may further contain a block moiety formed of the conjugated diene compound or the additional aromatic vinyl compound.

[0027]

The amount of the aromatic vinyl compound (i.e., the total amount of the aromatic vinyl compound (B) and the additional aromatic vinyl compound) contained in the monomer group X is preferably 3 to 55 mass%, more preferably 5 to 50

mass%, relative to the total amount of the monomer group X used for the polymerization, from the viewpoint of a good balance between the low hysteresis loss property and wet skid resistance 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 $^1\text{H-NMR}$.

[0028]

In order to achieve sufficient improvements in the tensile strength and low-heat-generating property of the vulcanized rubber, the total amount of the vinylsilane compound (A) and aromatic vinyl compound (B) used is preferably 0.001 mmol/g or more, more preferably 0.002 mmol/g or more, still more preferably 0.003 mmol/g or more, relative to the total amount of the compounds of the monomer group X. From the viewpoint of sufficiently high reactivity, the maximum total amount of the vinylsilane compound (A) and aromatic vinyl compound (B) used is preferably 130 mmol/g or less, more preferably 100 mmol/g or less, still more preferably 70 mmol/g or less, relative to the total amount of the compounds of the monomer group X.

[0029]

The monomer group X may contain an additional compound other than the conjugated diene compound, the vinylsilane compound (A), and the aromatic vinyl compound (hereinafter the additional compound may be referred to as an "additional monomer"). Examples of the additional monomer include acrylonitrile, methyl (meth)acrylate, ethyl (meth)acrylate,

and hydroxyethyl (meth)acrylate. The amount of the additional monomer used is preferably 5 mass% or less, more preferably 3 mass% or less, relative to the total amount of the monomers used for the polymerization.

[0030]

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

[0031]

At least one of an alkali metal compound and an alkaline-earth metal compound is preferably used as the initiator for polymerization of the monomer group X. Examples of the initiator include alkylolithiums such as methylolithium, ethylolithium, n-propylolithium, n-butyllithium, sec-butyllithium, and tert-butyllithium, 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, and calcium stearate. Among these, lithium compounds are preferable. The total amount of the

polymerization initiator(s) used is preferably 0.2 to 20 mmol relative to the amount (100 g) of the monomer used for the polymerization.

[0032]

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 (hereinafter the compound may be referred to as a "modifying initiator"). The term "functional group that interacts with silica" used herein refers to a group that includes at least one atom (e.g., a nitrogen atom, a sulfur atom, a phosphorus atom, an oxygen atom, or a silicon atom) that interacts with silica. The term "interaction" used herein refers to 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.

[0033]

The modifying initiator 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-butyldimethylsilyl)piperazine, and 1,3-ditrimethylsilyl-1,3,5-triazinane. The modifying initiator may be used singly or in combination of two or more species.

[0034]

In the case of polymerization in the presence of the aforementioned mixture, at least one of the alkali metal compound and the alkaline earth metal compound may be preliminarily mixed with the modifying initiator, and the resultant mixture may be added to the polymerization system. Alternatively, at least one of the alkali metal compound and the alkaline earth metal compound and the modifying initiator may be added to the reaction system, and the compound(s) and the modifying initiator may be mixed together in the polymerization system.

[0035]

The randomizer may be used to adjust the vinyl bond content (i.e., the amount of vinyl bonds) of 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 either alone or in combination.

[0036]

The organic solvent used for polymerization may be any organic solvent that is inert to the reaction. Examples of the organic solvent include aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic hydrocarbons. In particular, the organic solvent is preferably a C3 to C8 hydrocarbon. Specific examples of the C3 to C8 hydrocarbon 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.

[0037]

In the case of the solution polymerization, the monomer concentration of the reaction solvent is preferably 5 to 50 mass%, more preferably 10 to 30 mass%, for maintaining the balance between productivity and polymerization controllability. The polymerization reaction temperature is preferably -20°C to 150°C, more preferably 0 to 120°C. The polymerization reaction is preferably carried out under a pressure sufficient to maintain the monomer substantially in a liquid phase. Such a pressure can be achieved by, for example, pressurizing the reactor by use of a gas inert to the polymerization reaction.

