

DESCRIPTION

BRANCHED CONJUGATED DIENE-AROMATIC VINYL COPOLYMER AND PRODUCTION METHOD FOR THE SAME

Technical Field

[0001]

The present invention relates to a branched conjugated diene-aromatic vinyl copolymer and a production method for the same.

Background Art

[0002]

For automobile tires, in view of ensuring safety, it is important to use a material having excellent wet skid resistance and practically sufficient abrasion resistance and fracture characteristics. Meanwhile, recently, environmental concern such as reduction of carbon dioxide emission has been socially demanded and a desire for developing fuel-efficient cars has increased. In such circumstances, it has been desired to develop a material having low rolling-resistance, for automobile tires, in particular, for tire treads to be in contact with the ground.

[0003]

Furthermore, in view of life cycle of tires, reduction in energy consumption during their manufacturing step is a matter of growing concern. In particular, a rubber material requiring less energy consumption in kneading compounds and having satisfactory processability has been desired. Moreover, also synthetic rubber, as a raw material of tire, having satisfactory productivity with lower energy consumption has been demanded.

[0004]

As a main material for tire treads, there is a styrene-butadiene rubber (SBR). There are two kinds of SBR polymerization methods; an emulsion-polymerization method (E-SBR), in which monomers suspended in water is radically polymerized, and a solution polymerization method (S-SBR) in which monomers in a hydrocarbon solvent is subjected to anionic polymerization using an organic alkaline metal. Of these, consumption of solution polymerized SBR (S-SBR) has increased, since S-SBR has a lot of flexibility in polymer structure design and an excellent balance between fuel efficiency and wet skid resistance, particularly in tires using silica as a filler.

[0005]

Polymerizing processes for solution polymerized SBR (S-SBR) are roughly divided into two types, i.e., a batch polymerization process and a continuous polymerization process.

[0006]

In the batch polymerization process, a functional group is relatively easily introduced by adding a modifier to an active polymer end. As a result, a rubber providing low rolling-resistance when used as a material for tire treads can be obtained (see, for example, Patent Document 1). However, the batch polymerization process also has disadvantages such as; lower processability of the produced rubber, due to its narrow molecular weight distribution; the rubber compound viscosity increase during kneading, due to formation of bonds between modified polymer and silica, and large energy consumption in the polymerization process due to inevitable process of heating and cooling in every batch of polymerization.

[0007]

In the continuous polymerization process, on the other hand, since heat generated in an exothermic reaction of polymerization can be used for heating required for initiating and accelerating polymerization, energy consumption per production is low compared to the batch polymerization process. In addition, since the molecular weight distribution thereof is wide, relatively satisfactory processability is obtained. The continuous polymerization process has these advantages. However, solution polymerized SBR (S-SBR) has disadvantages in that S-SBR consumes large energy in kneading compounds when a composition is produced and has poor processability, compared to the emulsion polymerized SBR (E-SBR) in which a large number of branches are formed during polymerization.

[0008]

As other techniques, there are a method of coupling, for example, a conjugated diene-aromatic vinyl copolymer obtained by anionic polymerization in a continuous polymerization process, with a silicon coupling agent having 3 or more functional groups such as silicon tetrachloride (see, for example, Patent Document 2), a method of coupling with e.g., a halogen-containing silicon compound, an alkoxysilane compound or an alkoxysulfide compound (see, for example, Patent Document 3), a method of coupling with a compound having 2 or more epoxy groups (see, for example, Patent Document 4), etc.

[0009]

Patent Document 1: Japanese Patent Laid-Open No. 2003-171418

Patent Document 2: Japanese Patent Laid-Open No. 61-255917

Patent Document 3: Japanese Patent Laid-Open No. 11-199712

Patent Document 4: International Publication No. WO 01/23467

Summary of the Invention

Problems to be Solved by the Invention

[0010]

However, there remains a room for improvement to obtain a conjugated diene-aromatic vinyl copolymer having satisfactory processability when it is processed into a vulcanizate, providing a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and further having practically sufficient abrasion resistance in combination with fracture characteristics.

[0011]

Furthermore, the techniques disclosed in Patent Documents 2 to 4 require polymerization performed under relatively low temperature conditions in order to obtain a high coupling rate. Therefore, there is still a room for improving productivity.

[0012]

The present invention was made in the aforementioned circumstances, and aims at providing a branched conjugated diene-aromatic vinyl copolymer, which has satisfactory processability when it is processed into a vulcanizate, provides a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and satisfying practically sufficient abrasion resistance and fracture characteristics, and further has excellent productivity; and a production method thereof.

Means for Solving the Problems

[0013]

The present inventor intensively studied for solving the aforementioned problems. As a result, the present inventor have found that the aforementioned problems can be overcome by forming a branched conjugated diene-aromatic vinyl copolymer such that a bound aromatic vinyl content, a vinyl linkage content in total linkage units of a conjugated diene, a weight average molecular weight (M_w -C), and a weight average molecular weight (M_w -C)/a number average molecular weight (M_n -C) ratio fall within the predetermined numerical ranges, and that Mooney viscosity (ML-C) and Mooney stress relaxation rate (MSR-C) measured at 120°C satisfy a predetermined relational expression. Based on the findings, the present invention has been accomplished.

[0014]

More specifically, the present invention is as described below.

[1]

A branched conjugated diene-aromatic vinyl copolymer (C) being a random copolymer, wherein

a bound aromatic vinyl content in the conjugated diene-aromatic vinyl copolymer (C) is from 30 to 38 % by mass,

a vinyl linkage content in total linkage units of a conjugated diene is from 30 to 43 mol%,

a polystyrene-equivalent weight average molecular weight (M_w -C) of the conjugated diene-aromatic vinyl copolymer (C) obtained by gel permeation chromatography (GPC) is from 700,000 to 1,000,000,

a ratio $((M_w-C)/(M_n-C))$ of a weight average molecular weight (M_w -C) to a number average molecular weight (M_n -C) is from 1.7 to 3.0, and

a Mooney viscosity (ML-C) and a Mooney stress relaxation rate (MSR-C) measured at 120°C satisfy the relationship represented by the following Expression (1):

$$\{214-(ML-C)\}/300 \leq (MSR-C) \leq \{260-(ML-C)\}/300 \dots (1)$$

where $100 \leq (ML-C) \leq 140$.

[2]

The branched conjugated diene-aromatic vinyl copolymer (C) according to [1], obtained by coupling a conjugated diene-aromatic vinyl copolymer (I), having a polystyrene-equivalent weight average molecular weight (Mw-I) of from 500,000 to 700,000 and a Mooney viscosity (ML-I) and a Mooney stress relaxation rate (MSR-I) measured at 120°C satisfying the relationship represented by the following Expression (2):

$$\{260-(ML-I)\}/300 \leq (MSR-I) \leq \{310-(ML-I)\}/300 \dots (2)$$

where $65 \leq (ML-I) \leq 100$,

with a multifunctional modifier having 4 or more functional groups.

[3]

A composition of a branched conjugated diene-aromatic vinyl copolymer comprising
the branched conjugated diene-aromatic vinyl copolymer (C) according to [1] or [2] and
an inorganic filler.

[4]

A method for producing the branched conjugated diene-aromatic vinyl copolymer (C) according to [1] or [2], comprising
a step of continuously supplying a solution containing a conjugated diene compound, an aromatic vinyl compound and an anionic polymerization initiator to a reactor, thereby conducting a polymerization reaction to obtain a

solution of a conjugated diene-aromatic vinyl copolymer having an active polymer end, and

a step of coupling the conjugated diene-aromatic vinyl copolymer by using a multifunctional modifier having 4 or more functional groups which can react with the active polymer end.

[5]

A method for producing the branched conjugated diene-aromatic vinyl copolymer (C) according to [1] or [2], comprising

a step of continuously supplying a solution containing a conjugated diene compound, an aromatic vinyl compound and an anionic polymerization initiator to a reactor equipped with a stirrer to conduct a polymerization reaction;

a step of continuously obtaining a solution of a conjugated diene-aromatic vinyl copolymer having an active polymer end from an outlet of the reactor; and

a step of coupling the conjugated diene-aromatic vinyl copolymer by using a multifunctional modifier having 4 or more functional groups which can react with the active polymer end,

wherein

in the polymerization reaction, the polymerization reaction is continuously conducted for an average residence time of 15 minutes or more and 35 minutes or less while maintaining the internal temperature at the outlet of the reactor at from 95 to 110°C.

[6]

The method for producing the branched conjugated diene-aromatic vinyl copolymer according to [4] or [5], wherein the multifunctional modifier is used such that a total mole number of functional groups of the multifunctional

modifier is from 0.1 to 0.5 times based on a mole number of the anionic polymerization initiator.

Advantageous Effects of the Invention

[0015]

According to the present invention, it is possible to provide a branched conjugated diene-aromatic vinyl copolymer, which has excellent processability when it is processed into a vulcanizate, provides a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and satisfying practically sufficient abrasion resistance and fracture characteristics, and further has excellent productivity thereof, and provide a production method thereof.

Modes for Carrying Out the Invention

[0016]

An embodiment of the present invention (hereinafter referred to as "the present embodiment") will be more specifically described below. The present embodiment below is an example for explaining the present invention, and therefore, the present invention is not limited to the present embodiment described below. The present invention can be appropriately modified within the range of the gist thereof and carried out.

[0017]

[Branched conjugated diene-aromatic vinyl copolymer]

The branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is

a conjugated diene-aromatic vinyl copolymer (C), which is a random copolymer; and in which

the bound aromatic vinyl content in the conjugated diene-aromatic vinyl copolymer (C) is from 30 to 38 % by mass;

the vinyl linkage content in total linkage units of the conjugated diene is from 30 to 43 mol%;

the polystyrene-equivalent weight average molecular weight (Mw-C) of the conjugated diene-aromatic vinyl copolymer (C), obtained by GPC is from 700,000 to 1,000,000;

the ratio ((Mw-C)/(Mn-C)) of the weight average molecular weight to the number average molecular weight is from 1.7 to 3.0; and

the Mooney viscosity (ML-C) and the Mooney stress relaxation rate (MSR-C) measured at 120°C satisfy the relationship represented by the following Expression (1):

$$\{214-(ML-C)\}/300 \leq (MSR-C) \leq \{260-(ML-C)\}/300 \dots (1)$$

where $100 \leq (ML-C) \leq 140$.

[0018]

The branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is a random copolymer. The random copolymer here refers to a copolymer in which the content of a component having an aromatic vinyl chain length of 30 or more is low or zero.

[0019]

The branched conjugated diene-aromatic vinyl copolymer of the present embodiment is not limited as long as it is a random copolymer of a conjugated diene compound and an aromatic vinyl compound. As the conjugated diene compound and the aromatic vinyl compound, the compounds described later can be appropriately used. As the conjugated diene-aromatic vinyl copolymer, a styrene-butadiene copolymer, a styrene-

isoprene copolymer and a styrene-butadiene-isoprene copolymer are preferable; and a styrene-butadiene copolymer is more preferable.

[0020]

For example, in the case where the branched conjugated diene-aromatic vinyl copolymer (C) is a butadiene-styrene copolymer, when an amount of polystyrene insoluble in methanol is analyzed after decomposing the branched conjugated diene-aromatic vinyl copolymer (C) by the Kolthoff method (the method described in I. M. KOLTHOFF, et al., J. Polym. Sci. 1,429 (1946)), the amount of polystyrene based on the total amount of branched conjugated diene-aromatic vinyl copolymer (C) is preferably 5 % by mass or less and more preferably 3 % by mass or less.

