

DESCRIPTION

CONJUGATED DIENE-BASED POLYMER AND RUBBER COMPOSITION COMPRISING THE SAME

5

TECHNICAL FIELD

[0001] [Cross-reference to Related Applications]

[0002] The present application claims the benefit of priority
based on Korean Patent Application No. 10-2020-0153156, filed
10 on November 16, 2020, the entire contents of which are
incorporated herein by reference.

[0003] [Technical Field]

[0004] The present invention relates to a conjugated diene-
based polymer which has excellent wet skid resistance and
15 abrasion resistance in a balanced way, and a rubber composition
comprising the same.

BACKGROUND ART

[0005] According to the recent demand for cars having a low
20 fuel consumption ratio, a conjugated diene-based polymer
having modulational stability represented by wet skid
resistance as well as low running resistance, and excellent
abrasion resistance and tensile properties is required as a
rubber material for tires.

25 [0006] In order to reduce the running resistance of tires,

there is a method of reducing hysteresis loss of vulcanized rubber, and rebound resilience at 50°C to 80°C, $\tan \delta$, Goodrich heating, or the like is used as an evaluation index of the vulcanized rubber. That is, it is desirable to use a rubber material having high rebound resilience at the above temperature or a low $\tan \delta$, Goodrich heating.

[0007] Natural rubbers, polyisoprene rubbers, or polybutadiene rubbers are known as rubber materials having low hysteresis loss, but these rubbers have a limitation of low wet skid resistance. Thus, recently, conjugated diene-based polymers or copolymers such as styrene-butadiene rubbers (hereinafter, referred to as "SBR") and butadiene rubbers (hereinafter, referred to as "BR"), are prepared by emulsion polymerization or solution polymerization to be used as rubbers for tires. Among these polymerization methods, the greatest advantage of the solution polymerization in comparison to the emulsion polymerization is that the vinyl structure content and the styrene content, which specify physical properties of the rubber, may be arbitrarily adjusted and its molecular weight and physical properties may be controlled by coupling or modification. Thus, the SBR prepared by the solution polymerization is widely used as a rubber material for tires because it is easy to change a structure of the finally prepared SBR or BR, and movement of chain terminals may be reduced and a coupling force with a filler such as silica and

carbon black may be increased by coupling or modification of the chain terminals.

[0008] The solution-polymerized SBR is prepared by using an anionic polymerization initiator and is being used by coupling
5 or modifying the chain terminals of the polymer thus formed using various modifiers. For example, U.S. Patent No. 4,397,994 discloses a method of coupling active anions of the chain terminals of a polymer obtained by polymerizing styrene-butadiene using alkyllithium which is a monofunctional
10 initiator in a non-polar solvent, using a coupling agent such as a tin compound.

[0009] In addition, if the solution-polymerized SBR is used as a rubber material, physical properties required for tires such as running resistance may be controlled by increasing the
15 vinyl content in the SBR, but if the vinyl content is high, braking performance and abrasion resistance tend to become unfavorable, and accordingly, the styrene content in the SBR is required to a certain level or higher, but in this case, effects expressed by the high vinyl content may not be shown.

[0010] Due to such problems, attempts for improving running
20 resistance and wet skid resistance in a balanced way have been made using block copolymer SBR including two block copolymer units which have styrene and vinyl content gradients by using the solution-polymerized SBR, but the improvement was just
25 insignificant, and in the case of applying SBR having a low

glass transition temperature to improve abrasion resistance,
wet skid resistance tends to get worse.

[0011] Accordingly, it is necessary to develop a polymer that
may improve wet skid resistance and abrasion resistance
5 simultaneously, in a state basically satisfying the required
performance of products on tensile properties and fuel
consumption properties.

[0012] [Prior Art Document]

[0013] (Patent Document 1) US 4,397,994 A (1983. 08. 09.)

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DISCLOSURE OF THE INVENTION

TECHNICAL PROBLEM

[0014] The present invention has been devised to solve the
above-mentioned problems of the related arts, and an object is
15 to provide a conjugated diene-based polymer having a specific
tan δ peak through controlling the microstructure of the
polymer to accomplish tires having improved properties of wet
skid resistance and abrasion resistance in a balanced way in
a state of maintaining excellent tensile properties and fuel
20 consumption properties.

[0015] In addition, another object of the present invention
is to provide a modified conjugated diene-based polymer having
improved abrasion resistance and wet skid resistance through
controlling the microstructure of the polymer itself, and
25 additionally having even further improved fuel consumption

properties and processability through the introduction of a modifier.

[0016] In addition, the present invention provides a rubber composition including the conjugated diene-based polymer
5 and/or modified conjugated diene-based polymer.

TECHNICAL SOLUTION

[0017] To solve the above-described tasks, according to an embodiment of the present invention, there is provided a
10 conjugated diene-based polymer comprising a repeating unit derived from a conjugated diene-based monomer, wherein, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), a full width at half maximum (FWHM)
15 value of a $\tan \delta$ peak shown in a temperature range of -100°C to 100°C is 20°C or higher, and the Advanced Rheometric Expansion System is measured using a dynamic mechanical analyzer with a torsional mode under conditions of a frequency of 10 Hz, a strain of 0.5%, and a temperature rise rate of
20 $5^{\circ}\text{C}/\text{min}$.

[0018] In addition, the present invention provides a rubber composition comprising the conjugated diene-based polymer and a filler.

ADVANTAGEOUS EFFECTS

[0019] The conjugated diene-based polymer according to the present invention may improve wet skid resistance in a state maintaining abrasion resistance excellent even with a low glass transition temperature, by controlling the microstructure of the polymer.

[0020] In addition, since the conjugated diene-based polymer according to the present invention may achieve abrasion resistance and wet skid resistance through controlling the microstructure by additionally introducing a modifier, excellent processability and fuel consumption properties as well as tensile properties could be achieved through an alkoxysilane-based modifier and the control of the degree of branching, separately from the microstructure of the polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] The accompanying drawings in the present disclosure illustrate particular embodiments of the present invention and are included together with the above description to provide a further understanding of the inventive concept. The inventive concept, however, should not be construed as limited to the accompanying drawings.

[0022] FIG. 1 is an embodiment of a stress change graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES).

BEST MODE FOR CARRYING OUT THE INVENTION

[0023] Hereinafter, the present invention will be described in more detail in order to assist the understanding of the present invention.

[0024] It will be understood that words or terms used in the description and claims of the present invention shall not be interpreted as the meaning defined in commonly used dictionaries. It will be further understood that the words or terms should be interpreted as having a meaning that is consistent with their meaning of the technical idea of the invention, based on the principle that an inventor may properly define the meaning of the words or terms to best explain the invention.

[0025] Definition

[0026] The term "polymer" as used in the present disclosure refers to a polymer compound prepared by polymerizing monomers, irrespective of the same or different types. Like this, a general term polymer covers the term homopolymer which is generally used to refer to a polymer prepared from one type of a monomer, and the term copolymer which is regulated below.

[0027] The term "copolymer" as used in the present disclosure refers to a polymer prepared by polymerizing at least two different types of monomers. Like this, a general term

copolymer refers to a polymer prepared from two different types of monomers and includes a generally used binary copolymer and a polymer prepared from two or more different types of monomers.

[0028] In the present disclosure, the term "1,2-vinyl bond content" refers to the mass(or weight) percent of butadiene contained at 1,2-positions in a polymer chain of a polymer based on the portion derived from a conjugated diene-based monomer (butadiene, etc.) (the total amount of polymerized butadiene) in a polymer.

[0029] In the present disclosure, the term "styrene bond content" refers to the mass (or weight) percent of styrene contained in a polymer chain of a polymer derived from an aromatic vinyl-based monomer (styrene, etc.) in a polymer.

[0030] In the present disclosure, the term "room temperature" means a temperature in a natural state without heating or cooling, and is a temperature of $20\pm 5^{\circ}\text{C}$.

[0031] In the present disclosure, the term "substituted" may mean that hydrogen of a functional group, an atomic group or a compound is substituted with a specific substituent, and if the hydrogen of a functional group, an atomic group or a compound is substituted with a specific substituent, one or a plurality including two or more substituents may be present according to the number of hydrogen present in the functional group, the atomic group or the compound, and if there are a plurality of substituents, each substituent may be the same or

different.

[0032] In the present disclosure, the term "alkyl group" may mean monovalent aliphatic saturated hydrocarbon, and may include a linear alkyl group such as methyl, ethyl, propyl and butyl; a branched alkyl group such as isopropyl, sec-butyl, tert-butyl and neo-pentyl; and cyclic saturated hydrocarbon, or cyclic unsaturated hydrocarbon including one or two or more unsaturated bonds.

[0033] In the present disclosure, the term "alkylene group" may mean divalent aliphatic saturated hydrocarbon such as methylene, ethylene, propylene and butylene.

[0034] In the present invention, the term "cycloalkyl group" may mean cyclic saturated hydrocarbon.

[0035] In the present disclosure, the term "aryl group" may mean aromatic hydrocarbon, and may include both monocyclic aromatic hydrocarbon in which one ring is formed, and polycyclic aromatic hydrocarbon in which two or more rings are bonded.

[0036] In the present disclosure, the term "aralkyl group" is also referred to as aralkyl and may mean the combination of an alkyl group and an aryl group, formed by substituting a hydrogen atom bonded to carbon constituting an alkyl group with an aryl group.

[0037] In the present disclosure, the term "single bond" may mean a single covalent bond itself excluding a separate atomic

or molecular group.

[0038] In the present disclosure, the terms "derived unit", "derived repeating unit" and "derived functional group" may mean a component or a structure comes from a certain material, or the material itself.

[0039] In the present disclosure, the terms "comprising", and "having" and the derivatives thereof, though these terms are particularly disclosed or not, do not intended to preclude the presence of optional additional components, steps, or processes. In order to avoid any uncertainty, all compositions claimed by using the term "comprising" may include optional additional additives, auxiliaries, or compounds, including a polymer or any other materials, unless otherwise described to the contrary. In contrast, the term "consisting essentially of ~" excludes unnecessary ones for operation and precludes optional other components, steps or processes from the scope of optional continuous description. The term "consisting of ~" precludes optional components, steps or processes, which are not particularly described or illustrated.

[0040] **Measurement methods and conditions**

[0041] In the present disclosure, the "1,2-vinyl bond content" and "styrene bond content" are the vinyl content and the styrene content in a polymer unit, measured and analyzed using Varian VNMRs 500 MHz NMR. For the NMR measurement, 1,1,2,2-

tetrachloroethane was used as a solvent, 6.0 ppm was calculated as a solvent peak, and the 1,2-vinyl content and the styrene bond content in total polymer were respectively calculated and measured considering the peaks of 7.2-6.9 ppm as random styrene, 6.9-6.2 ppm as block styrene, 5.8-5.1 ppm as 1,4-vinyl and 1,2-vinyl, and 5.1-4.5 ppm as 1,2-vinyl.

[0042] In the present disclosure, a "weight average molecular weight (Mw), a "number average molecular weight (Mn)", "molecular weight distribution (MWD)" and "unimodal properties" were obtained by measuring a weight average molecular weight (Mw) and a number average molecular weight (Mn) by gel permeation chromatograph (GPC) (PL GPC220, Agilent Technologies), obtaining a molecular weight distribution curve, and calculating molecular weight distribution (PDI, MWD, Mw/Mn) from each of the molecular weights measured.

[0043] - Column: using two of PLgel Olexis (Polymer Laboratories Co.) and one of PLgel mixed-C (Polymer Laboratories Co.) in combination

[0044] - Solvent: using a mixture of tetrahydrofuran and 2 wt% of an amine compound

[0045] - Flow rate: 1 ml/min

[0046] - Specimen concentration: 1-2 mg/ml (diluted in THF)

[0047] - Injection amount: 100 μ l

[0048] - Column temperature: 40°C

[0049] - Detector: Refractive index

[0050] - Standard: Polystyrene (calibrated by cubic function)

[0051] In the present disclosure, "glass transition temperature (T_g)" is obtained based on ISO 22768:2006 using a differential scanning calorimetry (DSCQ100, TA Co.). Under
5 the circulation of nitrogen in a rate of 50 ml/min, a differential scanning calorimetry (DSC) curve is recorded while elevating the temperature from -100°C in a rate of 20°C/min, and the peak top (inflection point) of the DSC differential curve is regarded as the glass transition
10 temperature.

[0052] In the present disclosure, a "tan δ peak" is a peak shown in a tan δ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), and is measured using a
15 dynamic mechanical analyzer (TA Co., ARES-G2) with a torsional mode under conditions of a frequency of 10 Hz, a strain of 0.5%, a temperature rise rate of 5°C/min.

[0053] In the present disclosure, the "Si content" was measured by an ICP analysis method using an inductively coupled
20 plasma optical emission spectroscopy (ICP-OES; Optima 7300DV), and by using the inductively coupled plasma optical emission spectroscopy, measurement was performed by adding about 0.7 g of a specimen to a platinum (Pt) crucible, adding about 1 mL of concentrated sulfuric acid (98 wt%, electronic grade)
25 thereto, heating at 300°C for 3 hours, incinerating the

specimen in an electrical furnace (Thermo Scientific, Lindberg Blue M) by the following program of steps 1 to 3:

[0054] 1) step 1: initial temp 0°C, rate (temp/hr) 180°C/hr, temp (holdtime) 180°C (1hr),

5 **[0055]** 2) step 2: initial temp 180°C, rate (temp/hr) 85°C/hr, temp (holdtime) 370°C (2hr), and

[0056] 3) step 3: initial temp 370°C, rate (temp/hr) 47°C/hr, temp (holdtime) 510°C (3hr),

[0057] adding 1 mL of concentrated nitric acid (48 wt%) and
10 20 µl of concentrated hydrofluoric acid (50 wt%) to a residue, sealing the platinum crucible and shaking for 30 minutes or more, adding 1 mL of boric acid to the specimen, storing at 0°C for 2 hours or more, diluting in 30 ml ultrapure water, and performing incineration.