[0038]

A conjugated diene-based polymer having an active

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

[0039]

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

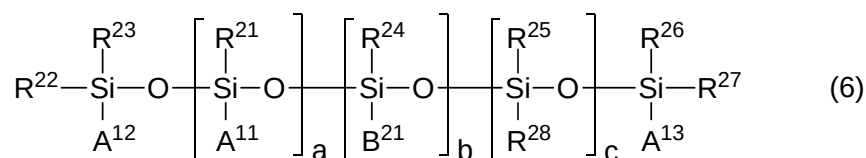
[0040]

[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 is two or more (hereinafter the polyorganosiloxane may be referred to as a "specific polyorganosiloxane").

[0041]

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 (6):



wherein R^{21} to R^{28} each represent a hydrocarbyl group; A^{11} represents a group having the specific functional group; A^{12} and A^{13} each represent a hydrocarbyl group or a group having the specific functional group; B^{21} 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^{21} to R^{28} , A^{11} , and B^{21} may be identical to or different from one another between structural units.

[0042]

Examples of the hydrocarbyl group represented by R^{21} to

R^{28} , A^{12} , or A^{13} in the formula (6) 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^{11} to A^{13} 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, 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.

[0043]

Examples of the polyether structure represented by B^{21} 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 (6), 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 (6), 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.

[0044]

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 0.01 mol or more, more preferably 0.05 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 1.0 mol, more preferably less than 0.7 mol, relative to 1 mol of the metal atom (responsible for the polymerization) of the polymerization initiator.

[0045]

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.

[0046]

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. The additional modifying agent may be a compound (coupling agent) having two or more groups capable of reacting with the active terminal. 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.

[0047]

In the case where the specific polyorganosiloxane is used, a polymerization terminator (e.g., an alcohol) or another modifying agent may be added to the polymerization

system before reaction between the conjugated diene-based polymer having the active terminal and the specific polyorganosiloxane to thereby inactivate a portion of the conjugated diene-based polymer, for the purpose of adjusting the amount of the conjugated diene-based polymer to be reacted with the specific polyorganosiloxane.

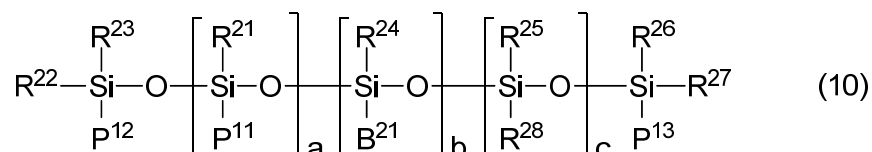
[0048]

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 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 resultant crosslinked polymer exhibits excellent tensile strength and low-heat-generating property. 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.

[0049]

The modified conjugated diene-based polymer of the present disclosure is preferably produced by use of the compound represented by the aforementioned formula (6) as the specific polyorganosiloxane. The modified conjugated diene-

based polymer is represented by the following formula (10):



wherein R^{21} to R^{28} each represent a hydrocarbyl group; P^{11} represents a group 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, or a conjugated diene-based polymer chain having a monomer unit derived from at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) and a monomer unit derived from the conjugated diene compound; P^{12} and P^{13} each represent the group having the specific functional group, the conjugated diene-based polymer chain, or a hydrocarbyl group; B^{21} 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; R^{21} to R^{28} , P^{11} , and B^{21} may be identical to or different from one another between structural units; and the number of the conjugated diene-based polymer chains present in the molecule is two or more.

The conjugated diene-based polymer contained in the reaction solution can be isolated by, for example, a known solvent removal method (e.g., steam stripping) and a drying operation (e.g., thermal treatment).

[0050]

The modified conjugated diene-based polymer of the present disclosure has a weight average molecular weight (M_w) (in terms of polystyrene) of preferably 1.0×10^5 to 3.0×10^6 as measured by means of GPC. 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 .