[0021]

Furthermore, according to a method in which the branched conjugated diene-aromatic vinyl copolymer (C) is decomposed by a method of ozonolysis and the styrene chain distribution is analyzed by gel permeation chromatography (GPC), it is preferred that isolated styrene (in other words, styrene having a chain formed of a single styrene unit) contains 40 % by mass or more of the total bound styrene content and it is more preferred that a long-chain block styrene (in other words, a styrene having a chain formed of 8 or more styrene units) contains 5 % by mass or less of the total bound styrene content.

[0022]

The bound aromatic vinyl content in the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is from 30 to 38 % by mass and preferably from 32 to 37 % by mass. The bound aromatic vinyl bond content can be determined by measuring the ultraviolet absorption by a phenyl group of the branched conjugated diene-aromatic vinyl copolymer (C).

[0023]

Furthermore, the vinyl linkage content in the total linkage units of the conjugated diene is from 30 to 43 mol% and preferably from 32 to 42 mol%. For example, in the case where the branched conjugated diene-aromatic vinyl copolymer (C) is a butadiene-styrene copolymer, the vinyl linkage content (1,2-linkage content) in a butadiene bond unit can be determined by the Hampton method (the method described in R. R. Hampton, Analytical Chemistry 21, 923 (1949)).

[0024]

A conjugated diene-aromatic vinyl copolymer is generally, in most cases, mixed with a natural rubber, a butadiene rubber, etc., to obtain a vulcanizate. When the bound aromatic vinyl content and the vinyl linkage content of the branched conjugated diene-aromatic vinyl copolymer (C) fall within the aforementioned range, the copolymer (C) can be mixed while keeping a satisfactory balance with these rubbers without excessively compatibilizing with them and excessively separating from them. Because of this, a vulcanizate excellent in balance between low hysteresis loss property and wet skid resistance can be obtained.

[0025]

The glass transition temperature of the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is preferably from -40 to -15°C and more preferably from -35 to -18°C. If the glass transition temperature falls within the range, a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance can be obtained. The glass transition temperature is obtained by recording a DSC curve in accordance with ISO 22768:2006 while increasing a temperature

within a predetermined temperature range and employing a peak top of the DSC differentiation curve (inflection point) as the glass transition temperature. [0026]

The branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment has a polystyrene-equivalent weight average molecular weight (Mw-C) of from 700,000 to 1,000,000, and preferably from 750,000 to 950,000, as described above. For obtaining satisfactory abrasion resistance and strength, Mw-C is 700,000 or more. For maintaining satisfactory processability, Mw-C is 1,000,000 or less. Furthermore, the ratio of ((Mw-C)/(Mn-C)) of the weight average molecular weight (Mw-C) to the number average molecular weight (Mn-C) is from 1.7 to 3.0 and preferably from 2.0 to 2.8. For obtaining satisfactory processability, the ratio of ((Mw-C)/(Mn-C)) is 1.7 or more. For obtaining satisfactory mechanical property, the ratio is 3.0 or less. The molecular weight and molecular weight distribution are determined by a chromatogram obtained by GPC measurement with reference to a calibration curve formed by using standard polystyrene. [0027]

In the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment, Mooney viscosity (ML-C) and Mooney stress relaxation rate (MSR-C) measured at 120°C satisfy the relationship represented by the following Expression (1):

$$\{214-(ML-C)\}/300 \leq (MSR-C) \leq \{260-(ML-C)\}/300 \dots (1)$$

where $100 \leq (ML-C) \leq 140$.

[0028]

Mooney stress relaxation rate (MSR) is obtained by a method specified by ISO289-4: 2003. More specifically, after Mooney viscosity is measured, a rotor is stopped. In the period of 1.6 seconds to 5 seconds after the

termination of the rotor, double logarithmic graph of torque (T) and time (t (seconds)) is obtained by plotting them. The absolute value of the slope of the resultant liner line is referred to as MSR. In the case where copolymers have the same Mooney viscosity, the larger the number of branches, the smaller the MSR value. Therefore, this value may be used an index showing extent of branching. More specifically, MSR can be determined by the method described in Examples (later described). Mooney viscosity and Mooney stress relaxation rate are usually measured at 100°C; however, in the present embodiment, Mooney viscosity and Mooney stress relaxation rate measured at 120°C are employed.

[0029]

In the case where it is the aforementioned upper limit value of Expression (1) or less and a copolymer thus has a sufficient extent of branching, the copolymer is excellent in processability and a vulcanizate of the copolymer has an excellent balance between low hysteresis loss property and wet skid resistance and also satisfies practically sufficient abrasion resistance and fracture characteristics. The higher the extent of branching and the lower the MSR-C value, the more excellent processability and the more excellent the balance between low hysteresis loss property and wet skid resistance of a vulcanizate. However, in the case where it is less than the aforementioned lower limit value, a higher-level coupling reaction must be performed, with the result that productivity decreases. This case is practically unfavorable.

[0030]

The present inventor investigated on the behavior of conjugated diene-aromatic vinyl copolymers and obtained the following findings. In the case of copolymers having the same microstructure (bound aromatic vinyl content

and vinyl linkage content in total conjugated diene linkage units) and having the same extent of branching and being different in molecular weight, if ML-C values of the copolymers are plotted on the X axis and MSR-C values thereof are plotted on the Y axis, the slope (MSR-C/ML-C) can be approximated to - 1/300. Furthermore, if the state of branching is varied by, e.g., changing the polymerization temperature and the content of e.g., a multibranching modifier, the plotted linear line shifts up or down (while the slope is maintained at - 1/300, only a Y-intercept shifts). From these findings, it was found that if MSR-C and ML-C of a conjugated diene-aromatic vinyl copolymer (C) satisfy the conditions specified by Expression (1), a preferable state of branching can be defined, and that if the vinyl linkage content, the weight average molecular weight (Mw-C) and the ratio ((Mw-C)/(Mn-C)) of a weight average molecular weight to a number average molecular weight are each controlled so as to fall within a specific range, it is possible to obtain a copolymer, which has satisfactory processability when it is processed into a vulcanizate, provides a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and satisfying practically sufficient abrasion resistance and fracture characteristics, and further has excellent productivity.

[0031]

Furthermore, ML-C and MSR-C preferably satisfy the relationship represented by the following Expression (1a). If the relationship represented by the following Expression (1a) is satisfied, the effect of the present embodiment becomes further remarkable.

$$\{220-(ML-C)\}/300 \leq (MSR-C) \leq \{255-(ML-C)\}/300 \dots (1a)$$

where $106 \leq (ML-C) \leq 135$.

[0032]

The branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is preferably obtained by coupling a conjugated diene-aromatic vinyl copolymer by use of a multifunctional modifier having 4 or more functional groups. In this manner, the extent of branching and the molecular weight can be effectively increased to obtain a copolymer having satisfactory productivity thereof, processability when the copolymer is processed into a vulcanizate and providing a vulcanizate having an excellent balance between properties.

[0033]

Furthermore, the conjugated diene-aromatic vinyl copolymer (C) is more preferably a conjugated diene-aromatic vinyl copolymer (I) having a polystyrene-equivalent weight average molecular weight (M_w-I) of from 500,000 to 700,000 and having a Mooney viscosity ($ML-I$) and a Mooney stress relaxation rate ($MSR-I$) measured at 120°C satisfying the following Expression (2). As a result, it is possible to provide a copolymer, which has satisfactory processability when it is processed into a vulcanizate, provides a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and satisfying practically sufficient abrasion resistance and fracture characteristics, and further has excellent productivity.

$$\{260-(ML-I)\}/300 \leq (MSR-I) \leq \{310-(ML-I)\}/300 \dots (2)$$

where $65 \leq (ML-I) \leq 100$.

[0034]

Furthermore, Mooney viscosity ($ML-I$) measured at 120°C and Mooney stress relaxation rate ($MSR-I$) measured at 120°C more preferably satisfy the following Expression (2a).

$$\{268-(ML-I)\}/300 \leq (MSR-I) \leq \{300-(ML-I)\}/300 \dots (2a)$$

where $66 \leq (ML-I) \leq 89$.

[0035]

[Method for producing branched conjugated diene-aromatic vinyl copolymer]

A preferable method for producing the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment comprises

a step of continuously supplying a solution containing a conjugated diene compound, an aromatic vinyl compound and an anionic polymerization initiator to a reactor, thereby conducting a polymerization reaction to obtain a solution of a conjugated diene-aromatic vinyl copolymer having an active polymer end, and

a step of coupling the conjugated diene-aromatic vinyl copolymer by using a multifunctional modifier having 4 or more functional groups which can react with the active polymer end.

[0036]

A more preferable method for producing a branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment comprises

a step of continuously supplying a solution containing a conjugated diene compound, an aromatic vinyl compound and an anionic polymerization initiator to a reactor equipped with a stirrer to conduct a polymerization reaction;

a step of continuously obtaining a solution of a conjugated diene-aromatic vinyl copolymer having an active polymer end from an outlet of the reactor; and

a step of performing coupling by using a multifunctional modifier having 4 or more functional groups which can react with the active polymer end.

[0037]

According to the aforementioned production methods, it is possible to efficiently produce the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment, which has excellent processability when it is processed into a vulcanizate, provides a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and satisfying practically sufficient abrasion resistance and fracture characteristics. For example, conventionally, when a compound containing SBR as mentioned above is kneaded, an internal mixer such as Banbury mixer is used. Compared to the case of using a small-volume mixer (for example, a volume of several liters or less) as used in a laboratory level, in the case of using a large-volume mixer (for example, a volume of several hundreds liters or more) as used in a step of manufacturing a rubber product such as a tire, kneading processability significantly decreases. Therefore, the processability becomes a more significant issue. As a result, the viscosity of a compound increases and the skin and edge of the compound sheet tend to be coarse. In the production method of the present embodiment, excellent processability can be maintained even in such a scale-up production. Thus, the branched conjugated diene-aromatic vinyl copolymer (C) can be efficiently produced without the aforementioned problems.

[0038]

(Conjugated diene compound)

The conjugated diene compound for use in producing the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is not particularly limited and examples thereof may include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 3-methyl-1,3-pentadiene, 1,3-heptadiene and 1,3-hexadiene. These may be used singly

or in combination with two or more. Of these, 1,3-butadiene and isoprene are preferred in view of availability and the economic efficiency.

[0039]

(Aromatic vinyl compound)

Examples of the aromatic vinyl compound for use in producing the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment may include styrene, p-methylstyrene, α -methylstyrene, vinylethylbenzene, vinylxylene, vinylnaphthalene and diphenylethylene. These may be used singly or in combination with two or more. Of these, styrene is preferred.

[0040]

Allenes and acetylenes which may possibly be contained as impurities in a conjugated diene compound and an aromatic vinyl compound become a factor of inhibiting a polymerization reaction and a coupling reaction. Therefore, the concentration of them in the total monomer is preferably specified to less than 200 ppm.

[0041]

(Polymerization solvent)

In the present embodiment, a conjugated diene compound and an aromatic vinyl compound are generally copolymerized in a solvent. The solvent is not particularly limited and examples thereof may include a solvent of a hydrocarbon such as a saturated hydrocarbon and an aromatic hydrocarbon. Specific examples thereof may include a linear or branched aliphatic hydrocarbon such as butane, pentane, hexane and heptane; an alicyclic hydrocarbon such as cyclopentane, cyclohexane, methylcyclopentane and methylcyclohexane; an aromatic hydrocarbon such as benzene, toluene and xylene and a hydrocarbon mixture of these.