15 **[0058]** In the present disclosure, the "N content" may be measured through an NSX analysis method, and measurement by the NSX analysis method may use a quantitative analyzer of a trace amount of nitrogen (NSX-2100H). Particularly, the quantitative analyzer of a trace amount of nitrogen (Auto
20 sampler, Horizontal furnace, PMT & Nitrogen detector) was turned on, carrier gas flow amounts were set to 250 ml/min for Ar, 350 ml/min for O₂, and 300 ml/min for ozonizer, a heater was set to 800°C, and the analyzer was stood for about 3 hours for stabilization. After stabilizing the analyzer, a
25 calibration curve with calibration curve ranges of 5 ppm, 10

ppm, 50 ppm, 100 ppm and 500 ppm was made using Nitrogen standard (AccuStandard S-22750-01-5 ml), an area corresponding to each concentration was obtained, and then, by using the ratios of concentrations to areas, a straight line was made.

5 After that, a ceramic boat holding 20 mg of a specimen was put in the auto sampler of the analyzer and measurement was conducted to obtain an area. By using the area of the specimen thus obtained and the calibration curve, the N content was calculated.

10 **[0059]** In this case, the specimen used in the NSX analysis method may be a modified conjugated diene-based polymer from which solvents are removed by putting the specimen in hot water heated by steam and stirring, and may be a specimen from which remaining monomer and remaining modifier are removed. In
15 addition, if oil was added to the specimen, the specimen may be one from which oil was extracted (removed).

[0060] Conjugated diene-based polymer

[0061] The conjugated diene-based polymer according to the
20 present invention is characterized in including a repeating unit derived from a conjugated diene-based monomer, wherein, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), a full width at half maximum (FWHM)
25 value of a $\tan \delta$ peak shown in a temperature range of -100°C

to 100°C is 20°C or higher, and the Advanced Rheometric Expansion System is measured using a dynamic mechanical analyzer with a torsional mode under conditions of a frequency of 10 Hz, a strain of 0.5%, and a temperature rise rate of 5°C/min.

[0062] According to an embodiment of the present invention, since the conjugated diene-based polymer achieved a polymer having a specific structure through the application of a specific preparation method, which will be explained later, the dynamic viscoelasticity behavior may be controlled to have a specific $\tan \delta$ peak, and through this, tensile properties may become excellent, and wet skid resistance and abrasion resistance may be excellent in a balanced way.

[0063] Dynamic viscoelasticity behavior of polymer

[0064] According to an embodiment of the present invention, the conjugated diene-based polymer is characterized in having a full width at half maximum (FWHM) value of a $\tan \delta$ peak shown in a temperature range of -100°C to 100°C of 20°C or higher, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES).

[0065] In the case of a polymer which is prepared by a general polymerization method and the microstructure thereof is not controlled, the two or more $\tan \delta$ peaks are shown, or the width

of a peak is formed very narrow, and the width of a peak formed is not wide. This may be related to the glass transition temperature, and in the case where units are partitioned in a polymer as in a block copolymer, and there is a glass transition temperature difference between the blocks, the $\tan \delta$ peak may have a narrow width and two or more peaks may be shown. In addition, in the case of a random copolymer, if the vinyl content or styrene content in a final polymer is controlled without fine control of the microstructure, the width of a peak is generally shown very narrow.

[0066] In this case, the glass transition temperature may be the same for both the block copolymer and the random copolymer, but there is a large difference in wet skid resistance, and to solve such defects, there have been efforts to improve the wet skid resistance while reducing the change of the glass transition temperature. However, if the glass transition temperature changes, there are problems in that abrasion resistance changes, and basic physical properties of the polymer change, and the task of achieving a polymer having improved performance is still present. That is, the adjustment of balance between abrasion resistance and wet skid resistance is difficult and remains as a difficult task to solve considering that these two properties are hard to improve through a modification process. However, the conjugated diene-based polymer according to an embodiment of the present

invention is prepared by a preparation method controlling the microstructure of the polymer, and though having the same glass transition temperature as that of the conventional modified conjugated diene-based polymer, a specific $\tan \delta$ peak may be shown, and improving effects of the wet skid resistance and abrasion resistance simultaneously, may be achieved.

[0067] In this case, the $\tan \delta$ peak is characterized in being shown in a temperature range of -100°C to 100°C , and the full width at half maximum of the $\tan \delta$ peak is 20°C or higher, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES). The number of the $\tan \delta$ peaks shown in the temperature range may be commonly one, or two or more, and in the case of showing two or more peaks, it may mean that the full width at half maximum of one peak among multiple peaks is 20°C or higher.

[0068] The full width at half maximum of the $\tan \delta$ peak may be 20°C or higher, preferably, 25°C or higher, more preferably, 30°C or higher. In addition, the full width at half maximum may be 80°C to the maximum, preferably, 70°C or less. If the full width at half maximum is less than 20°C , there arise defects of markedly reducing wet skid resistance at the same glass transition temperature, and it is unlikely to achieve a case where the full width at half maximum of the peak is greater than 80°C , but though achieved, phase separation may

occur, defects of increasing hysteresis at a high temperature may be inevitably accompanied, and there may arise defects of degrading fuel consumption properties.

5 **[0069]** In addition, the $\tan \delta$ peak may be shown at -100°C to 100°C , preferably, -80°C to 20°C , more preferably, -70°C to 0°C . If the peak is shown within the range, more favorable effects of abrasion resistance may be expected.

10 **[0070]** Dynamic viscoelasticity analysis by the Advanced Rheometric Expansion System corresponds to measuring $\tan \delta$ in accordance with temperature in a temperature range of -100°C to 100°C using a dynamic mechanical analyzer (TA Co., ARES-G2) with a torsional mode under a frequency of 10 Hz, a strain of 0.5%, and a temperature rise rate of $5^{\circ}\text{C}/\text{min}$, and in this case, a graph derived is a $\tan \delta$ value with respect to temperature.

15

[0071] Repeating unit derived from monomer

20 **[0072]** According to an embodiment of the present invention, the conjugated diene-based polymer has a repeating unit derived from a conjugated diene-based monomer as a main unit, and the conjugated diene-based monomer may be, for example, one or more selected from the group consisting of 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, piperylene, 3-butyl-1,3-octadiene, isoprene, 2-phenyl-1,3-butadiene and 2-halo-1,3-butadiene (halo means a halogen atom).

25 **[0073]** In addition, the conjugated diene-based polymer

additionally includes an aromatic vinyl-based monomer in addition to the conjugated diene-based monomer and may further include a repeating unit derived therefrom, and the aromatic vinyl-based monomer may be, for example, one or more selected from the group consisting of styrene, α -methylstyrene, 3-methylstyrene, 4-methylstyrene, 4-propylstyrene, 1-vinylnaphthalene, 4-cyclohexylstyrene, 4-(p-methylphenyl)styrene, 1-vinyl-5-hexylnaphthalene, 3-(2-pyrrolidino ethyl)styrene, 4-(2-pyrrolidino ethyl)styrene and 3-(2-pyrrolidino-1-methyl ethyl)- α -methylstyrene.

[0074] In another embodiment, the conjugated diene-based polymer may be a copolymer further including a repeating unit derived from a diene-based monomer of 1 to 10 carbon atoms together with the repeating unit derived from the conjugated diene-based monomer. The repeating unit derived from a diene-based monomer may be a repeating unit derived from a diene-based monomer which is different from the conjugated diene-based monomer, and the diene-based monomer which is different from the conjugated diene-based monomer may be, for example, 1,2-butadiene. If the conjugated diene-based polymer is a copolymer further including a diene-based monomer, the conjugated diene-based polymer may include a repeating unit derived from the diene-based monomer in greater than 0 wt% to 1 wt%, greater than 0 wt% to 0.1 wt%, greater than 0 wt% to 0.01 wt%, or greater than 0 wt% to 0.001 wt%, and within this

range, effects of preventing gel formation may be achieved.

[0075] According to an embodiment of the present invention, if two or more monomers are included in the chain of the conjugated diene-based polymer, a chain structure of a middle
5 type of a random copolymer and a block copolymer may be formed, and in this case, the control of microstructure may be easy, and excellent effects of balance among physical properties may be achieved. The random copolymer may mean arrangement of repeating units forming the copolymer in disorder.

10

[0076] Glass transition temperature of polymer

[0077] According to an embodiment of the present invention, the glass transition temperature of the modified conjugated diene-based polymer may be -100°C to 20°C . The glass
15 transition temperature is a value changing according to the microstructure of the polymer, but in order to improve abrasion resistance, the polymer is preferably prepared to satisfy the range, more preferably, -100°C to 0°C , more preferably, -90°C to -10°C , further more preferably, -80°C to -20°C .

20 **[0078]** The glass transition temperature may be flexibly controlled by the bonding method of the conjugated diene-based monomer in a polymer unit (1,2-bond or 1,4-bond), the presence or absence of a repeating unit derived from an aromatic vinyl-based monomer, the content of the repeating unit derived from
25 an aromatic vinyl-based monomer, and the microstructure in

each unit (1,2-vinyl bond content and styrene bond content) according to polymerization methods and polymerization conditions.

[0079] For example, the conjugated diene-based polymer may include the repeating unit derived from an aromatic vinyl-based monomer in 0 wt% to 50 wt%, particularly, 0 wt% to 45 wt%, preferably, 0 wt% to 30 wt%, and here, the inclusion of 0 wt% of the repeating unit derived from an aromatic vinyl-based monomer means that the repeating unit derived from an aromatic vinyl-based monomer is not included, and the polymer is composed of only the conjugated diene-based monomer. In addition, the 1,2-vinyl bond content may be 10 parts by weight to 80 parts by weight, preferably, 20 to 60 parts by weight, more preferably, 20 to 50 parts by weight with respect to 100 parts by weight of the modified conjugated diene-based polymer. If the microstructure is controlled like this, the improvement of abrasion resistance and wet skid resistance in a balanced way may be expected, with excellent tensile properties and fuel consumption properties.

[0080] Modified conjugated diene-based polymer

[0081] According to an embodiment of the present invention, there is provided a modified conjugated diene-based polymer including a repeating unit derived from a conjugated diene-based monomer and a functional group derived from a modifier,

wherein, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), a full width at half maximum (FWHM) value of a $\tan \delta$ peak shown in a temperature
5 range of -100°C to 100°C is 20°C or higher, and the Advanced Rheometric Expansion System is measured using a dynamic mechanical analyzer with a torsional mode under conditions of a frequency of 10 Hz, a strain of 0.5%, and a temperature rise rate of $5^{\circ}\text{C}/\text{min}$.

10 **[0082]** The explanation on the $\tan \delta$ peak has been provided in the aforementioned conjugated diene-based polymer, and the explanation thereon will be omitted.

[0083] Si and N contents of polymer

15 **[0084]** Meanwhile, the modified conjugated diene-based polymer according to an embodiment of the present invention may have the Si and N contents of 50 ppm or more, or 50 ppm to 1000 ppm each, based on the total weight of the polymer. The lower limit may preferably be 100 ppm or more, and 150 ppm or more
20 each, and the upper limit may preferably be 700 ppm or less, preferably, 500 ppm or less each. Within these ranges, the mechanical properties such as tensile properties and viscoelasticity properties of a rubber composition including the modified conjugated diene-based polymer may be excellent.
25 Meanwhile, since a compound having a modification functional

group such as a modifier which will be explained later, a modification initiator and a modification monomer is introduced, the Si and N may be derived therefrom.

5 **[0085]** Alkoxysilane-based modifier

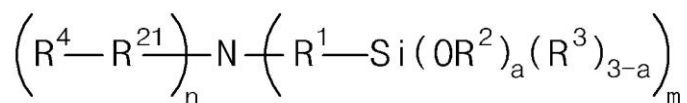
[0086] According to an embodiment of the present invention, the modified conjugated diene-based polymer includes a functional group derived from a modifier, and the modifier is for modifying the terminals of a polymer, and particularly,
10 may be an alkoxysilane-based modifier as a modifier having affinity with silica. The modifier having affinity with silica may mean a modifier containing a functional group having affinity with silica in a compound used as the modifier, and the functional group having affinity with silica may mean a
15 functional group having excellent affinity with a filler, particularly, a silica-based filler, and is capable of making interaction between the silica-based filler and the functional group derived from the modifier.