[0051]

<Polymer composition>

The polymer composition of the present disclosure contains a rubber component containing the aforementioned modified conjugated diene-based polymer, an inorganic filler, and a crosslinking agent. The amount of the modified 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 amount of the rubber component contained in the polymer composition. The inorganic filler is preferably at least one of silica and carbon black. In the case of combination with the modified conjugated diene-based polymer of the present disclosure, silica is preferably used in view of achieving highly effective improvements in properties for tire.

[0052]

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.

[0053]

Examples of the carbon black include, but are not particularly limited to, GPF, FEF, HAF, ISAF, and SAF. The use of carbon black as an inorganic filler achieves a good reinforcing effect.

[0054]

The polymer composition may contain, in addition to silica or carbon black, any reinforcing filler (e.g., clay or calcium carbonate). 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.

[0055]

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.

[0056]

The polymer composition of the present disclosure, which contains the above-prepared modified conjugated diene-based polymer of the present disclosure, may contain an additional rubber component different from the modified conjugated diene-based polymer. 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 amount of the additional rubber component is preferably 5 to 60 parts by mass, more preferably 10 to 50 parts by mass, relative to 100 parts by mass of the total amount of polymer components contained in the polymer composition.

[0057]

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, a vulcanization accelerator, a silane coupling agent, a compatibilizer, a vulcanization aid, a process oil, a processing aid, and an anti-scorching agent. The amount of

such an additive incorporated into the polymer composition may be appropriately determined, so long as the advantageous effects of the present disclosure are not impaired.

[0058]

The polymer composition of the present disclosure can be prepared through kneading of the polymer components, the inorganic filler, the crosslinking agent, and an optional component by means of, for example, 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.

[0059]

The production method of the present disclosure can produce a modified conjugated diene-based polymer capable of

preparing a vulcanized rubber that achieves excellent low fuel consumption performance, tensile strength, and wet grip property. Thus, the polymer composition containing the modified conjugated diene-based polymer of the present disclosure is particularly suitable for use as a material of a tire tread or sidewall.

[0060]

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

[0061]

The present invention will next be described in detail by way of examples, which should not be construed as limiting the invention 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.

[0062]

[Evaluation of properties of polymer]

Vinyl bond content (%): determined by means of ^1H -NMR (400 MHz).

Bonded styrene content (%): determined by means of ^1H -NMR (400 MHz).

Weight average molecular weight before modification (peak molecular weight before modification reaction): determined on the basis of a chart of molecular weight (in terms of polystyrene) obtained by means of gel permeation chromatography (GPC). Specific conditions for GPC are as follows.

(GPC conditions)

Chromatograph: HLC-8020 (manufactured by Tosoh Corporation)

Column: two columns of GMH-HR-H (manufactured by Tosoh Corporation) connected in series

Detector: differential refractometer RI-8020 (manufactured by Tosoh Corporation)

Eluent: tetrahydrofuran

Column temperature: 40°C

Mooney viscosity (ML_{1+4} , 100°C): determined according to JIS K6300 by use of an L rotor under the following conditions: preheating: 1 minute, rotor operation time: 4 minutes, temperature: 100°C.

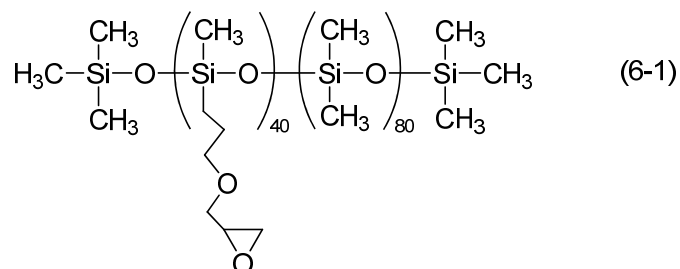
[0063]

[Example 1-1: Synthesis of modified conjugated diene-based rubber I]