[0042]

(Monomer concentration)

In the present embodiment, the monomer concentration of a conjugated diene compound and an aromatic vinyl compound in a polymerization solution in which a polymerization reaction is performed is not particularly limited; however, in view of productivity, the concentration is preferably from 5 to 50 % by mass and more preferably from 10 to 30 % by mass.

[0043]

(Anionic polymerization initiator)

In the present embodiment, an anionic polymerization initiator that may be used in a polymerization reaction is not particularly limited and examples thereof may include an alkaline metal-based initiator and an alkaline-earth metal-based initiator. As the alkaline metal-based initiator or alkaline-earth metal-based initiator, all alkaline metal-based initiators or alkaline-earth metal-based initiators may be used as long as they have polymerization initiation ability. Of them, at least one kind of compound of an organic alkaline metal compound and an organic alkaline-earth metal compound is preferably included.

[0044]

The organic alkaline metal compound is not particularly limited; however, in view of reactivity, etc., an organic lithium compound is preferred. Examples of the organic lithium compound may include a low molecular weight compound, an organic lithium compound of a solubilized oligomer, a compound having a single lithium in a single molecule, a compound having a plurality of lithium in a single molecule, compounds having lithium bonded to

an organic group such as a carbon-lithium bond, a compound having a nitrogen-lithium bond and a compound having a tin-lithium bond.

[0045]

Specifically, examples of the mono organic lithium compound may include n-butyllithium, sec-butyllithium, tert-butyllithium, n-hexyllithium, benzyllithium, phenyllithium and stilbenelithium.

[0046]

Examples of the multifunctional organic lithium compound may include 1,4-dilithiobutane, a reaction product of sec-butyllithium and diisopropenylbenzene, 1,3,5-trilithiobenzene, a reaction product of n-butyllithium and 1,3-butadiene and divinylbenzene, and a reaction product of n-butyllithium and a polyacetylene compound.

[0047]

Examples of a compound having a nitrogen-lithium bond may include lithium dimethylamide, lithium diethylamide, lithium dipropylamide, lithium di-n-hexylamide, lithium diisopropylamide, lithium hexamethyleneimide, lithium pyrrolidide, lithium piperidide, lithium heptamethyleneimide and lithium morpholide.

[0048]

Furthermore, organic alkaline metal compounds disclosed in U. S. Pat. No. 5,708,092, British Patent No. 2,241,239 and U. S. Pat. No. 5,527,753 can be also used. Particularly preferable ones are n-butyllithium and sec-butyllithium. The aforementioned organic lithium compounds may be used singly or as a mixture of two or more.

[0049]

Examples of other organic alkaline metal compounds may include an organic sodium compound, an organic potassium compound, an organic

rubidium compound and an organic cesium compound. Specific examples thereof may include sodium naphthalene and potassium naphthalene. Besides these, an alkoxides, sulfonate, carbonate and amide of lithium, sodium and potassium may be used.

The organic alkaline metal compound may be used in combination with other organic metal compounds.

[0050]

The alkaline-earth metal compound is not particularly limited and examples thereof may include an organic magnesium compound, an organic calcium compound and an organic strontium compound. Specific examples thereof may include dibutylmagnesium, ethylbutylmagnesium and propylbutylmagnesium. Furthermore, compounds such as an alkoxide, sulfonate, carbonate and amide of an alkaline-earth metal may be used. These organic alkaline-earth metal compounds may be used in combination with the organic alkaline metal-based initiator and other organic metal compounds.

[0051]

(Polar compound)

In the method for producing a branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment, a polar compound such as a Lewis base is preferably added in a small amount in order to randomly copolymerize an aromatic vinyl compound with a conjugated diene compound, in order to use as a vinyl agent for controlling a microstructure of a conjugated diene moiety of a copolymer, and in order to improve a polymerization rate.

[0052]

The polar compound is not particularly limited and examples thereof may include ethers such as tetrahydrofuran, diethyl ether, dioxane, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dimethoxybenzene, and 2,2-bis(2-oxolanyl)propane; tertiary amine compounds such as tetramethylethylenediamine, dipiperidinoethane, trimethylamine, triethylamine, pyridine and quinuclidine; alkali metal alkoxide compounds such as potassium-t-amylate, potassium-t-butyrate, sodium-t-butyrate and sodium amylate; metal salts of organic sulfonic acids such as potassium dodecylbenzene sulfonate and sodium dodecylbenzene sulfonate; and phosphine compounds such as triphenyl phosphine. These polar compounds may be used singly or in combination with two or more.

[0053]

The use amount of polar compound is selected depending upon the purpose and the degree of effect and not particularly limited; however, the use amount is usually from 0.01 to 100 moles based on one mole of an alkaline metal or an alkaline-earth metal atom in an anionic polymerization initiator.

[0054]

The polar compound may be used in an appropriate amount as a modifier for a microstructure of a polymer diene moiety depending upon desired vinyl linkage content. In this manner, the vinyl linkage content in total conjugated diene linkage units can be controlled. Most polar compounds simultaneously have an effective randomization effect in copolymerization between a conjugated diene compound and an aromatic vinyl compound. Thus, the distribution of an aromatic vinyl compound in a copolymer and the block amount of the aromatic vinyl compound (for

example, styrene block amount) can be controlled by using the polar compound.

[0055]

(Polymerization step)

The polymerization reaction of a conjugated diene compound and an aromatic vinyl compound is conducted by continuously supplying a conjugated diene compound, an aromatic vinyl compound, an anionic polymerization initiator, a polymerization solvent as mentioned above and a small amount of polar compound, if necessary to a predetermined reactor equipped with a stirrer and continuously letting out a solution of a conjugated diene-aromatic vinyl copolymer from the outlet of the reactor. Furthermore, a monomer and/or a polymerization solvent are brought into contact with an organic metal compound before they are supplied to a reactor by the method disclosed in Japanese Patent Laid-Open No. 2002-284814 to thereby inactivate a polymerization inhibitory action caused by a small amount of impurities.

[0056]

The supply site of e.g., a monomer solution and the let-out site of a copolymer solution are not particularly limited. Any site, e.g., the bottom portion and top portion of a reactor and an arbitrary site between them, may be used. It is preferred that a monomer solution be supplied from a site near the bottom portion and a copolymer solution is let out from a site near the top portion. Generally, in anionic copolymerization, since a conjugated diene compound is more preferentially polymerized than an aromatic vinyl compound, part of the conjugated diene compound may be supplied from the upper portion of the reactor for the purpose of randomization.

[0057]

The polymerization reaction is preferably conducted while maintaining the internal temperature at a reactor outlet at 95 to 110°C and at an average residence time of 15 minutes or more and 35 minutes or less. The internal temperature at the reactor outlet refers to the temperature of a copolymer solution at the reactor outlet. To improve productivity by increasing a reaction rate and form an appropriately branched structure before a coupling reaction by accelerating a thermal branching reaction by metalation, it is preferred that the internal temperature at the reactor outlet be set to 95°C or more. In contrast, to prevent inhibition of a coupling reaction by inactivation due to an excessive metalation reaction and the like, the internal temperature is preferably set to 110°C or less. The temperature of the copolymer solution can be controlled by heat exchange by means of an exterior heat exchanger and internal heat exchanger and temperature control of the monomer solution to be supplied.

[0058]

Furthermore, it is preferred that the temperature of a copolymer solution in the lower portion of the reactor be lower by 3 to 15°C than the internal temperature at the reactor outlet. The internal temperature of the lower portion of the reactor is more specifically defined as the temperature measured by a thermometer, which is provided at a position, which is soaked when a solution corresponding to 1/3 of the total volume is supplied to the reactor and which is not directly affected by the flow of the monomer solution to be supplied to the reactor. When the solution in the reactor is completely mixed, the internal temperature of the lower portion of a reactor is virtually the same as the internal temperature at the reactor outlet. Conversely, when the solution is in plug-flow conditions, there is a large temperature difference between the internal temperature of the lower portion of the

reactor and the internal temperature of the reactor outlet. If polymerization is performed while controlling stirring conditions such that a difference between the internal temperature of the lower portion of a reactor and the internal temperature of the reactor outlet falls within the range of from 3 to 15°C, an appropriate residence time distribution occurs, and a heat branching reaction of a copolymer can be appropriately conducted.

[0059]

Furthermore, in view of obtaining at least a predetermined conversion rate of a monomer and further sufficiently conducting a heat branching reaction, the average residence time is preferably 15 minutes or more. In view of productivity and suppressing an effect of inactivation upon a coupling reaction, the average residence time is preferably 35 minutes or less.

[0060]

The conversion rate of a monomer at the reactor outlet is preferably 95% or more, further preferably 98% or more and more preferably 99% or more. The higher the conversion rate, the better the unit of output. In addition, since a load on a solvent recovery step is low, excellent productivity is obtained. The conversion rate here can be determined by the method set forth in Examples (later described).

[0061]

The polystyrene-equivalent weight average molecular weight (M_w -I) (measured by GPC) of a conjugated diene-aromatic vinyl copolymer (I) obtained by a polymerization step prior to a coupling step, is not particularly limited; however, M_w -I is preferably from 500,000 to 700,000. In view of obtaining satisfactory abrasion resistance and strength, M_w -I is preferably 500,000 or more. In view of productivity and processability of a conjugated

diene-aromatic vinyl copolymer of the present embodiment obtained after coupling, Mw-I is preferably 700,000 or less.

[0062]

Furthermore, the conjugated diene-aromatic vinyl copolymer (I) obtained in the polymerization step before a coupling step preferably has a Mooney viscosity (ML-I) and a Mooney stress relaxation rate (MSR-I) measured at 120°C satisfying the relationship represented by the following Expression (2):

$$\{260-(ML-I)\}/300 \leq (MSR-I) \leq \{310-(ML-I)\}/300 \dots (2)$$

where $65 \leq (ML-I) \leq 100$.

[0063]

In order for the branched conjugated diene-aromatic vinyl copolymer (C) obtained after coupling to have a sufficient extent of branching, a polymerization reaction is preferably performed so as to satisfy the upper limit value or less in the Expression (2). To ensure an active polymer end sufficient to perform a coupling reaction performed after a polymerization reaction, a polymerization reaction is performed so as to satisfy the aforementioned lower limit value or more.

[0064]

As described above, with the solution of the conjugated diene-aromatic vinyl copolymer having an active polymer end let out from the reactor outlet, a multifunctional modifier having 4 or more functional groups and which can react with an active polymer end, is brought into contact to conduct a coupling reaction. In this manner, the branched conjugated diene-aromatic vinyl copolymer of the present embodiment can be obtained.

[0065]

The reactor may be a vessel-type reactor equipped with a stirrer, similarly to a polymerization vessel, a vessel-type reactor equipped with a stirrer, smaller than a polymerization vessel, or a static mixer. It is preferred that a conjugated diene-aromatic vinyl copolymer solution be sufficiently mixed with a multifunctional modifier, and a sufficient residence time for a reaction be obtained. From this point of view, when a vessel-type reactor equipped with a stirrer is used, the volume of the reactor is preferably from 1/20 to 1/5 of that of a polymerization vessel in the turbulence conditions.

[0066]

The residence time is not particularly limited; however in the aforementioned point of view, the residence time is preferably from one minute to one hour and more preferably from one minute to 15 minutes. The reaction temperature of a coupling reaction is not particularly limited; however, in view of obtaining a sufficient modification efficiency, the reaction temperature is preferably from 50 to 110°C and more preferably from 70 to 110°C.