[0087] The modifier may be an alkoxysilane-based modifier,
20 particularly, an alkoxysilane-based modifier containing one or more heteroatoms including a nitrogen atom, an oxygen atom, and a sulfur atom. If the alkoxysilane-based compound is used as a modifier, through substitution reaction between an anionic active part positioned at one terminal of an active polymer
25 and an alkoxy group of the alkoxysilane-based modifier, the

one terminal of the active polymer may be modified into a bonding state with a silyl group, and accordingly, the affinity with an inorganic filler of the modified conjugated diene-based polymer may be increased from the functional group derived from the modifier present at the one terminal of the polymer unit, and the viscoelasticity properties of a rubber composition including the modified conjugated diene-based polymer may be improved. Also, if the alkoxysilane-based compound contains a nitrogen atom, additional effects of improving physical properties due to the nitrogen atom may be anticipated in addition to the effects due to the silyl group. In order to embody such effects optimally, a compound including an N-containing functional group is preferably applied.

[0088] According to an embodiment of the present invention, the modifier may include a compound represented by Formula 1 below.

[0089] [Formula 1]



[0090] In Formula 1, R¹ may be a single bond, or an alkylene group of 1 to 10 carbon atoms, R² and R³ may be each independently an alkyl group of 1 to 10 carbon atoms, R⁴ may be hydrogen, an alkyl group of 1 to 10 carbon atoms, a divalent, trivalent, or tetravalent alkylsilyl group which is

substituted with an alkyl group of 1 to 10 carbon atoms, or a heterocycle of 2 to 10 carbon atoms, R^{21} may be a single bond, an alkylene group of 1 to 10 carbon atoms, or $-[R^{42}O]_j-$, where R^{42} may be an alkylene group of 1 to 10 carbon atoms, a and m may be each independently an integer selected from 1 to 3, n may be an integer of 0, 1 or 2, and j may be an integer selected from 1 to 30.

[0091] In a particular embodiment, in Formula 1, R^1 may be a single bond, or an alkylene group of 1 to 5 carbon atoms, R^2 and R^3 may be each independently hydrogen, or an alkyl group of 1 to 5 carbon atoms, R^4 may be hydrogen, an alkyl group of 1 to 5 carbon atoms, a tetravalent alkylsilyl group which is substituted with an alkyl group of 1 to 5 carbon atoms, or a heterocyclic group of 2 to 5 carbon atoms, R^{21} may be a single bond, an alkylene group of 1 to 5 carbon atoms, or $-[R^{42}O]_j-$, where R^{42} may be an alkylene group of 1 to 5 carbon atoms, a may be an integer of 2 or 3, m may be an integer selected from 1 to 3, n may be an integer of 0, 1 or 2, where $m+n=3$ may be satisfied, and j may be an integer selected from 1 to 10.

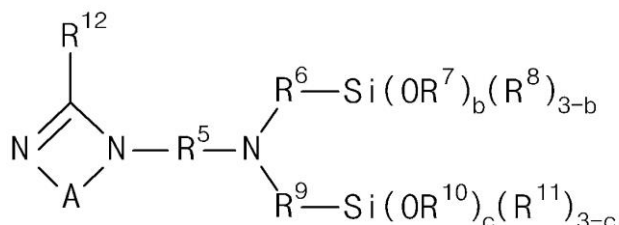
[0092] In Formula 1, if R^4 is a heterocyclic group, the heterocyclic group may be unsubstituted or substituted with a trisubstituted alkoxysilyl group, and if the heterocyclic group is substituted with a trisubstituted alkoxysilyl group, the trisubstituted alkoxysilyl group may be substituted via the connection with the heterocyclic group by an alkylene group

of 1 to 10 carbon atoms, and the trisubstituted alkoxy silyl group may mean an alkoxy silyl group which is substituted with an alkoxy group of 1 to 10 carbon atoms.

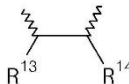
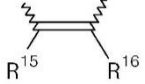
[0093] In a more particular embodiment, the compound
5 represented by Formula 1 may be one selected from the group
consisting of N,N-bis(3-(dimethoxy(methyl)silyl)propyl)-
methyl-1-amine, N,N-bis(3-(diethoxy(methyl)silyl)propyl)-
methyl-1-amine, N,N-bis(3-(trimethoxysilyl)propyl)-methyl-1-
amine, N,N-bis(3-(triethoxysilyl)propyl)-methyl-1-amine, N,N-
10 diethyl-3-(trimethoxysilyl)propan-1-amine, N,N-diethyl-3-
(triethoxysilyl)propan-1-amine, tri(trimethoxysilyl)amine,
tri(3-(trimethoxysilyl)propyl)amine, N,N-bis(3-
(diethoxy(methyl)silyl)propyl)-1,1,1-trimethylsilanamine,
N,N-bis(3-(1H-imidazol-1-yl)propyl)-(triethoxysilyl)methan-1-
15 amine, N-(3-(1H-1,2,4-triazole-1-yl)propyl)-3-
(trimethoxysilyl)-N-(3-trimethoxysilyl)propyl)propan-1-amine,
3-(trimethoxysilyl)-N-(3-(trimethoxysilyl)propyl)-N-(3-(1-(3-
(trimethoxysilyl)propyl)-1H-1,2,4-triazol-3-yl)propyl)propan-
1-amine, N,N-bis(2-(2-methoxyethoxy)ethyl)-3-
20 (triethoxysilyl)propan-1-amine, N,N-bis(3-
(triethoxysilyl)propyl)-2,5,8,11,14-pentaoxahexadecan-16-
amine, N-(2,5,8,11,14-pentaoxahexadecan-16-yl)-N-(3-
(triethoxysilyl)propyl)-2,5,8,11,14-pentaoxahexadecan-16-
amine and N-(3,6,9,12-tetraoxahexadecyl)-N-(3-
25 (triethoxysilyl)propyl)-3,6,9,12-tetraoxahexadecan-1-amine.

[0094] In another embodiment, the modifier may include a compound represented by Formula 2 below.

[0095] [Formula 2]



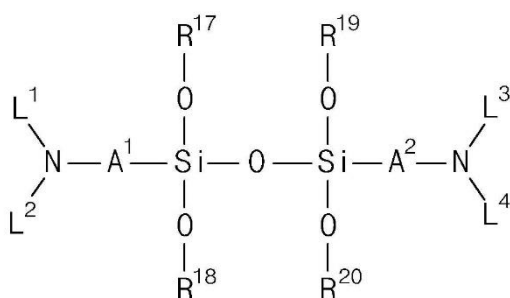
5 **[0096]** In Formula 2, R⁵, R⁶ and R⁹ may be each independently an alkylene group of 1 to 10 carbon atoms, R⁷, R⁸, R¹⁰ and R¹¹ may be each independently an alkyl group of 1 to 10 carbon atoms, R¹² may be hydrogen or an alkyl group of 1 to 10 carbon atoms, b and c may be each independently 0, 1, 2 or 3, where

10 b+c≥1 may be satisfied, and A may be  or , where R¹³, R¹⁴, R¹⁵ and R¹⁶ may be each independently hydrogen or an alkyl group of 1 to 10 carbon atoms.

[0097] In a particular embodiment, the compound represented by Formula 2 may be one selected from the group consisting of
 15 N-(3-(1H-imidazol-1-yl)propyl)-3-(triethoxysilyl)-N-(3-(triethoxysilyl)propyl)propan-1-amine and 3-(4,5-dihydro-1H-imidazol-1-yl)-N,N-bis(3-(triethoxysilyl)propyl)propan-1-amine.

[0098] In another embodiment, the modifier may include a
 20 compound represented by Formula 3 below.

[0099] [Formula 3]



[00100] In Formula 3, A¹ and A² may be each independently a divalent hydrocarbon group of 1 to 20 carbon atoms, which contains an oxygen atom or not, R¹⁷ to R²⁰ may be each independently a monovalent hydrocarbon group of 1 to 20 carbon atoms, L¹ to L⁴ may be each independently a divalent, trivalent, or tetravalent alkylsilyl group which is substituted with an alkyl group of 1 to 10 carbon atoms, or a monovalent hydrocarbon group of 1 to 20 carbon atoms, where L¹ and L², and L³ and L⁴ each may be combined with each other to form rings of 1 to 5 carbon atoms, and if L¹ and L², and L³ and L⁴ each are combined with each other to form rings, the rings thus formed may include one to three of one or more types of heteroatoms selected from the group consisting of N, O and S.

[00101] In a particular embodiment, in Formula 3, A¹ and A² may be each independently an alkylene group of 1 to 10 carbon atoms, R¹⁷ to R²⁰ may be each independently an alkyl group of 1 to 10 carbon atoms, L¹ to L⁴ may be each independently a tetravalent alkylsilyl group which is substituted with an alkyl group of

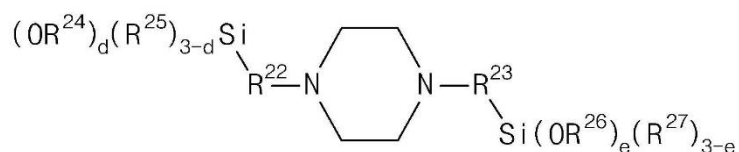
1 to 5 carbon atoms, or an alkyl group of 1 to 10 carbon atoms, where L¹ and L², and L³ and L⁴ each may be combined with each other to form rings of 1 to 3 carbon atoms, and if L¹ and L², and L³ and L⁴ each are combined with each other to form rings, the rings thus formed may include one to three of one or more types of heteroatoms selected from the group consisting of N, O and S.

[00102] In a more particular embodiment, the compound represented by Formula 3 may be one selected from the group consisting of 3,3'-(1,1,3,3-tetramethoxydisiloxane-1,3-diyl)bis(N,N-dimethylpropan-1-amine), 3,3'-(1,1,3,3-tetraethoxydisiloxane-1,3-diyl)bis(N,N-dimethylpropan-1-amine), 3,3'-(1,1,3,3-tetrapropoxydisiloxane-1,3-diyl)bis(N,N-dimethylpropan-1-amine), 3,3'-(1,1,3,3-tetramethoxydisiloxane-1,3-diyl)bis(N,N-diethylpropan-1-amine), 3,3'-(1,1,3,3-tetramethoxydisiloxane-1,3-diyl)bis(N,N-dipropylpropan-1-amine), 3,3'-(1,1,3,3-tetraethoxydisiloxane-1,3-diyl)bis(N,N-diethylpropan-1-amine), 3,3'-(1,1,3,3-tetrapropoxydisiloxane-1,3-diyl)bis(N,N-diethylpropan-1-amine), 3,3'-(1,1,3,3-tetraethoxydisiloxane-1,3-diyl)bis(N,N-dipropylpropan-1-amine), 3,3'-(1,1,3,3-tetrapropoxydisiloxane-1,3-diyl)bis(N,N-dipropylpropan-1-amine), 3,3'-(1,1,3,3-tetramethoxydisiloxane-1,3-diyl)bis(N,N-diethylmethan-1-amine), 3,3'-(1,1,3,3-tetraethoxydisiloxane-1,3-diyl)bis(N,N-diethylmethan-1-amine),

3,3'-(1,1,3,3-tetrapropoxydisiloxane-1,3-diyl)bis(N,N-
 diethylmethan-1-amine), 3,3'-(1,1,3,3-tetramethoxydisiloxane-
 1,3-diyl)bis(N,N-dimethylmethan-1-amine), 3,3'-(1,1,3,3-
 tetramethoxydisiloxane-1,3-diyl)bis(N,N-dipropylmethan-1-
 5 amine), 3,3'-(1,1,3,3-tetrapropoxydisiloxane-1,3-
 diyl)bis(N,N-dimethylmethan-1-amine), 3,3'-(1,1,3,3-
 tetrapropoxydisiloxane-1,3-diyl)bis(N,N-dipropylmethan-1-
 amine), 3,3'-(1,1,3,3-tetraethoxydisiloxane-1,3-diyl)bis(N,N-
 dimethylmethan-1-amine), 3,3'-(1,1,3,3-tetraethoxydisiloxane-
 10 1,3-diyl)bis(N,N-dipropylmethan-1-amine), N,N'-((1,1,3,3-
 tetramethoxydisiloxane-1,3-diyl)bis(propan-3,1-
 diyl))bis(1,1,1-trimethyl-N-(trimethylsilyl)silanamine, N,N'-
 ((1,1,3,3-tetraethoxydisiloxane-1,3-diyl)bis(propan-3,1-
 diyl))bis(1,1,1-trimethyl-N-(trimethylsilyl)silanamine, N,N'-
 15 ((1,1,3,3-tetrapropoxydisiloxane-1,3-diyl)bis(propan-3,1-
 diyl))bis(1,1,1-trimethyl-N-(trimethylsilyl)silanamine, N,N'-
 ((1,1,3,3-tetramethoxydisiloxane-1,3-diyl)bis(propan-3,1-
 diyl))bis(1,1,1-trimethyl-N-phenylsilanamine, N,N'-((1,1,3,3-
 tetraethoxydisiloxane-1,3-diyl)bis(propan-3,1-
 20 diyl))bis(1,1,1-trimethyl-N-phenylsilanamine, N,N'-((1,1,3,3-
 tetrapropoxydisiloxane-1,3-diyl)bis(propan-3,1-
 diyl))bis(1,1,1-trimethyl-N-phenylsilanamine, 1,3-bis(3-(1H-
 imidazol-1-yl)propyl)-1,1,3,3-tetramethoxydisiloxane, 1,3-
 bis(3-(1H-imidazol-1-yl)propyl)-1,1,3,3-tetraethoxydisiloxane,
 25 and 1,3-bis(3-(1H-imidazol-1-yl)propyl)-1,1,3,3-

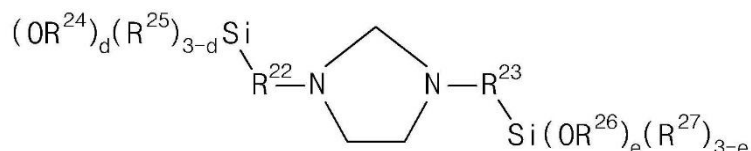
[00107] More particularly, the compound represented by Formula 4 may be a compound represented by Formula 4a, Formula 4b, or Formula 4c below.