Cyclohexane (4,000 g), tetrahydrofuran (0.083 mmol), 1,3-butadiene (306.6 g), and styrene (113.4 g) were added to an autoclave equipped with an agitator in a nitrogen

atmosphere. Subsequently, a solution of bis(diethylamino)methylvinylsilane (11.5 mmol) in cyclohexane and a solution of n-butyllithium (14.1 mmol) in n-hexane were added, to thereby initiate polymerization at 40°C. Ten minutes after initiation of the polymerization, 1,3-butadiene (167.4 g) and styrene (12.6 g) were continuously added over 60 minutes. The maximum temperature during polymerization reaction was 60°C. After completion of the continuous addition, the polymerization reaction was continued for 20 minutes. After determination of a polymerization conversion of 95% to 100%, a 20 mass% solution of polyorganosiloxane A represented by the following formula (6-1) in xylene was added so that the epoxy group content was 1.42 mmol (corresponding to 0.33-fold mole of the n-butyllithium used), and then reaction was allowed to proceed for 30 minutes. Thereafter, methanol (serving as a polymerization terminator) was added in an amount corresponding to 2-fold mole of the n-butyllithium used, to thereby prepare a solution containing a modified conjugated diene-based rubber I. The solution was mixed with Irganox 1520L (manufactured by Ciba Specialty Chemicals) serving as an antioxidant (0.15 parts relative to 100 parts of the modified conjugated diene-based rubber), and then the solvent was removed through steam stripping, followed by vacuum drying at 60°C for 24 hours, to thereby produce a modified conjugated diene-based rubber I in a solid form. The polymerization formulation of the modified conjugated diene-based rubber I is shown in Table 1, and the

properties of the modified conjugated diene-based rubber I are shown in Table 2.



[0064]

[Example 1-2]

The procedure of Example 1-1 was repeated, except that bis(diethylamino)methylvinylsilane was replaced with 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene (11.5 mmol), to thereby produce a modified conjugated diene-based rubber II. The properties of the modified conjugated diene-based rubber II are shown in Table 2.

[0065]

[Comparative Example 1-1]

The procedure of Example 1-1 was repeated, except that polyorganosiloxane A was not added, and methanol (serving as a polymerization terminator) was added in an amount corresponding to 2-fold mole of the n-butyllithium used, to thereby produce a modified conjugated diene-based rubber i.

[Comparative Example 1-2]

The procedure of Example 1-2 was repeated, except that polyorganosiloxane A was not added, and methanol (serving as a polymerization terminator) was added in an amount corresponding to 2-fold mole of the n-butyllithium used, to

thereby produce a modified conjugated diene-based rubber ii.

[Comparative Example 1-3]

The procedure of Example 1-1 was repeated, except that bis(diethylamino)methylvinylsilane was not added, to thereby produce a modified conjugated diene-based rubber iii.

[Comparative Example 1-4]

The procedure of Example 1-1 was repeated, except that neither bis(diethylamino)methylvinylsilane nor polyorganosiloxane A was added, and methanol (serving as a polymerization terminator) was added in an amount corresponding to 2-fold mole of the n-butyllithium used, to thereby produce an unmodified conjugated diene-based rubber iv.

The properties of the modified conjugated diene-based rubbers i to iii and the unmodified conjugated diene-based rubber iv are shown in Table 2.

[0066]

[Table 1]

	Example 1-1	Example 1-2	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3	Comparative Example 1-4
Type of (modified) conjugated diene-based rubber	I	II	i	ii	iii	iv
Polymerization component						
Cyclohexane (g)	4000	4000	4000	4000	4000	4000
Tetrahydrofuran (mmol)	0.083	0.083	0.083	0.083	0.083	0.083
Monomer group X						
: Styrene (g)	113.4	113.4	113.4	113.4	113.4	113.4
: 1,3-Butadiene (g)	306.6	306.6	306.6	306.6	306.6	306.6
: X-1 (mmol)	11.5	-	11.5	-	-	-
: X-2 (mmol)	-	11.5	-	11.5	-	-
: Supplemental styrene (g)	12.6	12.6	12.6	12.6	12.6	12.6
: Supplemental butadiene (g)	167.4	167.4	167.4	167.4	167.4	167.4
n-Butyllithium (mmol)	14.1	14.1	14.1	14.1	14.1	14.1
Terminal-modifying agent						
: Polyorganosiloxane A (mmol)	1.42	1.42	-	-	1.42	-
Antioxidant (g)	1.50	1.50	1.50	1.50	1.50	1.50