[0067]

(Multifunctional modifier having 4 or more functional group)

The multifunctional modifier having 4 or more functional groups which can react with the active polymer end of a conjugated diene-aromatic vinyl copolymer having an active polymer end used in the present embodiment is not particularly limited. Examples thereof may include a compound having at least one functional group selected from the group consisting of an epoxy group, a carbonyl group, a carboxylic acid ester group, a carboxylic acid amide group, an acid anhydride group, a phosphoric acid ester group, a phosphorous acid ester group, an epithio group, a thiocarbonyl group, a thiocarboxylic acid ester group, a dithiocarboxylic acid ester group, a

thiocarboxylic acid amide group, an imino group, an ethyleneimino group, a halogen group, an alkoxysilyl group, an isocyanate group, a thioisocyanate group, a conjugated diene group, and an arylvinyl group.

[0068]

Note that, in calculating the mole number of a functional group, in view of reactivity with the active polymer end of a conjugated diene-aromatic vinyl copolymer having an active polymer end, an epoxy group, a carbonyl group, an epithio group, a thiocarbonyl group, an imino group, an ethyleneimino group, a halogen group, a conjugated diene group, an arylvinyl group and an alkoxy group of an alkoxysilyl compound is regarded as a single functional group; a carboxylic acid ester group, a carboxylic acid amide group, an acid anhydride group, a thiocarboxylic acid ester group, a dithiocarboxylic acid ester group, a thiocarboxylic acid amide group, an isocyanate group and a thioisocyanate group are regarded as a bifunctional group, a phosphoric acid ester group and a phosphorous acid ester group are regarded as trifunctional group. The multifunctional modifier used in the present embodiment has a total of 4 or more of the functional groups per molecule.

[0069]

Examples of the multifunctional modifier having an epoxy group may include polyepoxy compounds such as polyepoxylated liquid polybutadiene; glycidyl amino compounds such as tetraglycidylmetaxylenediamine, tetraglycidylaminodiphenylmethane, tetraglycidyl-p-phenylenediamine and tetraglycidyl-1,3-bisaminomethylcyclohexane; and compounds having an epoxy group and another functional group such as a 3-glycidoxypropyl trimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropyl tributoxysilane, epoxylated soybean oil and epoxylated linseed oil.

[0070]

Furthermore, examples of a multifunctional modifier having an alkoxysilyl group may include alkoxysilane compounds such as tetramethoxysilane, tetraethoxysilane, tetrabutoxysilane, bis(triethoxysilyl)methane, bis(trimethoxysilyl)ethane, 1,6-bis(trimethoxysilyl)hexane, bis(triethoxysilyl)octane, bis(triethoxysilyl)ethylene, 1,1-bis(trimethoxysilylmethyl)ethylene, 1,4-bis(triethoxysilyl)benzene and bis(3-trimethoxysilylpropyl)-N-methyl amine; and compounds having an imino group and an alkoxysilyl group such as N-(1,3-dimethylbutylidene)-3-(triethoxysilyl)-1-propane amine, N-(1,3-dimethylbutylidene)-3-(tributoxysilyl)-1-propane amine, N-(1-methylpropylidene)-3-(triethoxysilyl)-1-propane amine, N-ethylidene-3-(triethoxysilyl)-1-propane amine and N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole.

[0071]

Furthermore, examples of a multifunctional modifier having a halogen group may include halogenated silane compounds such as silicon tetrachloride, silicon tetrabromide, silicon tetraiodide, bistrichlorosilylethane, 2,2,4,4,6,6-hexachloro-2,4,6-trisilaheptane and 1,2,3,4,5,6-hexakis[2-(methyldichlorosilyl)ethyl]benzene; and alkoxy halogenated silane compounds such as monochlorotrimethoxysilane, monobromotrimethoxysilane, dichlorodimethoxysilane, dibromodimethoxysilane, trichloromethoxysilane and tribromomethoxysilane.

[0072]

Furthermore, examples thereof may include halogenated tin compounds such as tin tetrachloride, tin tetrabromide and bistrichlorostannylethane; and polyhalogenated phosphorus compounds such as trichlorophosphine and tribromophosphine.

[0073]

Of them, examples of further preferable multifunctional modifiers may include a compound having a functional group having high affinity for silica, a polyepoxy compound having 4 to 6 functional groups having a large effect of improving the molecular weight by coupling and a compound having, in total, 4 to 6 functional groups of an epoxy group and an alkoxysilyl group.

Examples of further preferable multifunctional modifiers may include a glycidyl compound having an amino group in a molecule and a compound having 2 or 3 diglycidylamino groups in a molecule. Specific examples thereof may include tetraglycidylmetaxylenediamine, tetraglycidylaminodiphenylmethane, tetraglycidyl-p-phenylenediamine, and tetraglycidyl-1,3-bisaminomethylcyclohexane.

The aforementioned multifunctional modifiers may be used singly or in combination with 2 or more.

[0074]

The addition amount of each of these multifunctional modifiers, more specifically, the total mole number of functional groups in the multifunctional modifier is preferably from 0.1 to 0.5 times and more preferably from 0.2 to 0.4 times based on the mole number of an anionic polymerization initiator. To improve processability by branching and to improve strength by increasing a molecular weight, it is preferred to add 0.1 time or more the amount of the multifunctional modifier. In view of the economic efficiency, 0.5 times or less the amount of the multifunctional modifier is preferably added.

[0075]

As described above, a coupling reaction is conducted by bringing a multifunctional modifier having 4 or more functional groups which can react with an active polymer end into contact with a solution of a conjugated diene-

aromatic vinyl copolymer having the active polymer end to obtain the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment.

[0076]

As described above, after the coupling reaction is conducted, if necessary, e.g., a predetermined inactivator and a neutralizer, may be added to the solution. Examples of the inactivator may include water, alcohols such as methanol, ethanol and isopropanol. Examples of the neutralizer may include carboxylic acids such as stearic acid, oleic acid and versatic acid, aqueous inorganic acid solutions and carbon dioxide gas.

[0077]

Furthermore, since the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment itself has high viscosity, in view of preventing gelation in a finishing step after polymerization and in view of improving stability during processing, if necessary, a known rubber stabilizer is preferably added, which may include 2,6-di-tert-butyl-4-hydroxytoluene (BHT), n-octadecyl-3-(4'-hydroxy-3',5'-di-tert-butylphenol)propionate and 2-methyl-4,6-bis[(octylthio)methyl]phenol.

[0078]

In view of further improve processability of the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment, it is preferred to add extender oil. An addition method thereof is not particularly limited; however, it is preferred that extender oil be added to a polymer solution and mixed to obtain a solution of an oil extended copolymer, followed by removing the solvent. The extender oil is not particularly limited and, for example, aromatic oil, naphthenic oil and paraffinic oil may be used and preferably substitute for aromatic oil containing 3 % by mass or less of a

polycyclic aromatic hydrocarbon component defined by Method IP346 is used. Of them, substitute for aromatic oil containing 3 % by mass or less of a polycyclic aromatic hydrocarbon component is preferred in view of environmental safety and prevention of oil bleed, and further in view of wet grip property. Examples of more preferable substitute for aromatic oil may include TDAE (Treated Distillate Aromatic Extracts) and MES (Mild Extraction Solvate) described in Kautschuk Gummi Kunststoffe 52(12)799 (1999), and RAE (Residual Aromatic Extracts). The use amount of extender oil is not particularly limited; however it is usually preferably from 10 to 60 parts by mass based on 100 parts by mass of the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment and more preferably from 20 to 37.5 parts by mass.

[0079]

A method for obtaining the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment from a polymerization solution is not particularly limited and a conventionally known method can be applied. For example, a method of separating a solvent by steam stripping, etc. and thereafter separating a polymer by filtration, followed by dewatering and drying to obtain a polymer; a method of concentrating the obtained polymer in flashing tank and further devolatilizing it by vent-extruder, etc.; or a method of directly removing a solvent by drum-dryer etc. can be applied.

[0080]

[Branched conjugated diene-aromatic vinyl copolymer composition]

The branched conjugated diene-aromatic vinyl copolymer composition refers to a composition prepared by mixing predetermined materials with the aforementioned branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment. Examples of the predetermined materials may

include a rubbery polymer other than the branched conjugated diene-aromatic vinyl copolymer, an inorganic filler, a silane coupling agent, a rubber softener, a vulcanizing agent and a vulcanizing accelerator/vulcanization aid. Of these compositions, a composition at least containing an inorganic filler is preferred. More specifically, a branched conjugated diene-aromatic vinyl copolymer composition containing the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment and an inorganic filler is preferred.

[0081]

Examples of the rubbery polymer other than the branched conjugated diene-aromatic vinyl copolymer (C) may include a conjugated diene-based polymer or a hydrogenated polymer thereof, a random copolymer of a conjugated diene compound and a vinyl aromatic compound or a hydrogenated polymer thereof, a block copolymer of a conjugated diene compound and a vinyl aromatic compound or a hydrogenated polymer thereof; a non-diene-based polymer and a natural rubber.

[0082]

Specific examples thereof may include a butadiene rubber or a hydrogenated rubber thereof, an isoprene rubber or a hydrogenated rubber thereof, a styrene-based elastomer such as a styrene-butadiene rubber or a hydrogenated rubber thereof, a styrene-butadiene block copolymer or a hydrogenated copolymer thereof and a styrene-isoprene block copolymer or a hydrogenated copolymer thereof; and an acrylonitrile-butadiene rubber or a hydrogenated rubber thereof.

[0083]

Furthermore, examples of the non-diene polymer may include an olefin elastomer such as an ethylene-propylene rubber, an ethylene-propylene-

diene rubber, an ethylene-butene-diene rubber, an ethylene-butene rubber, an ethylene-hexene rubber and an ethylene-octene rubber; a butyl rubber, a brominated butyl rubber, an acryl rubber, a fluorine rubber, a silicone rubber, a chlorinated polyethylene rubber, an epichlorohydrin rubber, an α,β -unsaturated nitrile-acrylic acid ester-conjugated diene copolymer rubber, a urethane rubber and a polysulfide rubber.

[0084]

The aforementioned rubbery polymer may be a modified rubbery polymer having a functional group. The molecular weight thereof is preferably from 2,000 to 2,000,000 and further preferably from 5,000 to 1,500,000. A so-called liquid rubber of a low molecular weight may be used.

These rubbery polymers may be used singly or in combination with two or more.

[0085]

In the case where the branched conjugated diene-aromatic vinyl copolymer (C) of the present embodiment is used in combination with the aforementioned rubbery polymer, the ratio of them is not particularly limited; however, in view of obtaining a vulcanizate having an excellent balance between low hysteresis loss property and wet skid resistance and satisfying practically sufficient abrasion resistance and fracture characteristics, the ratio of the branched conjugated diene-aromatic vinyl copolymer (C)/the aforementioned rubbery polymer is preferably, from 20/80 to 100/0, more preferably from 30/70 to 90/10 and further more preferably from 50/50 to 80/20.

[0086]

Examples of the inorganic filler may include a silica-based inorganic filler and carbon black.