[00108] [Formula 4a]

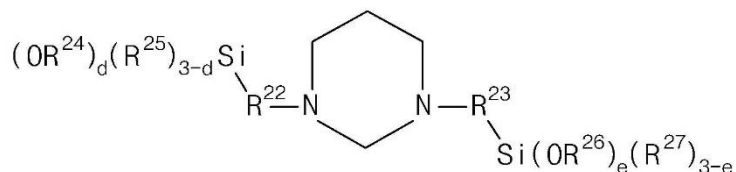


5

[00109] [Formula 4b]



[00110] [Formula 4c]



10 **[00111]** In Formula 4a, Formula 4b and Formula 4c, R^{22} to R^{27} , d and e are the same as described above.

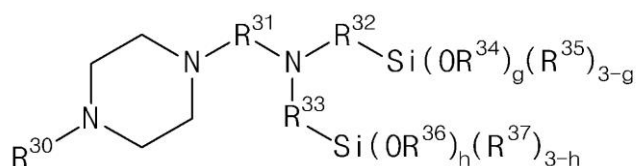
[00112] In a more particular embodiment, the compound represented by Formula 4 may be one selected from the group consisting of 1,4-bis(3-(3-

15 (triethoxysilyl)propoxy)propyl)piperazine, 1,4-bis(3-(triethoxysilyl)propyl)piperazine, 1,4-bis(3-(trimethoxysilyl)propyl)piperazine, 1,4-bis(3-

(dimethoxymethylsilyl)propyl)piperazine, 1-(3-
 (ethoxydimethylsilyl)propyl)-4-(3-
 (triethoxysilyl)propyl)piperazine, 1-(3-
 (ethoxydimethyl)propyl)-4-(3-
 5 (triethoxysilyl)methyl)piperazine, 1-(3-
 (ethoxydimethyl)methyl)-4-(3-
 (triethoxysilyl)propyl)piperazine, 1,3-bis(3-
 (triethoxysilyl)propyl)imidazolidine, 1,3-bis(3-
 (dimethoxyethylsilyl)propyl)imidazolidine, 1,3-bis(3-
 10 (trimethoxysilyl)propyl)hexahydropyrimidine, 1,3-bis(3-
 (triethoxysilyl)propyl)hexahydropyrimidine and 1,3-bis(3-
 (tributoxysilyl)propyl)-1,2,3,4-tetrahydropyrimidine.

[00113] In another embodiment, the modifier may include a compound represented by Formula 5 below.

15 **[00114]** [Formula 5]

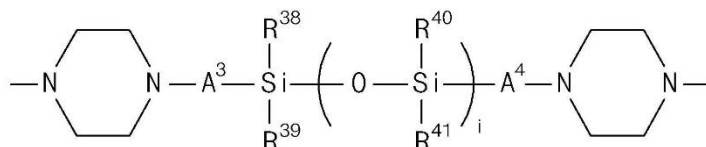


[00115] In Formula 5, R^{30} may be a monovalent hydrocarbon group of 1 to 30 carbon atoms, R^{31} to R^{33} may be each independently an alkylene group of 1 to 10 carbon atoms, R^{34} to R^{37} may be
 20 each independently an alkyl group of 1 to 10 carbon atoms, and
 g and h may be each independently 0 or an integer selected

from 1 to 3, where g+h may be an integer of 1 or more.

[00116] In another embodiment, the modifier may include a compound represented by Formula 6 below.

[00117] [Formula 6]



5

[00118] In Formula 6, A³ and A⁴ may be each independently an alkylene group of 1 to 10 carbon atoms, R³⁸ to R⁴¹ may be each independently an alkyl group of 1 to 10 carbon atoms, or an alkoxy group of 1 to 10 carbon atoms, and i may be an integer selected from 1 to 30.

10

[00119] In another embodiment, the modifier may include one or more selected from the group consisting of 3,4-bis(2-methoxyethoxy)-N-(4-(triethoxysilyl)butyl)aniline, N,N-diethyl-3-(7-methyl-3,6,8,11-tetraoxa-7-silatridecan-7-yl)propan-1-amine, 2,4-bis(2-methoxyethoxy)-6-((trimethylsilyl)methyl)-1,3,5-triazine and 3,14-dimethoxy-3,8,8,13-tetramethyl-2,14-dioxa-7,9-dithia-3,8,13-trisilapentadecane.

15

[00120] In another embodiment, the modifier may include a compound represented by Formula 7 below.

20

[00121] [Formula 7]



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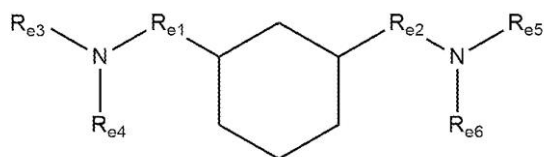
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35

[00126] In Formula 8, R_{b2} to R_{b4} are each independently an alkylene group of 1 to 10 carbon atoms, R_{b5} to R_{b8} are each independently an alkyl group of 1 to 10 carbon atoms, R_{b13} and R_{b14} are each independently an alkylene group of 1 to 10 carbon
5 atoms, R_{b15} to R_{b18} are each independently an alkyl group of 1 to 10 carbon atoms, and m_1 , m_2 , m_3 and m_4 are each independently an integer of 1 to 3.

[00127] In another embodiment, the modifier may include a compound represented by Formula 9 below.

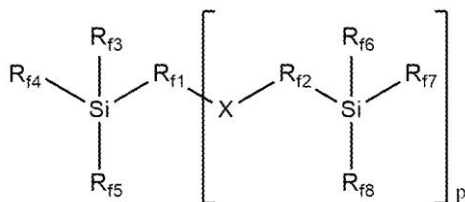
10 **[00128]** [Formula 9]



[00129] In Formula 9, R_{e1} and R_{e2} are each independently an alkylene group of 1 to 10 carbon atoms, R_{e3} to R_{e6} are each independently hydrogen, an alkyl group of 1 to 10 carbon atoms
15 or $-R_{e7}SiR_{e8}R_{e9}R_{e10}$, where at least one among R_{e3} to R_{e6} is $-R_{e7}SiR_{e8}R_{e9}R_{e10}$, wherein R_{e7} is a single bond or an alkylene group of 1 to 10 carbon atoms, R_{e8} to R_{e10} are each independently an alkyl group of 1 to 10 carbon atoms or an alkoxy group of 1 to 10 carbon atoms, where at least one among R_{e8} to R_{e10} is an
20 alkoxy group of 1 to 10 carbon atoms.

[00130] In another embodiment, the modifier may include a compound represented by Formula 10 below.

[00131] [Formula 10]

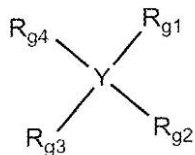


[00132] In Formula 10, X is O or S, R_{f1} and R_{f2} are each independently a single bond or an alkylene group of 1 to 10 carbon atoms,

[00133] R_{f3} to R_{f8} are each independently hydrogen, an alkyl group of 1 to 10 carbon atoms, an alkoxy group of 1 to 10 carbon atoms, an aryl group of 6 to 10 carbon atoms, a cycloalkyl group of 5 to 10 carbon atoms or an aralkyl group of 7 to 14 carbon atoms, and p is an integer of 0 or 1, where if p is 0, R_{f1} is an alkyl group of 1 to 10 carbon atoms or an alkoxy group of 1 to 10 carbon atoms.

[00134] In another embodiment, the modifier may include a compound represented by Formula 11 below.

[00135] [Formula 11]

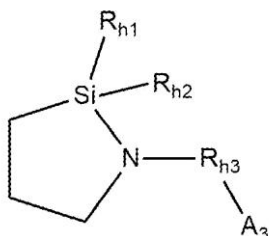


[00136] In Formula 11, R_{g1} to R_{g4} are each independently hydrogen, an alkyl group of 1 to 10 carbon atoms, an alkoxy group of 1 to 10 carbon atoms, an aryl group of 6 to 12 carbon

atoms or $-R_{g5}SiOR_{g6}$, where at least one among R_{g1} to R_{g4} is $-R_{g5}SiOR_{g6}$, wherein R_{g5} is a single bond or an alkylene group of 1 to 10 carbon atoms, R_{g6} is an alkyl group of 1 to 10 carbon atoms, and Y is C or N, where if Y is N, R_{g4} is not present.

5 **[00137]** In another embodiment, the modifier may include a compound represented by Formula 12 below.

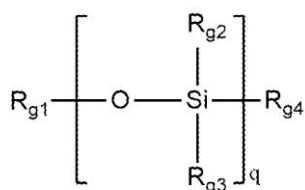
[00138] [Formula 12]



[00139] In Formula 12, R_{h1} and R_{h2} are each independently an
 10 alkyl group of 1 to 10 carbon atoms or an alkoxy group of 1 to 10 carbon atoms, R_{h3} is a single bond or an alkylene group of 1 to 10 carbon atoms, and A_3 is $-Si(R_{h4}R_{h5}R_{h6})$ or $-N[Si(R_{h7}R_{h8}R_{h9})]_2$, where R_{h4} to R_{h9} are each independently an alkyl group of 1 to 10 carbon atoms or an alkoxy group of 1 to 10 carbon atoms.

15 **[00140]** In another embodiment, the modifier may include a compound represented by Formula 13 below.

[00141] [Formula 13]



[00142] In Formula 13, R_{g1} to R_{g3} are each independently an

alkyl group of 1 to 10 carbon atoms or an alkoxy group of 1 to 10 carbon atoms, R_{q4} is an alkoxy group of 1 to 10 carbon atoms, and q is an integer of 2 to 100.

5 **[00143]** Shrink factor

[00144] The conjugated diene-based polymer according to an embodiment of the present invention has a shrink factor (g') obtained by the measurement by a gel permeation chromatography-light scattering method equipped with a viscosity detector of
10 0.1 or more, preferably, 0.1 to 1.0, more particularly, 0.3 to 0.9.

[00145] Here, the shrink factor (g') obtained through the measurement by the gel permeation chromatography-light scattering method is a ratio of the intrinsic viscosity of a
15 branched polymer with respect to the intrinsic viscosity of a linear polymer, which have the same absolute molecular weight, and may be used as the index of the branch structure of the branched polymer, that is, the index of the ratio occupied by branches. For example, according to the decrease of the shrink
20 factor, the number of branches of the corresponding polymer tends to increase, and accordingly, in case of comparing polymers having the same absolute molecular weight, the shrink factor decreases with the increase of the branches, and the shrink factor may be used as the index of the degree of
25 branching.

[00146] In addition, the shrink factor is obtained by measuring chromatogram using a gel chromatography-light scattering measurement apparatus equipped with a viscosity detector and computing based on a solution viscosity and a light scattering method, and particularly, absolute molecular weights and intrinsic viscosity corresponding to each absolute molecular weight were obtained using a GPC-light scattering measurement apparatus equipped with a light scattering detector in which two columns using a polystyrene-based gel as a filler are connected and a viscosity detector, the intrinsic viscosity of a linear polymer corresponding to the absolute molecular weight was computed, and the shrink factor was obtained as a ratio of intrinsic viscosity corresponding to each absolute molecular weight. For example, the shrink factor was shown by obtaining absolute molecular weights from a light scattering detector by injecting a specimen into a GPC-light scattering measurement apparatus (Viscotek TDMax, Malvern Co.) equipped with a light scattering detector and a viscosity detector, obtaining intrinsic viscosity $[\eta]$ on the absolute molecular weight from the light scattering detector and the viscosity detector, computing the intrinsic viscosity $[\eta]_0$ of a linear polymer on the absolute molecular weight through Mathematical Equation 1 below, and showing an average value of the ratio of intrinsic viscosities $([\eta]/[\eta]_0)$ corresponding to each absolute molecular weight as the shrink factor. In this case, a mixture

solution of tetrahydrofuran and N,N,N',N'-tetramethylethylenediamine (controlled by mixing 20 mL of N,N,N',N'-tetramethylethylenediamine with 1 L of tetrahydrofuran) was used as an eluent, PL Olexis (Agilent Co.)
5 was used as a column, measurement was conducted under conditions of an oven temperature of 40°C and a flow rate of 1.0 mL/min, and a specimen was prepared by dissolving 15 mg of a polymer in 10 mL of THF.

[00147] [Mathematical Equation 1]

10
$$[\eta]_0 = 10^{-3.883} M^{0.771}$$

[00148] In Mathematical Equation 1, M is an absolute molecular weight.

[00149] In addition, the modified conjugated diene-based
15 polymer may have the vinyl content of 5 wt% or more, 10 wt% or more, or 10 wt% to 60 wt%. Here, the vinyl content may mean the amount of not 1,4-added but 1,2-added conjugated diene-based monomer based on 100 wt% of a conjugated diene-based polymer composed of a monomer having a vinyl group and an
20 aromatic vinyl-based monomer.