[0067]

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

X-1: bis(diethylamino)methylvinylsilane

X-2: 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene

polyorganosiloxane A : a compound represented by the
aforementioned formula (6-1)

[0068]

[Table 2]

Type of (modified) conjugated diene-based rubber	I	II	i	ii	iii	iv
Bonded styrene content (%)	20	20	20	20	20	20
Vinyl bond content (%)	54	53	54	54	54	53
Weight average molecular weight before polymerization ($\times 10^4$)	38	37	37	38	38	36
Mooney viscosity (ML1+4, 100°C)	36	37	38	40	38	41

[0069]

[Example 2-1: Preparation of rubber composition and
evaluation of physical properties thereof]

A rubber composition having the formulation shown in Table 3 was prepared from the above-produced modified conjugated diene-based rubber I. The rubber composition was vulcanized and evaluated for its physical properties. The rubber composition was kneaded and evaluated by the methods described below.

[0070]

[Table 3]

Compounding formulation		Parts by mass
(Modified) conjugated diene-based rubber		70
Butadiene rubber	*1	30
Silica	*2	50
Silane coupling agent	*3	6
Oil	*4	25
Silica	*2	25
Zinc oxide		2.5
Stearic acid	*5	2
Antioxidant	*6	2
Sulfur		1.5
Vulcanization accelerator	*7	1.7
Vulcanization accelerator	*8	2

[0071]

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

*1: Nipol BR1220 manufactured by Zeon Corporation

*2: Zeosil 1165MP manufactured by Rhodia

*3: Si69 manufactured by Degussa

*4: Fukkol Eramic 30 manufactured by Nippon Oil Corporation

*5: SA-300 manufactured by Adeka Corporation

*6: Nocrac 6C manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

*7: Nocceler NS manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

*8: Nocceler D manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

[0072]

Methods for kneading and evaluating rubber composition

The modified conjugated diene-based rubber I produced in Example 1-1 (70 parts) and butadiene rubber (trade name

"Nipol BR1220," manufactured by Zeon Corporation) (30 parts) were masticated by means of a Banbury mixer (volume: 250 mL). Subsequently, silica (trade name "Zeosil 1165MP," manufactured by Rhodia, nitrogen adsorption specific surface area (BET): 163 m²/g) (50 parts), a silane coupling agent (bis(3-(triethoxysilyl)propyl) tetrasulfide, trade name "Si69," manufactured by Degussa) (6.0 parts), and process oil (trade name "Fukkol Eramic 30," manufactured by Nippon Oil Corporation) (25 parts) were added, and the resultant mixture was kneaded at 110°C (initiation temperature) for 1.5 minutes. The kneaded product was mixed with silica (trade name "Zeosil 1165MP," manufactured by Rhodia) (25 parts), zinc oxide (zinc white No. 1) (2.5 parts), stearic acid (trade name "SA-300," manufactured by Adeka Corporation) (2 parts), and an antioxidant (N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, trade name "Nocrac 6C," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.) (2 parts), and the mixture was kneaded for 2.5 minutes. Thereafter, the resultant rubber composition was discharged from the Banbury mixer. The temperature of the rubber composition was 150°C at the time of completion of kneading. After the rubber composition was cooled to room temperature, the rubber composition was kneaded again in the Banbury mixer for 3 minutes and then discharged from the Banbury mixer. Subsequently, the rubber composition was kneaded with sulfur (1.5 parts), and a crosslinking promoter (mixture of N-t-butyl-2-benzothiazole sulphenamide (trade name "Nocceler NS,"

manufactured by Ouchi Shinko Chemical Industrial Co., Ltd. (1.7 parts) and diphenylguanidine (trade name "Nocceler D," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd. (2.0 parts)) by means of an open roll mill at 50°C, and then a sheet-form rubber composition was discharged therefrom. [0073]