[0087]

Examples of the silica-based inorganic filler may include solid particles containing SiO_2 or Si_3Al as a main component of a constitutional unit. The main component here refers to a component containing 50 % by mass or more of the silica-based inorganic filler. Specific examples of the silica-based inorganic filler may include silica, clay, talc, mica, diatomaceous earth, wollastonite, montmorillonite, zeolite and an inorganic fibrous substance such as glass fiber. Furthermore, a silica-based inorganic filler with hydrophobic surface treatment and a mixture of a silica-based inorganic filler and a non silica-based inorganic filler can be also used. Of these, silica and a glass fiber are preferably used and silica is more preferably used. As the silica, for example, dry-process silica, wet-process silica and synthetic silicate silica may be used. Of these, wet-process silica is preferred since it has an excellent fracture-characteristics improving effect and an effect of balancing wet skid resistance with another property.

[0088]

In the branched conjugated diene-aromatic vinyl copolymer composition, in view of obtaining practical satisfactory abrasion resistance and fracture characteristics, the nitrogen adsorption specific surface area of the aforementioned silica-based inorganic filler, determined by the BET adsorption method, is preferably from 100 to 300 m^2/g and more preferably from 170 to 250 m^2/g .

[0089]

Furthermore, if a silica-based inorganic filler having a relatively small specific surface area (for example, specific surface area: less than 200 m^2/g) is used in combination with a silica-based inorganic filler having a relatively large specific surface area (for example, 200 m^2/g or more) as needed,

satisfactory abrasion resistance, fracture characteristics and low hysteresis loss property can be highly kept in balance.

[0090]

In the branched conjugated diene-aromatic vinyl copolymer composition, the content of the silica-based inorganic filler is not particularly limited; however, the content thereof is preferably from 0.5 to 300 parts by mass based on 100 parts by mass of the rubber component containing the branched conjugated diene-aromatic vinyl copolymer (C), more preferably from 5 to 200 parts by mass and further preferably from 20 to 100 parts by mass. In view of exerting an addition effect of a filler, the addition amount of 0.5 parts by mass or more is preferred. In contrast, in view of obtaining practically sufficient processability and mechanical strength of the composition by sufficiently dispersing a silica-based inorganic filler, 300 parts by mass or less is preferred.

[0091]

Carbon black is not particularly limited and, for example, carbon black belonging to each of the classes such as SRF, FEF, HAF, ISAF and SAF can be used. Carbon black having a nitrogen adsorption specific surface area of $50 \text{ m}^2/\text{g}$ or more and a DBP oil absorption amount of 80 mL/100 g or more is preferred.

[0092]

The content of carbon black is preferably from 0.5 to 100 parts by mass based on 100 parts by mass of a rubber component containing a branched conjugated diene-aromatic vinyl copolymer (C), more preferably from 3 to 100 parts by mass and further preferably from 5 to 50 parts by mass. In view of expressing performance such as dry grip performance and electrical conductivity required for the use in tires and the like, 0.5 parts by

mass or more is preferably added based on 100 parts by mass of the rubber component. In view of dispersibility, 100 parts by mass or less is preferably added based on 100 parts by mass of the rubber component.

[0093]

Note that, to the branched conjugated diene-aromatic vinyl copolymer composition, other than the aforementioned silica-based inorganic filler and carbon black, a metal oxide and a metal hydroxide may be added. The metal oxide here refers to solid particles containing a substance represented by chemical formula M_xO_y (M represents a metal atom, and x and y each represents an integer of from 1 to 6) as a main component of a constitutional unit. Examples thereof may include alumina, titanium oxide, magnesium oxide and zinc oxide. Furthermore, a mixture containing a metal oxide and an inorganic filler other than the metal oxide can be used. The metal hydroxide is not particularly limited and example thereof may include aluminum hydroxide, magnesium hydroxide and zirconium hydroxide.

[0094]

To the branched conjugated diene-aromatic vinyl copolymer composition, a silane coupling agent may be added. The silane coupling agent has a function of accelerating the interaction between a rubber component and a silica-based inorganic filler, and has a group having an affinity or a binding ability to each of a rubber component and a silica-based inorganic filler. Generally, a compound having a sulfur bonding moiety, an alkoxysilyl group and a silanol group moiety in a single molecule is used. In view of the above, a silane coupling agent is preferably used in combination with the aforementioned silica-based inorganic filler.

[0095]

Specific examples of the silane coupling agent may include bis-[3-(triethoxysilyl)-propyl]-tetrasulfide, bis-[3-(triethoxysilyl)-propyl]-disulfide, and bis-[2-(triethoxysilyl)-ethyl]-tetrasulfide.

[0096]

The content of the silane coupling agent is preferably from 0.1 to 30 parts by mass based on 100 parts by mass of the aforementioned silica-based inorganic filler, more preferably from 0.5 to 20 parts by mass and further preferably from 1 to 15 parts by mass. The content of the silane coupling agent is preferably 0.1 part by mass or more, in view of the blending effect and preferably 30 parts by mass or less in view of the economic efficiency.

[0097]

To the branched conjugated diene-aromatic vinyl copolymer composition, a rubber softener may be blended in order to improve processability. As the rubber softener, mineral oil or a liquid-state or low-molecular weight synthetic softener is mentioned. A mineral oil-based rubber softener called process oil or extender oil used for softening a rubber, increasing a volume thereof and improving processability thereof is a mixture of an aromatic ring, a naphthenic ring and a paraffinic chain. The softener in which the number of carbon atoms of a paraffinic chain occupies 50% or more of the total number of carbon atoms is called a paraffinic softener. The softener in which the number of carbon atoms of the naphthenic ring occupies from 30 to 45% is called as a naphthenic softener. The softener in which the number of aromatic carbon atoms exceeds 30% is called as an aromatic softener. As the rubber softener to be used in combination with the branched conjugated diene-aromatic vinyl copolymer (C), a softener in

which an aromatic compound is appropriately contained is preferred since it has good adaptability.

[0098]

The content of the rubber softener is preferably from 0 to 100 parts by mass based on 100 parts by mass of the rubber component containing a branched conjugated diene-aromatic vinyl copolymer (C), more preferably from 10 to 90 parts by mass and further preferably from 30 to 90 parts by mass. If the content of the rubber softener more than 100 parts by mass based on the rubber component, bleed-out easily occurs and the surface of the composition may become sticky. This case is unfavorable.

[0099]

A method for mixing a branched conjugated diene-aromatic vinyl copolymer (C), another rubbery polymer, and various additives such as a silica-based inorganic filler, carbon black or another filler, a silane coupling agent and a rubber softener is not particularly limited. For example, a melt kneading method using a general kneader such as an open roll, a Banbury mixer, a kneader, a single-screw extruder, a double-screw extruder and a multi-screw extruder; and a method in which components are dissolved and mixed and then heated to remove a solvent are mentioned. Of these, the melt kneading method by a roll, a Banbury mixer, a kneader or an extruder is preferred in view of productivity and satisfactory kneading property. A conjugated diene-aromatic vinyl copolymer and other components may be kneaded at a time or separately mixed multiple times.

[0100]

The aforementioned branched conjugated diene-aromatic vinyl copolymer composition may be vulcanized with a vulcanizing agent to obtain a vulcanized composition. A vulcanizing agent is not particularly limited and

for example, radical generators, such as an organic peroxide and an azo compound, oxime compounds, nitroso compounds, polyamine compounds, sulfur and sulfur compounds can be used. Examples of the sulfur compound may include sulfur monochloride, sulfur dichloride, a disulfide compound and a polymeric polysulfide compound.

[0101]

The use amount of a vulcanizing agent is not particularly limited and usually preferably from 0.01 to 20 parts by mass based on 100 parts by mass of the rubber component containing a branched conjugated diene-aromatic vinyl copolymer (C) and more preferably from 0.1 to 15 parts by mass.

[0102]

A vulcanization method is not particularly limited and a conventionally known method can be applied. The vulcanization temperature is, for example, from 120 to 200°C and preferably from 140 to 180°C. In vulcanization, if necessary, a vulcanizing accelerator, a vulcanization aid, etc. may be used. The vulcanizing accelerator is not particularly limited and a conventionally known material can be used. Examples thereof may include a sulfenamide-based, a guanidine-based, a thiuram-based, an aldehyde-amine-based, an aldehyde-ammonia-based, a thiazole-based, a thiourea-based, and a dithiocarbamate-based vulcanizing accelerators. The vulcanization aid is not particularly limited and a conventionally known material can be used. Examples thereof may include zinc oxide and stearic acid.

[0103]

The use amount of a vulcanizing accelerator is usually from 0.01 to 20 parts by mass based on 100 parts by mass of the rubber component containing a branched conjugated diene-aromatic vinyl copolymer (C) and

preferably from 0.1 to 15 parts by mass. The use amount of vulcanization aid is not particularly limited and preferably from 1 to 10 parts by mass based on 100 parts by mass of the aforementioned rubber component.

[0104]

To the branched conjugated diene-aromatic vinyl copolymer composition, as long as the purpose of the present embodiment is not impaired, various additives such as a softener and a filler, a thermal stabilizer, an antistatic agent, a weathering stabilizer, an anti-aging agent, a colorant and a lubricant other than the aforementioned ones may be used. Specific examples of the filler may include calcium carbonate, magnesium carbonate, aluminum sulfate and barium sulfate. As the thermal stabilizer, an antistatic agent, a weathering stabilizer, an anti-aging agent, a colorant and a lubricant, known materials can be applied.

Examples

[0105]

The present invention will be more specifically described below by way of Examples and Comparative Examples. Note that the present invention is not limited to the following Examples. Measurement and evaluation methods for physical properties applied to Examples and Comparative Examples will be described below.

[0106]

(1) Bound styrene amount

A chloroform solution of a measurement sample was prepared. Absorption by a phenyl group of styrene at UV254 nm was measured by a spectrophotometer for ultraviolet and visible region

(UV-2450 manufactured by Shimadzu Corporation) to obtain a bound styrene amount (mass%).

[0107]

(2) Microstructure of butadiene moiety (vinyl linkage content)

A carbon disulfide solution of a measurement sample was prepared. An infrared spectrum was measured within the range of from 600 to 1000 cm^{-1} by using a cell containing the solution and a Fourier transform infrared spectrophotometer (FT-IR230 manufactured by JASCO Corporation). A microstructure of a butadiene moiety (vinyl linkage content) was determined from the absorbance at a predetermined wavelength in accordance with the computation expression of the Hampton method.

[0108]

(3) Mooney viscosity and Mooney stress relaxation rate

A Mooney viscosity and a Mooney stress relaxation rate at a temperature of 120°C were measured in accordance with ISO289-1 and ISO289-4 by using a Mooney viscometer (VR1132, manufactured by Ueshima Seisakusho Co., Ltd.). First, a sample was preheated at 120°C for one minute, and then rotated at 2 rpm by a rotor. Four minutes later, torque was measured and determined as Mooney viscosity (ML_{1+4}). Immediately after that, rotation of the rotor was terminated. In the period of 1.6 to 5 seconds after the termination, torque was recorded in Mooney unit every 0.1 seconds. The double logarithmic graph of torque value and time (seconds) was obtained by plotting them. The slope of the resultant linear line was determined and the absolute value of the slope was regarded as Mooney stress relaxation rate (MSR).

[0109]

(4) Weight average molecular weight and molecular weight distribution

Using a gel permeation chromatographic apparatus in which three columns containing polystyrene gel as a filler were connected, measurement was performed to obtain a chromatogram. A weight average molecular weight was determined based on a calibration curve prepared by using standard polystyrene. Furthermore, the ratio of the weight average molecular to the number average molecular weight was obtained. From this, a molecular weight distribution (weight average molecular weight/number average molecular weight) was determined.