[00150] Mooney stress relaxation ratio

[00151] In another embodiment, the modified conjugated diene-based polymer may have a Mooney stress relaxation ratio
25 measured at 100°C of less than 0.7, and may be 0.7 to 3.0.

Particularly, in case of a polymer of a branch type having a large degree of branching, the Mooney stress relaxation ratio may be less than 0.7, preferably, 0.6 or less, more preferably, 0.5 or less, optimally 0.4 or less, and in case of a linear
5 polymer having a small degree of branching, the Mooney stress relaxation ratio may preferably be 0.7 to 2.5, more preferably, 0.7 to 2.0.

[00152] Here, the Mooney stress relaxation ratio represents the stress change shown as the response to the same amount of
10 strain, and may be measured using a mooney viscometer. Particularly, the Mooney stress relaxation ratio was obtained using a large rotor of MV2000E of Monsanto Co. in conditions of 100°C and a rotor speed of 2 ± 0.02 rpm, by standing a polymer at room temperature ($23 \pm 5^\circ\text{C}$) for 30 minutes or more, collecting
15 27 ± 3 g of the polymer and putting in a die cavity, applying torque by operating a Platen and measuring mooney viscosity, and measuring the slope value of the change of the mooney viscosity shown while releasing torque.

[00153] Meanwhile, the Mooney stress relaxation ratio may be
20 used as the index of the branch structure of a corresponding polymer. For example, in case of comparing polymers having the same mooney viscosity, the Mooney stress relaxation ratio decreases with the increase of branching and may be used as the index of the degree of branching.

[00154] Other properties of polymer

[00155] The (modified) conjugated diene-based polymer according to an embodiment of the present invention may include a functional group derived from a modification initiator at the other terminal in addition to one terminal including a functional group derived from a modifier, and here, the modification initiator may be a reaction product of an N-functional group-containing compound and an organometallic compound.

[00156] Particularly, the N-functional group-containing compound may be substituted with a substituent or unsubstituted aromatic hydrocarbon compound including an N-functional group including an amino group, amide group, imidazole group, imidazole group, pyrimidyl group or cyclic amino group, and the substituent may be an alkyl group of 1 to 20 carbon atoms, a cycloalkyl group of 3 to 20 carbon atoms, an aryl group of 6 to 20 carbon atoms, an alkylaryl group of 7 to 20 carbon atoms, an arylalkyl group of 7 to 20 carbon atoms or an alkoxysilyl group of 1 to 10 carbon atoms.

[00157] According to an embodiment of the present invention, the (modified) conjugated diene-based polymer may have a weight average molecular weight (Mw) measured by gel permeation chromatography (GPC) of 300,000 g/mol to 3,000,000 g/mol, 400,000 g/mol to 2,500,000 g/mol, or 500,000 g/mol to 2,000,000 g/mol, and within this range, running resistance and wet skid

resistance may be excellent in a balanced way even better.

[00158] In addition, the (modified) conjugated diene-based polymer according to an embodiment of the present invention may be a polymer having a high molecular weight with a weight
5 average molecular weight of 800,000 g/mol or more, preferably, 1,000,000 g/mol or more, and accordingly, a polymer having excellent tensile properties may be achieved, and if prepared by the above-described preparation method, effects of extending the chain of a polymer long may be achieved together
10 with the control of microstructure.

[00159] The (modified) conjugated diene-based polymer may have a number average molecular weight (M_n) of 1,000 g/mol to 2,000,000 g/mol, 10,000 g/mol to 1,500,000 g/mol, or 100,000 g/mol to 1,200,000 g/mol, and the number average molecular
15 weight may preferably be 400,000 g/mol or more, more preferably, 500,000 g/mol or more. In addition, a peak top molecular weight (M_p) may be 1,000 g/mol to 3,000,000 g/mol, 10,000 g/mol to 2,000,000 g/mol, or 100,000 g/mol to 2,000,000 g/mol. Within these ranges, excellent effects of rolling resistance
20 and wet skid resistance may be achieved.

[00160] In addition, the (modified) conjugated diene-based polymer may have a unimodal molecular weight distribution curve by gel permeation chromatography (GPC) and molecular weight distribution of 1.0 to 3.0, preferably, 1.0 to 2.5, more
25 preferably, 1.0 to 2.0, further more preferably, 1.0 to less

than 1.7, and here, the unimodal curve shape and molecular weight distribution may be satisfied at the same time by a continuous type polymerization, which will be explained later.

[00161] Generally, there are problems in that, in a continuous-
5 type polymerization, molecular weight distribution shows unimodal and broad, and processability is excellent, but tensile and viscoelasticity properties are poor, and in a batch-type polymerization, molecular weight distribution shows bimodal and narrow, and tensile and viscoelasticity properties
10 are excellent, but processability is poor, and productivity is low. However, if applying a preparation method which will be explained later according to an embodiment of the present invention, the molecular weight distribution may be selectively reduced to the maximum though prepared by a
15 continuous-type, and accordingly, the control of the balance among physical properties such as processability, tensile properties and viscoelasticity properties may become easy.

[00162] In addition, the (modified) conjugated diene-based polymer according to an embodiment of the present invention is
20 required to satisfy the mooney viscosity measured under conditions of ASTM D1646 of 40 to 140, preferably, 45 to 120. The measure for evaluating processability may be a lot, but if the mooney viscosity satisfies the above-described range, processability may be significantly excellent.

25 **[00163]** The (modified) conjugated diene-based polymer

according to an embodiment of the present invention specifies a polymer structure so as to have a difference between glass transition initiation temperature and termination temperature through the control of the microstructure of the polymer, such as the aforementioned styrene bond content and 1,2-vinyl bond content, and through the selective control of a weight average molecular weight, a molecular weight distribution curve shape, molecular weight distribution, N and Si atom contents, and mooney viscosity, effects of improving abrasion resistance and wet skid resistance in a balanced way could be expected, while maintaining excellent tensile properties, fuel consumption properties and processability.

[00164] Preparation method of conjugated diene-based polymer

[00165] In order to prepare the conjugated diene-based polymer, the present invention provides a method for preparing a conjugated diene-based polymer as follows.

[00166] The method for preparing a conjugated diene-based polymer is characterized in being a continuous-type preparation method and including polymerizing a conjugated diene-based monomer, or a conjugated diene-based monomer and an aromatic vinyl-based monomer in the presence of a hydrocarbon solvent, a polymerization initiator and a polar additive (S1), wherein step (S1) is performed in two or more polymerization reactors, a polymer is transported to a second

reactor at a point where a polymerization conversion ratio of a first reactor is 70% to 85%, and a polar additive, or a polar additive and a conjugated diene monomer are additionally added to the second reactor.

5 **[00167]** Hereinafter, the explanation on the physical properties of the conjugated diene-based polymer such as viscoelasticity behavior properties has been provided above, and the explanation will be given mainly with the preparation method.

10

[00168] The hydrocarbon solvent is not specifically limited, but may be, for example, one or more selected from the group consisting of n-pentane, n-hexane, n-heptane, isooctane, cyclohexane, toluene, benzene and xylene.

15 **[00169]** The polymerization initiator may be used in 0.1 equivalents to 3.0 equivalents, preferably, 0.1 equivalents to 2.0 equivalents, more preferably, 0.5 equivalents to 1.5 equivalents based on 1.0 equivalent of the monomer. In another embodiment, the polymerization initiator may be used in 0.01
20 mmol to 10 mmol, 0.05 mmol to 5 mmol, 0.1 mmol to 2 mmol, 0.1 mmol to 1 mmol, or 0.15 to 0.8 mmol based on total 100 g of the monomer. Here, the total 100 g of the monomer may be a conjugated diene-based monomer, or the sum of a conjugated diene-based monomer and an aromatic vinyl-based monomer.

25 **[00170]** Meanwhile, the polymerization initiator may be an

organometallic compound, for example, one or more selected from the group consisting of an organolithium compound, an organosodium compound, an organopotassium compound, an organorubidium compound and an organocesium compound.

5 **[00171]** Particularly, the organometallic compound may be one or more selected from the group consisting of methyllithium, ethyllithium, propyllithium, n-butyllithium, s-butyllithium, t-butyllithium, hexyllithium, n-decyllithium, t-octyllithium, phenyllithium, 1-naphthyl lithium, n-eicosyl lithium, 4-
10 butylphenyl lithium, 4-tolyl lithium, cyclohexyl lithium, 3,5-di-n-heptylcyclohexyl lithium, 4-cyclopentyl lithium, naphthyl sodium, naphthyl potassium, lithium alkoxide, sodium alkoxide, potassium alkoxide, lithium sulfonate, sodium sulfonate, potassium sulfonate, lithium amide, sodium amide, potassium
15 amide, and lithium isopropylamide.

[00172] In another embodiment, the polymerization initiator may be a modification initiator, and the modification initiator may be a reaction product of an N-functional group-containing compound and the organometallic compound.

20

[00173] Step S1

[00174] According to an embodiment of the present invention, step (S1) in the preparation method is a step of performing polymerization reaction of a conjugated diene-based monomer,
25 or a conjugated diene-based monomer and an aromatic vinyl-

based monomer by, for example, anionic polymerization. In a particular embodiment, the anionic polymerization may be a living anionic polymerization by which an anionic active part is formed at the polymerization terminal through a propagation reaction by anions. In addition, the polymerization of step (S1) may be a polymerization with heating, an isothermal polymerization, or a polymerization at a constant temperature (adiabatic polymerization). The polymerization at a constant temperature may mean a polymerization method including a step of polymerizing using self-generated heat of reaction without optionally applying heat after adding a polymerization initiator, the polymerization with heating may mean a polymerization method including injecting the polymerization initiator and then, increasing the temperature by optionally applying heat, and the isothermal polymerization may mean a polymerization method by which the temperature of a polymer is kept constant by increasing heat by applying heat or taking heat after injecting the polymerization initiator.

[00175] In addition, according to an embodiment of the present invention, the polymerization of step (S1) may be performed by further adding a diene-based compound of 1 to 10 carbon atoms in addition to the conjugated diene-based monomer, and in this case, effects of preventing the formation of gel on the wall of a reactor during operating for a long time may be achieved. The diene-based compound may be, for example, 1,2-butadiene.

[00176] In addition, according to an embodiment of the present invention, the polymerization of step (S1) is performed in two or more polymerization reactors, and a polymerization conversion ratio in the first polymerization reactor among the polymerization reactors may be 70% to 85%, 70% to 80%, or 70% to less than 80%. That is, the polymerization of step (S1) may be only performed until the polymerization conversion ratio in the first polymerization reactor becomes 70% or more, 70% to 85%, 70% to 80%, or 70% to less than 80%.

[00177] Within this range, side reactions occurring while forming a polymer after initiating polymerization reaction may be restrained and the microstructure of a polymer may be easily controlled, and accordingly, the full width at half maximum of a glass transition temperature peak is broadened in a dynamic mechanical analysis, and thus, the basis of improving abrasion resistance may be provided.

[00178] The polymerization in the first reactor may be performed, for example, in a temperature range of 80°C or less, -20°C to 80°C, 0°C to 80°C, 0°C to 70°C, or 10°C to 70°C, and in this range, the molecular weight distribution of the polymer may be controlled narrow, and excellent effects of improving physical properties may be achieved.

[00179] According to an embodiment of the present invention, step (S1) is performed in two or more reactors, and after performing polymerization until the aforementioned conversion

ratio in the first reactor is achieved, the polymer is transported to the second reactor, and the additional injection of a polar additive or a conjugated diene-based monomer to the second reactor may be performed.

5 **[00180]** In this case, the polar additive, or the polar additive and the conjugated diene-based monomer, additionally injected may be injected at once or in order, and may be injected in installments at various points among the points in the range or injected continuously within the point in the range.

10 **[00181]** The additional injection of the polar additive, or the polar additive and conjugated diene-based monomer may be a means for achieving the glass transition temperature properties of a polymer prepared together with for controlling the conversion ratio in the first reactor. Through the
15 additional injection of the polar additive, a power may be further applied to polymerization reaction after a specific conversion ratio to arise the deformation of a microstructure.

20 **[00182]** Particularly, in the case of homopolymerizing a conjugated diene-based monomer, the polar additive may control the ratio of 1,2-bond and 1,4-bond through the control of a reaction rate, and in the case of copolymerizing a conjugated diene-based monomer and an aromatic vinyl-based monomer, a reaction rate difference between the monomers may be corrected to show inducing effects of easy formation of a random
25 copolymer.

[00183] In this case, the polar additive additionally injected may be used in a suitable amount in a direction so that the full width at half maximum of a stress change peak may become broadened. For example, the polar additive additionally injected may be used in a ratio of 0.001 g to 10 g, or 0.01 g to 1.0 g, more preferably, 0.02 g to 0.5 g based on total 100 g of the monomer used when initiating polymerization.

[00184] In addition, the conjugated diene-based monomer selectively additionally injected may be used in an amount of 5 g to 25 g, or 5 g to 20 g based on 100 g of the monomer used when initiating polymerization. If the polar additive or the conjugated diene-based monomer additionally injected is controlled in the aforementioned amount, there are advantages in that the control of a glass transition temperature peak during dynamic mechanical analysis may be easy, finer control thereof may be possible, and the full width at half maximum of the peak may be broadened.