The rubber composition was press-crosslinked at 160°C for 20 minutes, to thereby prepare a test piece. The test piece was evaluated for tensile strength, wet grip property, and low-heat-generating property as described below. The results are shown in Table 4.

(i) Tensile strength: The vulcanized rubber was used as a sample for measurement. A tensile test was performed according to JIS K6251 by use of a dumbbell-shaped No. 3 test piece, to thereby determine a rupture strength. A higher rupture strength indicates a higher tensile strength of the vulcanized rubber.

(ii) Wet grip property: The vulcanized rubber was used as a sample for measurement. An impact resilience test was performed according to JIS K6255 by use of a test piece having a diameter of 29.0 mm and a thickness of 12.5 mm, to thereby determine an impact resilience at 0°C. The impact resilience was indicated by an index relative to that (taken as 100) of the sample (standard) of Comparative Example 2-1. A higher index indicates superior wet grip property of a tire produced from the vulcanized rubber.

(iii) Low-heat-generating property: The vulcanized

rubber was used as a sample for measurement. A test piece having a length of 50 mm, a width of 12.7 mm, and a thickness of 2 mm was tested by means of ARES (manufactured by Rheometrics) under the following conditions (dynamic strain: 2.5%, 10 Hz), to thereby determine a $\tan\delta$ at 60°C. The $\tan\delta$ value was indicated by an index relative to that (taken as 100) of the sample (standard) of Comparative Example 2-1. A lower index indicates superior low-heat-generating property of a tire produced from the vulcanized rubber.

The results of evaluation of these properties are shown in Table 4.

[0074]

[Example 2-2 and Comparative Examples 2-1 to 2-4]

The procedure of Example 2-1 was repeated, except that the type and amount of a rubber component used were changed as shown in Table 4, to thereby prepare a rubber composition. The prepared rubber composition was vulcanized and evaluated for the aforementioned properties. The results of evaluation of the properties are shown in Table 4.

[0075]

[Table 4]

Evaluation of properties	Example 2-1	Example 2-2	Comparative Example 2-1	Comparative Example 2-2	Comparative Example 2-3	Comparative Example 2-4
Type of (modified) conjugated diene-based rubber	I	II	i	ii	iii	iv
Tensile strength	101	107	92	94	97	86
Wet grip property (INDEX)	103	102	100	103	105	102
Low-heat-generating property (INDEX)	92	95	100	99	97	112

[0076]

As shown in the aforementioned results, the modified conjugated diene-based rubbers I and II of the Examples achieved preparation of vulcanized rubbers exhibiting excellent tensile strength and low-heat-generating property, as compared with the modified (or unmodified) conjugated diene-based rubbers of the Comparative Examples. The vulcanized rubbers of the Examples exhibited wet grip property comparable to that of the vulcanized rubbers of the Comparative Examples.

These results demonstrated that a modified conjugated diene-based polymer including a monomer unit derived from at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) and having a terminal modified with the specific polyorganosiloxane can prepare a vulcanized rubber achieving well-balanced properties in terms of tensile strength, wet grip property, and low-heat-generating property.