[0110]

As an eluting solution, tetrahydrofuran (THF) was used. As a column, a guard column: Tosoh Corporation, TSKguardcolumn HHR-H, column: Tosoh Corporation TSKgel G6000HHR, TSKgel G5000HHR, TSKgel G4000HHR were used. In the conditions: an oven temperature of 40°C and a THF flow rate of 1.0 mL/minute, an RI detector (HLC8020 manufactured by Tosoh Corporation) was used. A measurement sample (10 mg) was dissolved in 10 mL of THF to prepare a measurement solution. The measurement solution (200 μ L) was injected into the gel permeation chromatographic apparatus to perform measurement.

[0111]

(5) Glass transition temperature (T_g)

In accordance with ISO22768: 2006, T_g was measured by use of DSC3200S manufactured by Mac Science. While supplying helium at a flow rate of 50 mL/minute and increasing a temperature from -100°C at a rate of 20°C/minute, a DSC curve was recorded. The peak top of the DSC differentiation curve (inflection point) was regarded as a glass transition temperature.

[0112]

(6) Conversion rate

To a sealed 100 mL-bottle containing n-propyl benzene (0.50 mL) as an internal standard and toluene (about 20 mL), about 20 mL of a polymer solution obtained from a reactor outlet was poured to prepare a measurement sample. The obtained sample was measured by gas chromatography (GC) with a packed column in which apiezon grease is supported. Based on a calibration curve of 1,3-butadiene monomer and a calibration curve of a styrene monomer previously obtained, the amount of residual monomer in the polymer solution was determined. In this manner, conversion rates of 1,3-butadiene monomer and the styrene monomer were determined.

[0113]

[Example 1]

Two autoclaves (each having an interior volume of 10L and a ratio (L/D) of height (L) to diameter (D) being 4) having an inlet at the bottom portion and an outlet at the top portion and provided with a stirrer and a jacket for controlling temperature were connected in series. The first reactor was used as a polymerization reactor and the second reactor was used as a coupling reactor.

[0114]

1,3-Butadiene, styrene and n-hexane, from which impurities such as moisture were removed in advance, were added respectively at addition rates of 23.8 g/minute, 11.9 g/minute and 187.5 g/minute to prepare a solution mixture. To the obtained solution mixture, n-butyllithium (n-butyllithium for treatment) for use in an impurity inactivation treatment was added at an addition rate of 0.100 mmol/minute and mixed by use of a static mixer. The solution mixture was continuously supplied to the first reactor

(polymerization reactor), from the bottom portion. At the same time, 2,2-bis(2-oxolanyl)propane was used as a polar substance at an addition rate of 0.014 g/minute, and n-butyllithium was used as a polymerization initiator at an addition rate of 0.145 mmol/minute were supplied to the first reactor (polymerization reactor), from the bottom portion. In this manner, a polymerization reaction was continuously performed while controlling the internal temperature (temperature of the copolymer solution) at the outlet of the polymerization reactor to be 100°C. At this time, the average residence time in the reactor was 30 minutes.

[0115]

From the top portion of the first reactor (polymerization reactor), the polymer solution was continuously flowed out and supplied to the second reactor (coupling reactor). After the polymerization reaction in the first reactor (polymerization reactor) proceeded steadily, the polymer solution was sampled slowly with sufficient care so as not to bring the polymer solution into contact with the air from the inlet of the second reactor (coupling reactor), and added to a solution mixture of methanol (about 1 mL) and cyclohexane (about 30 mL). Subsequently, an antioxidant (BHT: 2,6-di-t-butyl-4-hydroxytoluene) was added to the solution mixture such that 0.2 g of the antioxidant was contained per polymer (100 g) and then the solvent was removed by a drum dryer to obtain a sample (conjugated diene-aromatic vinyl copolymer (I)) to be subjected to measurement of a molecular weight, Mooney viscosity and Mooney stress relaxation rate. Mooney viscosity and Mooney stress relaxation rate were measured after the sample was passed through 6-inch rolls set at 110°C, ten times.

[0116]

The Mooney viscosity (ML-I) of the sample (conjugated diene-aromatic vinyl copolymer (I)) at 120°C was 93.5, the Mooney stress relaxation rate (MSR-I) thereof was 0.687, and the polystyrene-equivalent weight average molecular weight (Mw-I) measured by GPC was 674,000. Furthermore, the polymerization conversion rates of 1,3-butadiene and styrene (measured at the inlet of the second reactor (coupling reactor)) reached to 98% and 96%, respectively.

[0117]

While keeping the temperature of the second reactor (coupling reactor) at 85°C, tetraglycidyl-1,3-bisaminomethylcyclohexane was added at an addition rate of 0.0184 mmol/minute to the second reactor (coupling reactor) from the bottom portion to conduct a coupling reaction. Tetraglycidyl-1,3-bisaminomethylcyclohexane was a compound having 4 epoxy groups per molecule and the ratio of the total mole number of functional groups to the mole number of n-butyllithium added (equivalent ratio) was 0.30. To the polymer solution taken out from the top portion of the second reactor (coupling reactor), an antioxidant (BHT) was continuously added at an addition rate of 0.071 g/minute (n-hexane solution) such that 0.2 g of BHT was added per polymer (100 g) to terminate the coupling reaction. Thereafter, the solvent was removed to obtain a branched conjugated diene-aromatic vinyl copolymer (C).

[0118]

The Mooney viscosity (ML-C) at 120°C of the branched conjugated diene-aromatic vinyl copolymer (C) after the coupling reaction was 134.2 and the Mooney stress relaxation rate (MSR-C) thereof was 0.401. The polystyrene-equivalent weight average molecular weight (Mw-C) measured by GPC was 886,000 and the ratio ((Mw-C)/(Mn-C)) of a weight average

molecular weight to a number average molecular weight was 2.32.

Furthermore, the bound styrene amount was 33 % by mass, the vinyl linkage content (1,2-linkage amount) in the butadiene bond unit was 34 mol% and the glass transition temperature measured by DSC was -31°C.

[0119]

To the branched conjugated diene-aromatic vinyl copolymer solution, further 37.5 parts by mass of S-RAE oil (NC-140 manufactured by Japan Energy Corporation) was added based on 100 parts by mass of the polymer. Thereafter, the solvent was removed to obtain an oil extended copolymer (Sample a). The properties of the obtained copolymer are shown in Table 1.

[0120]

[Examples 2, 3]

n-Butyllithium serving as a polymerization initiator, 2,2-bis(2-oxolanyl)propane and tetraglycidyl-1,3-bisaminomethylcyclohexane were used in the conditions shown in Table 1. Other conditions were the same as in Example 1. In this way, oil extended copolymers (Samples b, c) were obtained. The properties of the obtained copolymer are shown in Table 1.

[0121]

[Example 4]

As shown in Table 2, a polymerization reaction and a coupling reaction were conducted by employing the same amount ratio of 1,3-butadiene and styrene as in the method of Example 1, changing the supply amount of monomer, setting an average residence time to 25 minutes and the internal temperature of the reactor outlet to 105°C and changing the supply amounts of other substances as shown in Table 1. Thereafter, oil was added and the solvent was removed in the same manner as in Example 1 to obtain an oil

extended copolymer (Sample d). The properties of the obtained copolymer are shown in Table 2.

[0122]

[Example 5]

As shown in Table 2, an oil extended copolymer (Sample e) was obtained in the same manner as in Example 4 except that the addition amount of tetraglycidyl-1,3-bisaminomethylcyclohexane was changed. The properties of the obtained copolymer are shown in Table 2.

[0123]

[Example 6]

The addition amounts of n-butyllithium serving as a polymerization initiator, 2,2-bis(2-oxolanyl)propane and tetraglycidyl-1,3-bisaminomethylcyclohexane were as shown in Table 2. Other conditions were the same as in Example 4. In this way, an oil extended copolymer (Sample f) was obtained. The properties of the obtained copolymer are shown in Table 2.

[0124]

[Comparative Example 1]

As shown in Table 3, a polymerization reaction and a coupling reaction were conducted by employing the same amount ratio of 1,3-butadiene and styrene as in the method of Example 1, changing the supply amount of monomer, setting an average residence time to 45 minutes and the internal temperature of the reactor outlet to 90°C and changing the supply amounts of other substances as shown in Table 1. Thereafter, oil was added and the solvent was removed in the same manner as in Example 1 to obtain an oil extended copolymer (Sample g). The properties of the obtained copolymer are shown in Table 3.

[0125]

[Comparative Example 2]

As shown in Table 3, the addition amounts of n-butyllithium serving as a polymerization initiator and 2,2-bis(2-oxolanyl)propane were changed and further, tetraglycidyl-1,3-bisaminomethylcyclohexane was not added. Other conditions were the same as in Comparative Example 1. A polymerization reaction was performed in the same manner as in Comparative Example 1. Thereafter, oil was added and the solvent was removed in the same manner as in Example 1 to obtain an oil extended copolymer (Sample h).

[0126]

In Examples 1 to 4 and Comparative Example 1, a polymerization reaction was conducted in a single reactor, whereas in Comparative Example 2, a polymerization reaction was conducted in two reactors. A polymerization conversion rate was measured by use of a copolymer solution taken out from the top portion of the second reactor. The properties of the obtained copolymer are shown in Table 3.

[0127]

[Example 7]

As shown in Table 4, a polymerization reaction and a coupling reaction were performed by changing the amount ratio of 1,3-butadiene and styrene, changing the supply amount of monomer from those of the method of Example 1, setting an average residence time to 25 minutes and an internal temperature of the reactor outlet to 97°C and changing supply amounts of other substances. Thereafter, oil was added and the solvent was removed in the same manner as in Example 1 to obtain an oil extended copolymer (Sample i). The properties of the obtained copolymer are shown in Table 4.

[0128]

[Examples 8, 9]

The addition amounts of n-butyllithium serving as a polymerization initiator, 2,2-bis(2-oxolanyl)propane and tetraglycidyl-1,3-bisaminomethylcyclohexane were set as shown in Table 4. Oil extended copolymers (Samples j, k) were obtained by setting other conditions to be the same as shown in Example 7. The properties of the obtained copolymer are shown in Table 4.

[0129]

[Example 10]

As shown in Table 5, a polymerization reaction and a coupling reaction were conducted by employing the same amount ratio of 1,3-butadiene and styrene as in the method of Example 7, changing the supply amount of monomer, setting an average residence time to 22 minutes and the internal temperature of the reactor outlet to 102°C and by changing the supply amounts of other substances as shown in Table 1. Thereafter, oil was added and the solvent was removed in the same manner as in Example 1 to obtain an oil extended copolymer (Sample l). The properties of the obtained copolymer are shown in Table 5.

[0130]

[Comparative Example 3]

As shown in Table 5, the addition amount of tetraglycidyl-1,3-bisaminomethylcyclohexane was reduced from the amount in the method of Example 7. An oil extended copolymer (Sample m) was obtained by setting other conditions to be the same as shown in Example 7. The properties of the obtained copolymer are shown in Table 5.

[0131]

[Comparative Example 4]

As shown in Table 5, a polymerization reaction and a coupling reaction were conducted by employing the same amount ratio of 1,3-butadiene and styrene as in the method of Example 7, changing the supply amount of monomer, setting an average residence time to 45 minutes and the internal temperature of the reactor outlet to 90°C and changing the supply amounts of other substances as shown in Table 5. Thereafter, oil was added and the solvent was removed in the same manner as in Example 7 to obtain an oil extended copolymer (Sample n). The properties of the obtained copolymer are shown in Table 5.