[00185] The total amount used of the polar additive used in the polymerization of step (S1) may be in a ratio of 0.001 g to 50 g, or 0.002 g to 1.0 g based on total 100 g of the monomer. In another embodiment, the total amount used of the polar additive may be in a ratio of greater than 0 g to 1 g, 0.01 g to 1 g, or 0.1 g to 0.9 g based on total 100 g of the polymerization initiator. Here, the total amount used of the

polar additive includes the additionally injected amount of the polar additive.

[00186] The polymerization in the second reactor may be performed in a temperature range of 80°C or less, -20°C to 80°C, 0°C to 80°C, 0°C to 70°C, or 10°C to 70°C, and in this range, the molecular weight distribution of the polymer may be controlled narrow, and excellent effects of improving physical properties may be achieved.

[00187] Meanwhile, in additionally controlling the full width at half maximum of the glass transition temperature peak by the dynamic mechanical analysis, the polymerization temperatures in the first reactor and the second reactor may also influence, and in this case, it is preferable to control the polymerization temperature of the second reactor lower than the polymerization temperature of the first reactor, and the polymerization temperature of the second reactor is preferably 60°C or higher.

[00188] The polar additive may be, for example, one or more selected from the group consisting of tetrahydrofuran, 2,2-di(2-tetrahydrofuryl)propane, diethyl ether, cyclopentyl ether, dipropyl ether, ethylene methyl ether, ethylene dimethyl ether, diethyl glycol, dimethyl ether, tert-butoxy ethoxy ethane, bis(3-dimethylaminoethyl)ether, (dimethylaminoethyl) ethyl ether, trimethylamine, triethylamine, tripropylamine, N,N,N',N'-tetramethylethylenediamine, sodium mentholate and 2-

ethyl tetrahydrofurfuryl ether, and may preferably be 2,2-di(2-tetrahydrofuryl)propane, triethylamine, tetramethylethylenediamine, sodium mentholate or 2-ethyl tetrahydrofurfuryl ether.

5 **[00189]** Meanwhile, the polymerization conversion ratio may be determined, for example, by measuring the solid concentration in a polymer solution phase including the polymer during polymerization, and in a particular embodiment, in order to secure the polymer solution, a cylinder type container is
10 installed at the outlet of each polymerization reactor to fill up a certain amount of the polymer solution in the cylinder type container, and then, the cylinder type container is separated from the reactor, the weight (A) of the cylinder filled with the polymer solution is measured, the polymer
15 solution filled in the cylinder type container is transported to an aluminum container, for example, an aluminum dish, the weight (B) of the cylinder type container from which the polymer solution is removed is measured, the aluminum container containing the polymer solution is dried in an oven of 140°C
20 for 30 minutes, the weight (C) of a dried polymer is measured, and calculation is performed according to Mathematical Equation 2 below.

[00190] [Mathematical Equation 2]

$$\text{Polymerization conversion ratio (\%)} = \frac{\text{Weight (C)}}{[(\text{Weight (A)} - \text{Weight (B)}) \times \text{Total solid content (TSC)}]} \times 100$$

25 **[00191]** In Mathematical Equation 2, the total solid content is

the total solid (monomer) content in a polymer solution separated from each reactor and is the weight percent of the solid content with respect to 100% of the polymer solution. For example, if the total solid content is 20 wt%, calculation
5 may be performed by substituting 20/100, i.e., 0.2 in Mathematical Equation 2.

[00192] Meanwhile, the polymer polymerized in the second reactor may be transported to a final polymerization reactor in order, and polymerization may be performed until the final
10 polymerization conversion ratio becomes 95% or more. After performing the polymerization in the second reactor, the polymerization conversion ratio for each reactor of the third reactor to the final polymerization reactor, may be suitably controlled to control molecular weight distribution. After
15 that, a reaction terminator for deactivating an activation part may be injected, and in case of preparing a modified conjugated diene-based polymer, an active polymer may be transported to a modification reaction process, and the reaction terminator may use any materials commonly used in
20 this technical field, without limitation.

[00193] In addition, the active polymer prepared by step (S1) may mean a polymer in which a polymer anion and the organometallic cation of a polymerization initiator are combined.

[00194] Preparation method of modified conjugated diene-based polymer

[00195] According to an embodiment of the present invention, a preparation method of a modified conjugated diene-based polymer is provided and is characterized in further including
5 step (S2) of reacting the polymer of which activity of the polymer prepared in step (S1) is maintained, with a modifier, in the preparation method of the conjugated diene-based polymer.

[00196] In the preparation method of the modified conjugated
10 diene-based polymer, a method for preparing an active polymer is the same as the step (S1) of the conjugated diene-based polymer, and the description thereof will be omitted.

[00197] Step S2

15 **[00198]** The step (S2) is a modification step reacting an active polymer in a state of maintaining the activity of the polymer prepared in step (S1) with a modifier, and the anion active part of the active polymer and an alkoxy group bonded to the silane of the modifier may react. The modifier may be used in
20 an amount of 0.01 mmol to 10 mmol based on total 100 g of the monomer. In another embodiment, the modifier may be used in a molar ratio of 1:0.1 to 10, 1:0.1 to 5, or 1:0.1 to 1:3, based on 1 mol of the polymerization initiator of step (S1).

[00199] In addition, according to an embodiment of the present
25 invention, the modifier may be injected into a modification

reactor, and step (S2) may be conducted in the modification reactor. In another embodiment, the modifier may be injected into a transporting part for transporting the active polymer prepared in step (S1) to a modification reactor for conducting
5 step (S2), and the reaction may be performed by the mixing of the active polymer and the modifier in the transporting part. In this case, the reaction may be modification reaction for simply coupling the modifier with the active polymer, or coupling reaction for connecting the active polymer based on
10 the modifier.

[00200] Meanwhile, in the preparation method of the modified conjugated diene-based polymer, a step of additionally injecting a conjugated diene-based monomer to the active
15 polymer prepared in step (S1) and reacting may be further performed prior to the modification reaction of step (S2), and in this case, modification reaction afterward may become more favorable. In this case, the conjugated diene-based monomer may be injected in 1 mol to 100 mol based on 1 mol of the
20 active polymer.

[00201] The preparation method of a modified conjugated diene-based polymer according to an embodiment of the present invention is a method that may satisfy the properties of the aforementioned modified conjugated diene-based polymer, and as
25 described above, the effects to achieve in the present

invention may be achieved if the properties are satisfied, but through controlling other polymerization conditions diversely, the physical properties of the modified conjugated diene-based polymer according to the present invention may be achieved.

5

[00202] Rubber Composition

[00203] According to the present invention, a rubber composition including the conjugated diene-based polymer or the modified conjugated diene-based polymer is provided.

10 **[00204]** The rubber composition may include the (modified) conjugated diene-based polymer in an amount of 10 wt% or more, 10 wt% to 100 wt%, or 20 wt% to 90 wt%, and within this range, mechanical properties such as tensile strength and abrasion resistance are excellent, and effects of excellent balance
15 between physical properties may be achieved.

[00205] In addition, the rubber composition may further include other rubber components, as necessary, in addition to the (modified) conjugated diene-based polymer, and in this case, the rubber components may be included in an amount of 90
20 wt% or less based on the total weight of the rubber composition. In a particular embodiment, the other rubber components may be included in an amount of 1 part by weight to 900 parts by weight based on 100 parts by weight of the (modified) conjugated diene-based polymer.

25 **[00206]** The rubber component may be, for example, natural

rubber or synthetic rubber, and may particularly be natural rubber (NR) including cis-1,4-polyisoprene; modified natural rubber which is obtained by modifying or purifying common natural rubber, such as epoxidized natural rubber (ENR),
5 deproteinized natural rubber (DPNR), and hydrogenated natural rubber; and synthetic rubber such as a styrene-butadiene copolymer (SBR), a polybutadiene (BR), a polyisoprene (IR), butyl rubber (IIR), an ethylene-propylene copolymer, a polyisobutylene-co-isoprene, neoprene, a poly(ethylene-co-propylene),
10 a poly(styrene-co-butadiene), a poly(styrene-co-isoprene), a poly(styrene-co-isoprene-co-butadiene), a poly(isoprene-co-butadiene), a poly(ethylene-co-propylene-co-diene), polysulfide rubber, acryl rubber, urethane rubber, silicone rubber, epichlorohydrin rubber, and halogenated butyl
15 rubber, and any one or a mixture of two or more thereof may be used.

[00207] The rubber composition may include a filler in 0.1 parts by weight to 200 parts by weight, or 10 parts by weight to 120 parts by weight based on 100 parts by weight of the
20 (modified) conjugated diene-based polymer of the present invention. The filler may be, for example, a silica-based filler, particularly, wet silica (hydrated silicate), dry silica (anhydrous silicate), calcium silicate, aluminum silicate, colloid silica, etc., and preferably, the filler may
25 be wet silica which has the most significant improving effects

of destruction characteristics and compatible effects of wet grip. In addition, the rubber composition may further include a carbon-based filler, as necessary.

[00208] In another embodiment, if silica is used as the filler,
5 a silane coupling agent may be used together for the improvement of reinforcing and low exothermic properties. Particular examples of the silane coupling agent may include
bis(3-triethoxysilylpropyl)tetrasulfide, bis(3-
triethoxysilylpropyl)trisulfide, bis(3-
10 triethoxysilylpropyl)disulfide, bis(2-
triethoxysilylethyl)tetrasulfide, bis(3-
trimethoxysilylpropyl)tetrasulfide, bis(2-
trimethoxysilylethyl)tetrasulfide, 3-
mercaptopropyltrimethoxysilane, 3-
15 mercaptopropyltriethoxysilane, 2-
mercaptoethyltrimethoxysilane, 2-mercaptoethyltriethoxysilane,
3-trimethoxysilylpropyl-N,N-dimethylthiocarbamoyltetrasulfide,
3-triethoxysilylpropyl-N,N-dimethylthiocarbamoyltetrasulfide,
2-triethoxysilylethyl-N,N-dimethylthiocarbamoyltetrasulfide,
20 3-trimethoxysilylpropylbenzothiazolyltetrasulfide, 3-
triethoxysilylpropylbenzolyltetrasulfide, 3-
triethoxysilylpropylmethacrylatemonosulfide, 3-
trimethoxysilylpropylmethacrylatemonosulfide, bis(3-
diethoxymethylsilylpropyl)tetrasulfide, 3-
25 mercaptopropyldimethoxymethylsilane,

dimethoxymethylsilylpropyl-N,N-
dimethylthiocarbamoyltetrasulfide, or
dimethoxymethylsilylpropylbenzothiazolyltetrasulfide, and any
one or a mixture of two or more thereof may be used. Preferably,
5 bis(3-triethoxysilylpropyl)polysulfide or 3-
trimethoxysilylpropylbenzothiazolyltetrasulfide may be used in
consideration of the improving effects of reinforcing
properties.

[00209] In addition, in the rubber composition according to an
10 embodiment of the present invention, since a modified
conjugated diene-based polymer in which a functional group
having high affinity with silica is brought in an active part
is used as a rubber component, the mixing amount of the silane
coupling agent may be smaller than a common case. Thus, the
15 silane coupling agent may be used in an amount of 1 part by
weight to 20 parts by weight, or 5 parts by weight to 15 parts
by weight based on 100 parts by weight of silica, and within
the above range, effects as a coupling agent may be
sufficiently shown, and effects of preventing gelation of a
20 rubber component may be achieved.

[00210] The rubber composition according to an embodiment of
the present invention may be sulfur crosslinkable, and may
further include a vulcanizing agent. The vulcanizing agent
may particularly be a sulfur powder and may be included in an
25 amount of 0.1 parts by weight to 10 parts by weight based on

100 parts by weight of a rubber component, and within the above range, elasticity and strength required for a vulcanized rubber composition may be secured, and at the same time, an excellent low fuel consumption ratio may be achieved.

5 **[00211]** The rubber composition according to an embodiment of the present invention may further include various additives used in a common rubber industry in addition to the above components, particularly, a vulcanization accelerator, a process oil, a plasticizer, an antiaging agent, a scorch
10 preventing agent, a zinc white, stearic acid, a thermosetting resin, or a thermoplastic resin.

[00212] The vulcanization accelerator may include, for example, thiazole-based compounds such as 2-mercaptobenzothiazole (M), dibenzothiazyl disulfide (DM), and N-cyclohexyl-2-
15 benzothiazyl sulfenamide (CZ), or guanidine-based compounds such as diphenylguanidine (DPG), in 0.1 parts by weight to 5 parts by weight based on 100 parts by weight of the rubber component.

[00213] The process oil acts as a softener in a rubber
20 composition and may include, for example, paraffin-based, naphthene-based, or aromatic compounds. The aromatic process oil may be used in consideration of tensile strength and abrasion resistance, and the naphthene-based or paraffin-based process oil may be used in consideration of hysteresis loss
25 and properties at a low temperature. The process oil may be

included in an amount of 100 parts by weight or less based on 100 parts by weight of the rubber component. Within the above-described range, the deterioration of the tensile strength and low exothermic properties (low fuel consumption ratio) of the vulcanized rubber may be prevented.

[00214] The antiaging agent may include, for example, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, or a condensate of diphenylamine and acetone at a high temperature, in 0.1 parts by weight to 6 parts by weight based on 100 parts by weight of the rubber component.

[00215] The rubber composition according to an embodiment of the present invention may be obtained by mulling using a mulling apparatus such as a banbury mixer, a roll, and an internal mixer according to a mixing prescription, and a rubber composition having low exothermic properties and good abrasion properties may be obtained by a vulcanization process after a molding process.