CLAIMS

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

polymerizing a monomer group X containing at least one compound selected from the group consisting of a vinylsilane compound (A) and an aromatic vinyl compound (B) and a conjugated diene compound in the presence of a polymerization initiator, thereby preparing a polymer having an active terminal; and

reacting the polymer having the active terminal with a polyorganosiloxane (C), wherein

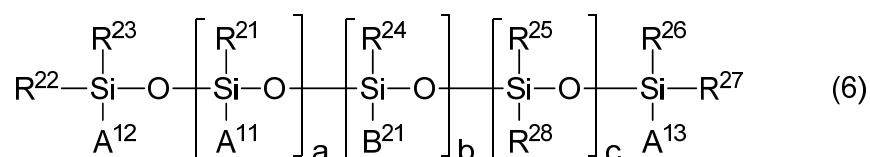
the vinylsilane compound (A) is a vinylsilane compound having a group $-\text{SiR}^1\text{R}^2\text{R}^3$, wherein R^1 represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen;

the aromatic vinyl compound (B) is an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom; and

the polyorganosiloxane (C) is 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 is two or more.

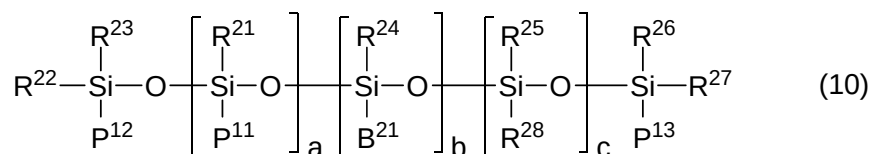
[Claim 2] The method for producing a modified conjugated diene-based polymer according to claim 1, wherein the polyorganosiloxane (C) is a compound represented by formula (6):



wherein R^{21} to R^{28} each represent a hydrocarbyl group; A^{11} represents a group having the specific functional group; A^{12} and A^{13} each represent a hydrocarbyl group or a group having the specific functional group; B^{21} 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^{21} to R^{28} , A^{11} , and B^{21} may be identical to or different from one another between structural units.

[Claim 3] The method for producing a modified conjugated diene-based polymer according to claim 1 or 2, wherein the monomer group X further contains an aromatic vinyl compound having none of a nitrogen atom, a phosphorus atom, and a sulfur atom.

[Claim 4] A modified conjugated diene-based polymer represented by formula (10):



wherein R^{21} to R^{28} each represent a hydrocarbyl group; P^{11} represents a group 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, or a conjugated diene-based polymer chain having a monomer unit derived from at least one compound selected from the group consisting of a vinylsilane compound (A) and an aromatic vinyl compound (B) and a monomer unit derived from a conjugated diene compound; P^{12} and P^{13} each represent the group having the specific functional group, the conjugated diene-based polymer chain, or a hydrocarbyl group; B^{21} 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; R^{21} to R^{28} , P^{11} , and B^{21} may be identical to or different from one another between structural units; and the number of the conjugated diene-based polymer chains present in the molecule is two or more, wherein

the vinylsilane compound (A) is a vinylsilane compound having a group " $-\text{SiR}^1\text{R}^2\text{R}^3$ ", wherein R^1 represents a monovalent group having at least one atom selected from the group

consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen; and

the aromatic vinyl compound (B) is an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom.

[Claim 5] A modified conjugated diene-based polymer produced by polymerizing a monomer group X containing at least one compound selected from the group consisting of a vinylsilane compound (A) and an aromatic vinyl compound (B) and a conjugated diene compound in the presence of a polymerization initiator to thereby prepare a polymer having an active terminal, and reacting the polymer having the active terminal with a polyorganosiloxane (C), wherein

the vinylsilane compound (A) is a vinylsilane compound having a group $-\text{SiR}^1\text{R}^2\text{R}^3$, wherein R^1 represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group

consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen;

the aromatic vinyl compound (B) is an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom; and

the polyorganosiloxane (C) is 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 is two or more.

[Claim 6] A polymer composition comprising a modified conjugated diene-based polymer produced by a method according to any one of claims 1 to 3 or a modified conjugated diene-based polymer according to claim 4 or 5, an inorganic filler, and a crosslinking agent.

[Claim 7] A crosslinked polymer produced through crosslinking of a polymer composition according to claim 6.

[Claim 8] A tire obtained by employing a crosslinked polymer according to claim 7 as a tread material, a sidewall material, or both.