[0132]

[Table 1]

Sample No.		Example 1	Example 2	Example 3
		a	b	c
Polymerization condition	1,3-Butadiene (g/minute)	23.8	23.8	23.8
	Styrene (g/minute)	11.9	11.9	11.9
	n-Hexane (g/minute)	187.5	187.5	187.5
	Polymerization temperature (°C)	100	100	100
	n-Butyllithium for treatment (mmol/minute)	0.100	0.100	0.100
	n-Butyllithium serving as polymerization initiator (mmol/minute)	0.145	0.158	0.182
	Polar substance ^{*1} Addition amount (g/minute)	0.014	0.015	0.017
	TGAMH ^{*2} Addition amount (mmol/minute)	0.0184	0.0192	0.0211
	Lithium equivalent ratio	0.30	0.30	0.30
	Average residence time (1st reactor) (minute)	30	30	30
	Monomer concentration (% by mass)	16	16	16
Analysis value	Polymerization conversion rate	1,3-Butadiene (%)	98	99
		Styrene (%)	96	99
	Bound styrene amount (% by mass)		33	33
	Vinyl linkage content (1,2-linkage content) (mol%)		34	34
	Glass transition temperature (°C)		-31	-31
	Analysis value of polymer before coupling	Weight average molecular weight (Mw-I) (10 ⁴ g/mol)	67.4	57.3
		Mooney viscosity at 120°C (ML-I)	93.5	70.8
		{260 - (ML-I)}/300	0.555	0.631
		{310 - (ML-I)}/300	0.722	0.797
		Mooney stress relaxation rate at 120°C (MSR-I)	0.687	0.772
	Analysis value of (final) polymer after coupling	Weight average molecular weight (Mw-C) (10 ⁴ g/mol)	88.6	71.3
		(Mw-C)/(Mn-C)	2.33	2.28
		Mooney viscosity at 120°C (ML-C)	134.2	108.9
		{214 - (ML-C)}/300	0.266	0.350
		{260 - (ML-C)}/300	0.419	0.504
		Mooney stress relaxation rate at 120°C (MSR-C)	0.401	0.478

*1 2,2-Bis(2-oxolanyl)propane

*2 Tetraglycidyl-1,3-bisaminomethylcyclohexane

[0133]

[Table 2]

Sample No.		Example 4	Example 5	Example 6
		d	e	f
Polymerization condition	1,3-Butadiene (g/minute)	28.6	28.6	28.6
	Styrene (g/minute)	14.3	14.3	14.3
	n-Hexane (g/minute)	225.1	225.1	225.1
	Polymerization temperature (°C)	105	105	105
	n-Butyllithium for treatment (mmol/minute)	0.120	0.120	0.120
	n-Butyllithium serving as polymerization initiator (mmol/minute)	0.185	0.185	0.200
	Polar substance ^{*1} Addition amount (g/minute)	0.025	0.025	0.027
	TGAMH ^{*2} Addition amount (mmol/minute)	0.0133	0.0236	0.248
	Lithium equivalent ratio	0.17	0.31	0.31
	Average residence time (1st reactor) (minute)	25	25	25
	Monomer concentration (% by mass)	16	16	16
Analysis value	Polymerization conversion rate	1,3-Butadiene (%)	98	98
		Styrene (%)	97	98
	Bound styrene amount (% by mass)		33	33
	Vinyl linkage content (1,2-linkage content) (mol%)		34	34
	Glass transition temperature (°C)		-31	-31
	Analysis value of polymer before coupling	Weight average molecular weight (Mw-I) (10 ⁴ g/mol)	67.9	62.7
		Mooney viscosity at 120°C (ML-I)	86.2	73.4
		{260 - (ML-I)}/300	0.579	0.622
		{310 - (ML-I)}/300	0.746	0.789
		Mooney stress relaxation rate at 120°C (MSR-I)	0.667	0.715
	Analysis value of (final) polymer after coupling	Weight average molecular weight (Mw-C) (10 ⁴ g/mol)	79.6	75.9
		(Mw-C)/(Mn-C)	2.48	2.35
		Mooney viscosity at 120°C (ML-C)	119.5	115.4
		{214 - (ML-C)}/300	0.315	0.329
		{260 - (ML-C)}/300	0.468	0.482
		Mooney stress relaxation rate at 120°C (MSR-C)	0.422	0.409

*1 2,2-Bis(2-oxolanyl)propane

*2 Tetraglycidyl-1,3-bisaminomethylcyclohexane

[0134]

[Table 3]

			Comparative Example 1	Comparative Example 2
Sample No.			g	h
Polymerization condition	1,3-Butadiene (g/minute)		16.0	16.0
	Styrene (g/minute)		8.0	8.0
	n-Hexane (g/minute)		125.6	125.6
	Polymerization temperature (°C)		90	90
	n-Butyllithium for treatment (mmol/minute)		0.067	0.067
	n-Butyllithium serving as polymerization initiator (mmol/minute)		0.100	0.090
	Polar substance ^{*1} Addition amount (g/minute)		0.0070	0.0065
	TGAMH ^{*2}	Addition amount (mmol/minute)	0.0125	-
		Lithium equivalent ratio	0.30	-
	Average residence time (1st reactor) (minute)		45	45
	Monomer concentration (% by mass)		16	16
Analysis value	Polymerization conversion rate	1,3-Butadiene (%)	98	99
		Styrene (%)		
			95	99
	Bound styrene amount (% by mass)		33	33
	Vinyl linkage content (1,2-linkage content) (mol%)		34	34
	Glass transition temperature (°C)		-31	-31
	Analysis value of polymer before coupling	Weight average molecular weight (Mw-I) (10 ⁴ g/mol)	63.4	-
		Mooney viscosity at 120°C (ML-I)	85.4	-
		{260 - (ML-I)}/300	0.582	-
		{310 - (ML-I)}/300	0.749	-
		Mooney stress relaxation rate at 120°C (MSR-I)	0.785	-
	Analysis value of (final) polymer after coupling	Weight average molecular weight (Mw-C) (10 ⁴ g/mol)	82.3	71.2
		(Mw-C)/(Mn-C)	2.30	2.12
		Mooney viscosity at 120°C (ML-C)	124.3	115.3
		{214 - (ML-C)}/300	0.299	0.329
		{260 - (ML-C)}/300	0.452	0.482
Mooney stress relaxation rate at 120°C (MSR-C)		0.498	0.712	

*1 2,2-Bis(2-oxolanyl)propane

*2 Tetraglycidyl-1,3-bisaminomethylcyclohexane

[0135]

[Table 4]

Sample No.		Example 7	Example 8	Example 9
		i	j	k
Polymerization condition	1,3-Butadiene (g/minute)	31.2	31.2	31.2
	Styrene (g/minute)	17.1	17.1	17.1
	n-Hexane (g/minute)	220.1	220.1	220.1
	Polymerization temperature (°C)	97	97	97
	n-Butyllithium for treatment (mmol/minute)	0.136	0.136	0.136
	n-Butyllithium serving as polymerization initiator (mmol/minute)	0.218	0.200	0.185
	Polar substance ^{*1} Addition amount (g/minute)	0.043	0.040	0.038
	TGAMH ^{*2} Addition amount (mmol/minute)	0.0292	0.0277	0.0265
	Lithium equivalent ratio	0.33	0.33	0.33
	Average residence time (1st reactor) (minute)	25	25	25
	Monomer concentration (% by mass)	18	18	18
Analysis value	Polymerization conversion rate	1,3-Butadiene (%)	99	99
		Styrene (%)	98	98
	Bound styrene amount (% by mass)		35	35
	Vinyl linkage content (1,2-linkage content) (mol%)		40	40
	Glass transition temperature (°C)		-21	-21
	Analysis value of polymer before coupling	Weight average molecular weight (Mw-I) (10 ⁴ g/mol)	59.0	63.8
		Mooney viscosity at 120°C (ML-I)	66.6	77.2
		{260 - (ML-I)}/300	0.645	0.609
		{310 - (ML-I)}/300	0.811	0.776
		Mooney stress relaxation rate at 120°C (MSR-I)	0.692	0.671
	Analysis value of (final) polymer after coupling	Weight average molecular weight (Mw-C) (10 ⁴ g/mol)	78.5	82.4
		(Mw-C)/(Mn-C)	2.35	2.32
		Mooney viscosity at 120°C (ML-C)	106.6	116.0
		{214 - (ML-C)}/300	0.358	0.327
		{260 - (ML-C)}/300	0.511	0.480
		Mooney stress relaxation rate at 120°C (MSR-C)	0.401	0.362

*1 2,2-Bis(2-oxolanyl)propane

*2 Tetraglycidyl-1,3-bisaminomethylcyclohexane

[0136]

[Table 5]

		Example 10	Comparative Example 3	Comparative Example 4
Sample No.		l	m	n
Polymerization condition	1,3-Butadiene (g/minute)	35.4	31.2	17.3
	Styrene (g/minute)	19.4	17.1	9.5
	n-Hexane (g/minute)	250.2	220.1	122.0
	Polymerization temperature (°C)	102	97	90
	n-Butyllithium for treatment (mmol/minute)	0.154	0.136	0.075
	n-Butyllithium serving as polymerization initiator (mmol/minute)	0.240	0.218	0.122
	Polar substance ^{*1} Addition amount (g/minute)	0.049	0.043	0.021
	TGAMH ^{*2} Addition amount (mmol/minute)	0.0345	0.0053	0.0492
	Lithium equivalent ratio	0.35	0.06	1.00
	Average residence time (1st reactor) (minute)	22	25	45
	Monomer concentration (% by mass)	18	18	18
Analysis value	Polymerization conversion rate	1,3-Butadiene (%)	99	99
		Styrene (%)	99	97
	Bound styrene amount (% by mass)		35	35
	Vinyl linkage content (1,2-linkage content) (mol%)		40	40
	Glass transition temperature (°C)		-21	-21
	Analysis value of polymer before coupling	Weight average molecular weight (Mw-I) (10 ⁴ g/mol)	59.7	65.2
		Mooney viscosity at 120°C (ML-I)	72.4	78.2
		{260 - (ML-I)}/300	0.625	0.606
		{310 - (ML-I)}/300	0.792	0.773
		Mooney stress relaxation rate at 120°C (MSR-I)	0.655	0.698
	Analysis value of (final) polymer after coupling	Weight average molecular weight (Mw-C) (10 ⁴ g/mol)	81.0	91.2
		(Mw-C)/(Mn-C)	2.42	2.15
		Mooney viscosity at 120°C (ML-C)	119.6	145.3
		{214 - (ML-C)}/300	0.315	0.229
		{260 - (ML-C)}/300	0.468	0.382
		Mooney stress relaxation rate at 120°C (MSR-C)	0.335	0.261

*1 2,2-Bis(2-oxolanyl)propane

*2 Tetraglycidyl-1,3-bisaminomethylcyclohexane

[0137]

[Examples 11 to 16], [Comparative Examples 5 to 8]

The samples (Samples a, b, d, e, g to i, l to n) shown in Tables 1 to 5 were used as raw-material rubbers to obtain rubber compositions containing the raw-material rubbers in accordance with the following formulations.