[00216] Therefore, the rubber composition may be useful to the manufacture of each member of a tire such as a tire tread, an under tread, a side wall, a carcass coating rubber, a belt coating rubber, a bead filler, a chafer, and a bead coating rubber, or to the manufacture of rubber products in various industries such as a vibration-proof rubber, a belt conveyor,

and a hose.

[00217] Also, the present invention provides a tire manufactured using the rubber composition.

5 **[00218]** The tire may be a tire or include a tire tread.

[00219] Examples

[00220] Hereinafter, the present invention will be explained in more detail referring to embodiments. Embodiments
10 according to the present invention may be modified into various other types, and the scope of the present invention should not be limited to the embodiments described below. The embodiments of the present invention are provided for completely explaining the present invention to a person having an average knowledge
15 in the art.

[00221] Experimental data I

[00222] Example 1

[00223] To a first reactor among three continuous stirring
20 liquid phase reactors (CSTR), continuously injected were n-hexane in a flow rate of 5 kg/hr, a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.16 kg/h, a monomer solution in which 60 wt% of styrene was dissolved in n-hexane in a flow rate of 0.31 kg/hr,
25 an initiator solution in which 6.6 wt% of n-butyllithium was

dissolved in n-hexane in a flow rate of 8.33 g/hr, a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate of 2.25 g/hr. In this case, the internal temperature of the reactor was maintained to 60°C, and when a polymerization conversion ratio reached 72%, a polymerization reactant was transported from the first reactor to a second reactor through a transport pipe.

[00224] Then, the temperature of the second reactor was maintained to 60°C, and to the second reactor, continuously injected were a solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 0.2 kg/hr, and a polar additive solution in which 10 wt% of ditetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate of 6 g/hr to participate in the reaction. When a polymerization conversion ratio reached 95% or more, the reaction was finished. After that, a polymerization reactant was transported from the second reactor to a third reactor through a transport pipe, and a solution in which 4.5 wt% of silicon tetrachloride was dissolved in n-hexane as a coupling agent was injected in a flow rate of 3.7 g/hr, and the reaction was performed for 30 minutes.

[00225] Then, an IR1520 (BASF Co.) solution in which 30 wt% of an antioxidant was dissolved, was injected in a rate of 100 g/h and stirred. The polymer thus obtained was injected in

hot water heated with steam, stirred to remove solvents and roll dried to remove remaining solvents and water to prepare an unmodified conjugated diene-based copolymer.

5 **[00226] Example 2**

[00227] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except for transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization
10 conversion ratio in the first reactor reached 70%, in Example 1.

[00228] Example 3

[00229] An unmodified conjugated diene-based polymer was
15 prepared by performing the same method as in Example 1 except for maintaining the temperature of the first reactor to 70°C, and the temperature of the second reactor to 65°C, and transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization
20 conversion ratio in the first reactor reached 80%, in Example 1.

[00230] Example 4

[00231] An unmodified conjugated diene-based polymer was
25 prepared by performing the same method as in Example 1 except

for transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 73%, and continuously injecting a polar additive solution in which 10 wt% of ditetrahydrofurylpropane was dissolved in n-hexane, which was additionally injected to the second reactor, in a flow rate of 15 g/hr, in Example 1.

[00232] Example 5

[00233] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except for transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 77%, and continuously injecting a polar additive solution in which 10 wt% of ditetrahydrofurylpropane was dissolved in n-hexane, which was additionally injected to the second reactor, in a flow rate of 1 g/hr, in Example 1.

[00234] Example 6

[00235] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except for injecting to the first reactor, a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.13 kg/hr, a monomer solution in which 60 wt% of

styrene was dissolved in n-hexane in a flow rate of 0.28 kg/hr, and a polar additive solution in which 2 wt% of dithetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate of 4.0 g/hr, and transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 75%, in Example 1.

[00236] Comparative Example 1

[00237] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except for transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 66%, in Example 1.

[00238] Comparative Example 2

[00239] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except for transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 83%, in Example 1.

[00240] Comparative Example 3

[00241] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except

for injecting to the first reactor, a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane in a flow rate of 5 g/hr, transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 75%, and not additionally injecting the polar additive solution to the second reactor, in Example 1.

[00242] Comparative Example 4

[00243] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 1 except for injecting to the first reactor, a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane in a flow rate of 5 g/hr, transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 75%, and not additionally injecting the 1,3-butadiene solution and the polar additive solution to the second reactor, in Example 1.

[00244] Experimental Example 1. Evaluation of properties of polymers

[00245] With respect to each of the unmodified conjugated diene-based polymers prepared in the Examples and Comparative Examples, the styrene bond content and 1,2-vinyl bond content

in each polymer, a weight average molecular weight (M_w , $\times 10^3$ g/mol), a number average molecular weight (M_n , $\times 10^3$ g/mol), molecular weight distribution (PDI, MWD), mooney viscosity (MV), and the full width at half maximum of a $\tan \delta$ peak were measured, and the results are shown in Table 1 below.

[00246] 1) Styrene bond content and 1,2-vinyl bond content (wt%)

[00247] The styrene bond content (SM) and 1,2-vinyl bond content in each polymer were measured and analyzed using Varian VNMRs 500 MHz NMR.

[00248] When measuring NMR, 1,1,2,2-tetrachloroethane was used as a solvent, and styrene unit and vinyl contents were calculated by calculating a solvent peak as 5.97 ppm, and regarding 7.2-6.9 ppm as random styrene peaks, 6.9-6.2 ppm as block styrene peaks, 5.8-5.1 ppm as 1,4-vinyl and 1,2-vinyl peaks, and 5.1-4.5 ppm as 1,2-vinyl peaks.

[00249] 2) Weight average molecular weight (M_w , $\times 10^3$ g/mol), number average molecular weight (M_n , $\times 10^3$ g/mol), and molecular weight distribution (PDI, MWD)

[00250] By gel permeation chromatography (GPC) (PL GPC220, Agilent Technologies), a number average molecular weight (M_n) and a weight average molecular weight (M_w) were measured, and molecular weight distribution was calculated by dividing the weight average molecular weight by the number average molecular

weight.

[00251] - Column: using two of PLgel Olexis (Polymer Laboratories Co.) and one of PLgel mixed-C (Polymer Laboratories Co.) in combination

5 **[00252]** - Solvent: using a mixture of tetrahydrofuran and 2 wt% of an amine compound

[00253] - Flow rate: 1 ml/min

[00254] - Specimen concentration: 1-2 mg/ml (diluted in THF)

[00255] - Injection amount: 100 μ l

10 **[00256]** - Column temperature: 40°C

[00257] - Detector: Refractive index

[00258] - Standard: Polystyrene (calibrated by cubic function)

[00259] 3) Mooney viscosity

15 **[00260]** The mooney viscosity (MV, (ML1+4, @100°C) MU) was measured by using MV-2000 (Alpha Technologies Co.) using Large Rotor at a rotor speed of 2 ± 0.02 rpm at 100°C. In this case, a specimen used was stood at room temperature ($23 \pm 3^\circ\text{C}$) for 30 minutes or more, and 27 ± 3 g of the specimen was collected and
20 put in a die cavity, and then, Platen was operated for 4 minutes for measurement.

[00261] 4) Full width at half maximum (FWHM) of $\tan \delta$ peak

[00262] With respect to the polymers prepared in the Examples
25 and Comparative Examples, in order for dynamic viscoelasticity

analysis by an Advanced Rheometric Expansion System (ARES),
tan δ in accordance with temperature in a temperature range of
-100°C to 100°C was measured using a dynamic mechanical
analyzer (TA Co., ARES-G2) with a torsional mode under a
5 frequency of 10 Hz, a strain of 0.5 %, and a temperature rise
rate of 5°C/min. A tan δ graph as in FIG. 1 was obtained, and
the full width at half maximum of the peak was obtained from
the graph.

[00263] [Table 1]

Division		Example						Comparative Example			
		1	2	3	4	5	6	1	2	3	4
NMR (wt%)	SM	17	17	17	17	17	15	17	17	17	17
	Vinyl	13	13	13	13	13	20	13	13	13	13
GPC	Mn (X10 ³ g/mol)	443	456	452	466	479	451	447	461	473	458
	Mw (X10 ³ g/mol)	828	834	823	853	877	857	822	848	856	847
	PDI	1.87	1.83	1.82	1.83	1.83	1.90	1.84	1.84	1.81	1.85
Mooney viscosity		99	97	96	101	102	101	98	99	101	101
FWHM of tan δ peak (°C)		32	43	27	35	38	23	17	13	15	14

10 **[00264]** Referring to Table 1, in the case of the polymers
prepared by the preparation method according to the present
invention, all the full width at half maximum values of the
tan δ peak were shown 20°C or higher, but it was confirmed
that all the Comparative Examples not following the preparation
15 method according to the present invention, showed the value of
less than 20°C. That is, it could be found that according to
the preparation method of the present invention, fine control
of the microstructure of the polymer may be possible, and the
full width at half maximum value of the tan δ peak may be

increased.

[00265] Experimental Example 2. Evaluation of properties of rubber composition

5 **[00266]** In order to compare and analyze the physical properties of rubber compositions including each of the unmodified conjugated diene-based polymers prepared in the Examples and Comparative Examples, and molded articles manufactured therefrom, viscoelasticity properties and abrasion resistance
10 weremeasured, respectively, and the results are shown in Table 3 below.

[00267] 1) Preparation of rubber specimen

[00268] Compounding was performed using each of the modified or unmodified conjugated diene-based polymers of the Examples,
15 Comparative Examples and Reference Examples as a raw material rubber under the compounding conditions shown in Table 2 below. The raw materials in Table 2 are represented by parts by weight based on 100 parts by weight of the raw material rubber.

[00269] [Table 2]

Division	Raw material	Amount (parts by weight)
First stage mulling	Rubber	100
	Silica	70
	Coupling agent (X50S)	11.2
	Process oil	37.5
	Zinc white	3
	Stearic acid	2

	Antioxidant	2
	Antiaging agent	2
	wax	1
Second stage mulling	Sulfur	1.5
	Rubber accelerator	1.75
	Vulcanization accelerator	2

[00270] Particularly, the rubber specimen was mulled via a first stage mulling and a second stage mulling. In the first stage mulling, a raw material rubber, silica (filler), an organic silane coupling agent (X50S, Evonik), a process oil (TADE oil), zinc oxide (ZnO), stearic acid, an antioxidant (TMQ (RD)) (2,2,4-trimethyl-1,2-dihydroquinoline polymer), an antiaging agent (6PPD ((dimethylbutyl)-N-phenyl-phenylenediamine) and wax (Microcrystalline Wax) were mulled using a banbury mixer equipped with a temperature controlling apparatus. In this case, the initial temperature of a mulling apparatus was controlled to 70°C, and after finishing compounding, a first compound mixture was obtained at a discharge temperature of 145°C. In the second stage mulling, the first compound mixture was cooled to room temperature, and the first compound mixture, sulfur, a rubber accelerator (DPG (diphenylguanidine)), and a vulcanization accelerator (CZ (N-cyclohexyl-2-benzothiazylsulfenamide)) were added to the mulling apparatus and mixed at a temperature of 100°C or less to obtain a second compound mixture. Then, via a curing process at 160°C for 20 minutes, a rubber specimen was formed.

[00271] 2) Viscoelasticity properties

[00272] With respect to the rubber specimens manufactured by including the polymers prepared in the Examples and Comparative

5 Examples, in order for dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), $\tan \delta$ in accordance with temperature in a temperature range of -100°C to 100°C was measured using a dynamic mechanical analyzer (TA Co., ARES-G2) with a torsional mode under a frequency of 10

10 Hz, a strain of 0.5 %, and a temperature rise rate of $5^{\circ}\text{C}/\text{min}$, and a $\tan \delta$ graph was obtained. In the $\tan \delta$ graph obtained, a $\tan \delta$ value at 0°C and a $\tan \delta$ value at 60°C were confirmed.

In this case, if the $\tan \delta$ value at a low temperature of 0°C increases, wet skid resistance becomes better, and if the $\tan$
15 δ value at a high temperature of 60°C decreases, hysteresis loss decreases, and running resistance (fuel consumption ratio) becomes better. The resultant values in Table 3 were indexed by setting the resultant values of Comparative Example 3 to 100, and thus, the higher numerical value means better results.

20

[00273] 3) Abrasion resistance (DIN abrasion test)

[00274] With respect to each rubber specimen, DIN abrasion test was conducted based on ASTM D5963 and represented by DIN loss index (loss volume index): abrasion resistance index (ARIA,
25 Method A). In Table 3 below, the resultant values were indexed

based on the measured resultant values of Comparative Example 3, and thus, the higher numerical value means better results.

[00275] [Table 3]

Division		Example						Comparative Example			
		1	2	3	4	5	6	1	2	3	4
Viscoelasticity properties	tan δ at 0°C	111	116	116	117	115	113	103	99	100	98
	tan δ at 60°C	99	100	100	101	100	100	102	97	100	99
Abrasion resistance		129	124	122	126	123	123	105	100	100	101

[00276] Referring to Table 3, it could be confirmed that in the case of a rubber specimen including a polymer having the full width at half maximum of a tan δ peak of 20°C or higher according to the present invention, improved properties of wet skid resistance and running resistance were shown in a balanced way and at the same time, markedly improved abrasion resistance shown.

[00277] On the contrary, it could be confirmed that in the case of a rubber specimen including a polymer of the Comparative Example, having the full width at half maximum of a tan δ peak of less than 20°C, markedly degraded wet skid resistance and running resistance were shown in contrast to the Examples, and very poor abrasion resistance was shown.

[00278] Experimental data II

[00279] Example 7

[00280] To a first reactor among three continuous stirring liquid phase reactors (CSTR), continuously injected were n-

hexane in a flow rate of 5 kg/hr, a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.16 kg/h, a monomer solution in which 60 wt% of styrene was dissolved in n-hexane in a flow rate of 0.31 kg/hr, 5 an initiator solution in which 6.6 wt% of n-butyllithium was dissolved in n-hexane in a flow rate of 8.33 g/hr, and a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate of 2.25 g/hr. In this case, the internal temperature of the 10 reactor was maintained to 60°C, and when a polymerization conversion ratio reached 70%, a polymerization reactant was transported from the first reactor to a second reactor through a transport pipe.

[00281] Then, the temperature of the second reactor was 15 maintained to 60°C, and to the second reactor, continuously injected were a solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 0.2 kg/hr, and a polar additive solution in which 10 wt% of ditetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate 20 of 6 g/hr to participate in the reaction. When a polymerization conversion ratio reached 95% or more, a polymerization reactant was transported from the second reactor to a third reactor through a transport pipe, and a solution in which 5 wt% of N,N-dimethyl-3- 25 (trimethoxysilyl)propan-1-amine was dissolved in n-hexane as

a modifier was injected in a flow rate of 11.6 g/hr, and the reaction was performed for 30 minutes.

[00282] Then, an IR1520 (BASF Co.) solution in which 30 wt% of an antioxidant was dissolved, was injected in a rate of 100 g/h and stirred. The polymer thus obtained was injected in hot water heated with steam, stirred to remove solvents and roll dried to remove remaining solvents and water to prepare a modified conjugated diene-based copolymer.

10 **[00283] Example 8**

[00284] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for continuously injecting a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.13 kg/hr, a monomer solution in which 60 wt% of styrene was dissolved in n-hexane in a flow rate of 0.28 kg/hr, and a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate of 4.0 g/hr, and transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 72%, in Example 7.

[00285] Example 9

25 **[00286]** A modified conjugated diene-based polymer was prepared

by performing the same method as in Example 7 except for maintaining the temperature of the first reactor to 70°C, and the temperature of the second reactor to 65°C, and transporting the polymerization reactant to the second reactor, when the
5 polymerization conversion ratio in the first reactor reached 80%, in Example 7.

[00287] Example 10

[00288] A modified conjugated diene-based polymer was prepared
10 by performing the same method as in Example 7 except for transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 77%, and not injecting a 1,3-butadiene solution to the second reactor, which
15 was additionally injected to the second reactor, in Example 7.

[00289] Example 11

[00290] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for
20 continuously injecting a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.13 kg/hr, a monomer solution in which 60 wt% of styrene was dissolved in n-hexane in a flow rate of 0.28 kg/hr, and an initiator solution in which 6.6 wt% of n-butyllithium was
25 dissolved in n-hexane in a flow rate of 6.06 g/hr, and

transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 72%, in Example 7.

5

[00291] Example 12

[00292] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for continuously injecting a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.08 kg/hr, a monomer solution in which 60 wt% of styrene was dissolved in n-hexane in a flow rate of 0.35 kg/hr, and a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane as a polar additive in a flow rate of 3.0 g/hr, transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 75%, and continuously injecting a 1,3-butadiene solution, which was additionally injected to the second reactor in a flow rate of 0.24 kg/hr, in Example 7.

[00293] Example 13

[00294] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for transporting the polymerization reactant from the first

reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 73%, and continuously injecting a polar additive solution in which 10 wt% of ditetrahydrofurylpropane was dissolved in n-hexane, which was additionally injected to the second reactor, in a flow rate of 15.0 g/hr, in Example 7.

[00295] Example 14

[00296] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for transporting the polymerization reactant from the first reactor to the second reactor, when the polymerization conversion ratio in the first reactor reached 73%, and continuously injecting a polar additive solution in which 10 wt% of ditetrahydrofurylpropane was dissolved in n-hexane, which was additionally injected to the second reactor, in a flow rate of 1 g/hr, in Example 7.

[00297] Example 15

[00298] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for continuously injecting a monomer solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane in a flow rate of 1.06 kg/hr, transporting the polymer from the first reactor to the second reactor, when the polymerization conversion ratio in

the first reactor reached 75%, and continuously injecting a 1,3-butadiene solution, which was additionally injected to the second reactor in a flow rate of 0.30 kg/hr, in Example 7.

5 **[00299] Comparative Example 5**

[00300] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for injecting to the first reactor, a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-
10 hexane in a flow rate of 17.5 g/hr, transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 78%, and not injecting 1,3-butadiene and a polar additive to the second reactor, in Example 7.

15

[00301] Comparative Example 6

[00302] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 12 except for injecting to the first reactor, a polar additive solution in
20 which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane in a flow rate of 6.0 g/hr, transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 73%, and not injecting a polar additive to the second reactor,
25 in Example 12.

[00303] Comparative Example 7

[00304] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 8 except for
5 injecting to the first reactor, a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-hexane in a flow rate of 17.5 g/hr, and not injecting a polar additive to the second reactor, in Example 8.

10 **[00305] Comparative Example 8**

[00306] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 12 except for injecting to the first reactor, a polar additive solution in which 2 wt% of ditetrahydrofurylpropane was dissolved in n-
15 hexane in a flow rate of 12.0 g/hr, transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 76%, injecting a solution in which 60 wt% of 1,3-butadiene was dissolved in n-hexane to the second reactor in a flow rate of
20 0.24 kg/hr, and not injecting a polar additive, in Example 12.

[00307] Comparative Example 9

[00308] A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for
25 transporting the polymerization reactant to the second reactor,

when the polymerization conversion ratio in the first reactor reached 65%, in Example 7.

[00309] Comparative Example 10

5 **[00310]** A modified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 87%, in Example 7.

10

[00311] Comparative Example 11

[00312] An unmodified conjugated diene-based polymer was prepared by performing the same method as in Example 7 except for injecting a polar additive solution in which 2 wt% of
15 ditetrahydrofurylpropane was dissolved in n-hexane to the first reactor in a flow rate of 5.0 g/hr, transporting the polymerization reactant to the second reactor, when the polymerization conversion ratio in the first reactor reached 75%, not injecting a polar additive solution to the second
20 reactor, and performing coupling reaction by continuously supplying a solution in which 4.5 wt% of silicon tetrachloride was dissolved in n-hexane in a flow rate of 3.7 g/hr as a coupling agent instead of the modifier, in Example 7.

25 **[00313] Experimental Example 3. Evaluation of properties of**

polymers

[00314] With respect to each of the modified and unmodified conjugated diene-based polymers prepared in Example 7 to Example 15, and Comparative Example 5 to Comparative Example 11, the styrene bond content and 1,2-vinyl bond content in each polymer, a weight average molecular weight (M_w , $\times 10^3$ g/mol), a number average molecular weight (M_n , $\times 10^3$ g/mol), molecular weight distribution (PDI, MWD), and the full width at half maximum of a $\tan \delta$ peak were measured by the same method as in Experimental Example 1 of Experimental data I. The results are shown in Table 4 below.

[00315] [Table 4]

Division		Example									Comparative Example						
		7	8	9	10	11	12	13	14	15	5	6	7	8	9	10	11
NMR (wt%)	SM	17	15	17	17	17	20	17	17	17	15	20	15	20	17	17	17
	Vinyl	13	20	13	13	13	13	13	13	13	25	13	20	20	13	13	13
GPC	M_n ($\times 10^3$ g/mol)	371	394	378	407	475	363	383	387	401	372	404	385	415	391	411	473
	M_w ($\times 10^3$ g/mol)	601	643	628	636	746	589	605	608	642	600	643	627	664	610	699	856
	PDI	1.62	1.63	1.66	1.56	1.57	1.62	1.58	1.57	1.60	1.61	1.59	1.63	1.61	1.57	1.70	1.81
Mooney viscosity		78	86	83	85	97	76	81	81	85	78	86	83	90	81	88	101
FWHM of $\tan \delta$ peak ($^{\circ}\text{C}$)		31	30	35	39	37	28	42	37	24	13	17	16	17	19	12	15

[00316] Referring to Table 4 above, it could be confirmed that all the polymers prepared by the preparation method according to the present invention showed the full width at half maximum values of a $\tan \delta$ peak of 20°C or more, but all the Comparative Examples which did not follow the preparation method according to the present invention showed the values of less than 20°C .

Through this, according to the preparation method of the present invention, it could be found that the fine control of the microstructure of the polymer was possible, and the full width at half maximum value of a $\tan \delta$ peak was increased.

5

[00317] Experimental Example 4. Evaluation of properties of rubber molded articles

[00318] In order to compare and analyze the physical properties of a rubber composition including each of the modified and unmodified conjugated diene-based polymers prepared in the Examples and Comparative Examples, and a molded article manufactured therefrom, viscoelasticity properties and abrasion resistance were measured by the same method as in Experimental Example 2 of Experimental data I. The results are shown in Table 5 below.

[00319] Meanwhile, in Table 5 below, the viscoelasticity properties and abrasion resistance of Examples 7 to 15, and Comparative Examples 5 to 11 are indexed based on the measured resultant values of Comparative Example 11, and the higher numerical represents better results.

[00320] [Table 5]

Division		Example										Comparative Example					
		7	8	9	10	11	12	13	14	15	5	6	7	8	9	10	11
Viscoelasticity properties	$\tan \delta$ at 0°C	118	118	116	117	113	114	117	115	113	100	101	98	99	106	101	100
	$\tan \delta$ at 60°C	108	107	108	109	113	112	111	109	110	107	108	111	108	110	107	100
Abrasion resistance		122	123	127	125	127	125	128	124	122	99	98	97	99	105	102	100

[00321] Referring to Table 5, in the case of a rubber specimen including a polymer having the full width at half maximum of a $\tan \delta$ peak of 20°C or more according to the present invention, it could be confirmed that wet skid resistance and running resistance showed improved properties in a balanced way and at the same time, abrasion resistance was markedly improved. On the contrary, in the case of a rubber specimen including a polymer of the Comparative Example, having the full width at half maximum of a $\tan \delta$ peak of less than 20°C, it could be confirmed that wet skid resistance and running resistance were markedly degraded in contrast to the Examples, and abrasion resistance was very poor.

CLAIMS

1. A conjugated diene-based polymer comprising a repeating unit derived from a conjugated diene-based monomer, wherein, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), a full width at half maximum (FWHM) value of a $\tan \delta$ peak shown in a temperature range of -100°C to 100°C is 20°C to 80°C , and the Advanced Rheometric Expansion System is measured using a dynamic mechanical analyzer with a torsional mode under conditions of a frequency of 10 Hz, a strain of 0.5%, and a temperature rise rate of $5^{\circ}\text{C}/\text{min}$.
2. The conjugated diene-based polymer of claim 1, wherein the full width at half maximum value of a $\tan \delta$ peak is 20°C to 80°C .
3. The conjugated diene-based polymer of claim 1, wherein the full width at half maximum value of a $\tan \delta$ peak is 30°C to 60°C .
4. The conjugated diene-based polymer of claim 1, wherein the $\tan \delta$ peak is shown in a temperature range of -80°C to 20°C .
5. The conjugated diene-based polymer of claim 1, further comprising a repeating unit derived from an aromatic vinyl-

based monomer.

6. The conjugated diene-based polymer of claim 1, wherein a molecular weight distribution curve by gel permeation chromatography is unimodal, and molecular weight distribution is 1.0 to 3.0.

7. A modified conjugated diene-based polymer comprising a repeating unit derived from a conjugated diene-based monomer and a functional group derived from a modifier, wherein, in a $\tan \delta$ graph in accordance with temperature, derived from dynamic viscoelasticity analysis by an Advanced Rheometric Expansion System (ARES), a full width at half maximum (FWHM) value of a $\tan \delta$ peak shown in a temperature range of -100°C to 100°C is 20°C to 80°C , and the Advanced Rheometric Expansion System is measured using a dynamic mechanical analyzer with a torsional mode under conditions of a frequency of 10 Hz, a strain of 0.5%, and a temperature rise rate of $5^{\circ}\text{C}/\text{min}$.

8. The modified conjugated diene-based polymer of claim 7, wherein the modifier is an alkoxysilane-based modifier, and the modified conjugated diene-based polymer has the Si and N contents of 50 ppm or more each, based on a total weight of the polymer.

9. The modified conjugated diene-based polymer of claim 7,

wherein a molecular weight distribution curve by gel permeation chromatography is unimodal, and molecular weight distribution is 1.0 to 3.0.

10. A rubber composition comprising a polymer and a filler, wherein the polymer is the conjugated diene-based polymer of claim 1 or the modified conjugated diene-based polymer of claim 7.

11. The rubber composition of claim 10, wherein the filler is comprised in 0.1 parts by weight to 200 parts by weight based on 100 parts by weight of the polymer.