[0138]

- Oil extended styrene-butadiene copolymer (Samples a, b, d, e, g to i, l to n): 96.25 parts by mass

- Polybutadiene rubber having a high content of 1,4-cis (hereinafter referred to as high-cis-polybutadiene rubber) (UBEPOL BR-150 manufactured by Ube Industries, Ltd., cis-linkage content: 98%): 30.00 parts by mass

- Silica (Ultrasil VN3 manufactured by Degussa): 75.00 parts by mass

- Carbon black (N339, Tokai Carbon Co., Ltd.): 5.00 parts by mass

- Silane coupling agent (Si75 manufactured by Degussa): 6.00 parts by mass

- S-RAE oil (JOMO process NC140 manufactured by Japan Energy Corporation): 15.75 parts by mass

- Zinc oxide: 2.50 parts by mass

- Stearic acid: 2.00 parts by mass

- Wax (Sunnock N, manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.): 1.50 parts by mass

- Age resister (N-isopropyl-N'-phenyl-p-phenylenediamine): 2.00 parts by mass

- Sulfur: 2.20 parts by mass

- Vulcanizing accelerator (N-cyclohexyl-2-benzothiazylsulfonamide): 1.70 parts by mass

- Vulcanizing accelerator (diphenylguanidine): 2.00 parts by mass

Total: 241.90 parts by mass

[0139]

A method for kneading a rubber composition will be described below.

Using a sealed kneader (content: 0.3L) equipped with a temperature controller, a raw-material rubber (Samples a, b, d, e, g to i, l to n, high-cis butadiene rubber), silica, an organic silane coupling agent and process oil were kneaded as first-stage kneading in the conditions: a fill factor of 72% and a rotor rotation number of 50/57 rpm. At this time, the temperature of the kneader was controlled and a discharge temperature (the rubber compound) was controlled to 155 to 160°C. In this manner, a rubber composition was obtained.

[0140]

Subsequently, as second-stage kneading, the obtained rubber compound was cooled to room temperature, and then carbon black, zinc oxide, stearic acid, wax and an age resister were added and kneaded again. In this case, the discharge temperature (the rubber compound) was controlled to 155 to 160°C by controlling the temperature of the mixer. After cooling, as third-stage kneading, sulfur and a vulcanizing accelerator were added and kneaded by an open roll set at 70°C. Thereafter, the kneaded product was molded and vulcanized by a vulcanization press at 160°C for 20 minutes. After the vulcanization, the physical properties of the rubber composition were measured. The physical property measurement results are shown in the following Tables 6 and 7.

[0141]

The physical properties of the rubber composition were measured by the following methods.

(1) Bound rubber content

After the second-stage kneading step, a blend (about 0.2 g) was cut into about 1 mm-cubic pieces and placed in a Harris basket (100-mesh, made of wire) and weighed. Thereafter, the wire mesh was soaked in toluene at 23°C for 24 hours, dried and the weight of components insoluble in toluene was measured. Based on the weight of the insoluble components, rubber bound to a filler (branched conjugated diene-aromatic vinyl copolymer + high-cis-butadiene rubber) was calculated to determine the ratio of rubber bound to a filler to the rubber content in the initial blend.

[0142]

(2) Compound Mooney viscosity

Mooney viscosity was measured by using a Mooney viscometer in accordance with JIS K6300-1. More specifically, preheating was performed at 130°C for one minute and thereafter a rotor was rotated at a rate of two turns per minute (2 rpm). Four minutes later, viscosity was measured. The smaller the Mooney viscosity value, the lower the energy consumption during kneading time, which means that processability is satisfactory.

[0143]

(3) Tensile strength

Tensile strength was measured in accordance with the drawing test method of JIS K6251. The tensile strength values of Examples 11 to 14 and Comparative Example 5 were expressed by indexes based on that of Comparative Example 6 as being 100, whereas the tensile strength values of Examples 15, 16 and Comparative Example 8 were expressed by indexes based on that of Comparative Example 7 as being 100.

[0144]

(4) Viscoelasticity parameter

A viscoelasticity parameter was measured in a torsion mode by using a viscoelasticity tester (ARES) manufactured by Rheometric Scientific Inc. Measurement values of Examples 11 to 14 and Comparative Example 5 were expressed by indexes based on that of Comparative Example 6 as being 100, whereas the values of Examples 15, 16 and Comparative Example 8 were expressed by indexes based on that of Comparative Example 7 as being 100. $\tan\delta$ (loss tangent) measured at 0°C, a frequency of 10 Hz and a strain of 1% was used as an index of wet skid resistance. The larger the value, the more satisfactory the wet skid resistance.

[0145]

Furthermore, $\tan\delta$ (loss tangent) measured at 50°C, a frequency of 10 Hz and a strain of 3% was used as an index for a fuel-efficient property. The lower the value, the more satisfactory the low hysteresis loss property. Furthermore, G' (storage modulus) measured in the same conditions was used as an index for handling stability. The larger the value and the larger the rigidity, the more satisfactory the handling stability.

[0146]

(5) Abrasion resistance

Abrasion loss at a load of 44.1 N and a rotation number of 1000 was measured by use of an Akron abrasion tester (manufactured by Yasuda Seiki Seisakusho Ltd.) in accordance with JIS-K6264-2. The abrasion loss values of Examples 11 to 14 and Comparative Example 5 were expressed by indexes based on that of Comparative Example 6 as being 100, whereas the abrasion loss values of Examples 15, 16 and Comparative Example 8 were expressed by indexes based on that of Comparative Example 7 as being 100. The larger the index, the more excellent the abrasion resistance.

[0147]

[Table 6]

			Example 11	Example 12	Example 13	Example 14	Comparative Example 5	Comparative Example 6
Oil-extended styrene-butadiene copolymer			a	b	d	E	g	h
Compound Mooney viscosity			55	52	53	54	54	61
Bound rubber content (%)			46	44	43	45	42	39
Vulcanizate physical property	Tensile strength	Index	108	103	102	107	104	100
	Abrasion resistance	Index	108	104	103	107	102	100
	0°C tan δ (Strain 1%)	Index	100	102	99	100	100	100
	50°C tan δ (Strain 3%)	Index	95	97	97	95	98	100
	50°C G' (Strain 3%)	Index	97	98	98	97	98	100

[0148]

[Table 7]

			Example 15	Example 16	Comparative Example 7	Comparative Example 8
Oil-extended styrene-butadiene copolymer			i	l	m	n
Compound Mooney viscosity			46	49	45	58
Bound rubber content (%)			42	45	37	54
Vulcanizate physical property	Tensile strength	Index	105	107	100	110
	Abrasion resistance	Index	105	108	100	115
	0°C tan δ (Strain 1%)	Index	103	103	100	101
	50°C tan δ (Strain 3%)	Index	98	96	100	92
	50°C G' (Strain 3%)	Index	99	98	100	94

[0149]

Examples and Comparative Examples which used oil extended styrene-butadiene copolymers having the same microstructure (bound styrene amount and vinyl linkage content) are compared and discussed.

[0150]

Copolymer g of Comparative Example 1 polymerized at low temperature was not sufficiently branched and thus failed to satisfy the requirements of the above Expression (1). As is apparent from comparison between Examples 1 to 6 and Comparative Example 1 in Tables 1 to 3, residence time of each of copolymers a to f of Examples 1 to 6 in a reactor for obtaining a sufficient polymerization conversion rate can be shorter than that of copolymer g of Comparative Example 1. Therefore, the copolymers of Examples 1 to 6 were found to have excellent productivity. Furthermore, when the rubber compositions of Examples 11 to 14 are compared to that of Comparative Example 5, the rubber compositions were found to have an excellent balance between properties (such as tensile strength, abrasion resistance, low hysteresis loss property and wet skid resistance) and processability.

[0151]

Copolymer h of Comparative Example 2, which was polymerized without performing a coupling reaction, was not sufficiently branched and thus failed to satisfy the requirements of the above Expression (1). In Examples 11 to 14 using copolymers a, b, d, e of Examples 1, 2, 4, 5, as compared to Comparative Example 6 using copolymer h of Comparative Example 2, the Mooney viscosity of the blend is low and processability is satisfactory. As is apparent from $\tan\delta$ values at 50°C and 0°C, Examples 11 to 14 were found to have an excellent balance between low hysteresis loss property and wet skid resistance, and have satisfactory tensile strength and

abrasion resistance and satisfy practically sufficient abrasion resistance and fracture characteristics.

[0152]

Copolymer m of Comparative Example 3 had a small weight average molecular weight and excessively low Mooney viscosity. When Examples 15 and 16 using copolymers i and l of Examples 8 and 11 are compared to Comparative Example 7 using copolymer m of Comparative Example 3, as is apparent from $\tan\delta$ values at 50°C and 0°C, Examples 15 and 16 were found to have an excellent balance between low hysteresis loss property and wet skid resistance, have satisfactory tensile strength and abrasion resistance, and satisfy practically sufficient abrasion resistance and fracture characteristics.

[0153]

In Comparative Example 8 using copolymer n of Comparative Example 4 which was enhanced in coupling efficiency by performing polymerization at lower temperature, as is apparent from comparison between Examples 7 to 10 and Comparative Example 4, residence time in a reactor for obtaining a sufficient polymerization conversion rate is long. From this, when copolymer n of Comparative Example 4 is compared to those of Examples 7 to 10, copolymer n is inferior in productivity. Furthermore, since Mooney viscosity of copolymer n is high, the Mooney viscosity of a rubber composition blend of Comparative Example 8 is high. Thus, copolymer n was found to be inferior in processability compared to Examples 15 and 16.

[0154]

The present application was based on Japanese Patent Application No. 2009-93252 filed on April 7, 2009 with the Japan Patent Office and the content thereof is incorporated herein by reference.

Industrial Applicability

[0155]

A conjugated diene-aromatic vinyl copolymer of the present invention is industrially applicable to e.g., a tire tread material, foot wear and industrial products.

CLAIMS

What is claimed is:

1. A branched conjugated diene-aromatic vinyl copolymer (C) being a random copolymer, wherein

a bound aromatic vinyl content in the conjugated diene-aromatic vinyl copolymer (C) is from 30 to 38 % by mass,

a vinyl linkage content in total linkage units of a conjugated diene is from 30 to 43 mol%,

a polystyrene-equivalent weight average molecular weight (M_w -C) of the conjugated diene-aromatic vinyl copolymer (C) obtained by gel permeation chromatography (GPC) is from 700,000 to 1,000,000,

a ratio $((M_w-C)/(M_n-C))$ of a weight average molecular weight (M_w -C) to a number average molecular weight (M_n -C) is from 1.7 to 3.0, and

a Mooney viscosity (ML-C) and a Mooney stress relaxation rate (MSR-C) measured at 120°C satisfy the relationship represented by the following Expression (1):

$$\{214-(ML-C)\}/300 \leq (MSR-C) \leq \{260-(ML-C)\}/300 \dots (1)$$

where $100 \leq (ML-C) \leq 140$.

2. The branched conjugated diene-aromatic vinyl copolymer (C) according to claim 1, obtained by coupling a conjugated diene-aromatic vinyl copolymer (I), having a polystyrene-equivalent weight average molecular weight (M_w -I) of from 500,000 to 700,000 and a Mooney viscosity (ML-I) and a Mooney stress relaxation rate (MSR-I) measured at 120°C satisfying the relationship represented by the following Expression (2):

$$\{260-(ML-I)\}/300 \leq (MSR-I) \leq \{310-(ML-I)\}/300 \dots (2)$$

where $65 \leq (ML-I) \leq 100$,

with a multifunctional modifier having 4 or more functional groups.

3. A composition of a branched conjugated diene-aromatic vinyl copolymer comprising
 - the branched conjugated diene-aromatic vinyl copolymer (C) according to claim 1 or 2 and
 - an inorganic filler.