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 (Mw-C), and a weight average molecular weight (Mw-C)/a number average molecular weight (Mn-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~~embodiments are 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 (Mw-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 ((Mw-C)/(Mn-C)) of a weight average molecular weight (Mw-C) to a number average molecular weight (Mn-C) is from 1.7 to 3.0, and

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

[0014A]

In accordance with a first aspect, there is provided a method for producing the branched conjugated diene-aromatic vinyl copolymer (C), 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; wherein the branched conjugated diene-aromatic vinyl copolymer (C) is characterized in that the branched conjugated diene-aromatic vinyl copolymer (C) is a random copolymer, an aromatic vinyl bonding content in the conjugated diene-aromatic vinyl copolymer (C) is from 30 to 38 % by mass, a vinyl bonding content in the total bonding units of the conjugated diene is from 30 to 43 mol%, a polystyrene-equivalent weight average molecular weight (Mw-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 ((Mw-C)/(Mn-C)) of a weight average molecular weight (Mw-C) to a number average molecular weight (Mn-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 of the following Expression (1):

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

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

[0014B]

In accordance with another aspect, there is provided a method for producing the branched conjugated diene-aromatic vinyl copolymer (C), 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 from 15 minutes to 35 minutes while maintaining the internal temperature at the outlet of the reactor at from 95 to 110°C; wherein the branched conjugated diene-aromatic vinyl copolymer (C) is characterized in that the branched conjugated diene-aromatic vinyl copolymer (C) is a random copolymer, an aromatic vinyl bonding content in the conjugated diene-aromatic vinyl copolymer (C) is from 30 to 38 % by mass, a vinyl bonding content in the total bonding units of the conjugated diene is from 30 to 43 mol%, a polystyrene-equivalent weight average molecular weight (Mw-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 ((Mw-C)/(Mn-C)) of a weight average molecular weight (Mw-C) to a number average molecular weight (Mn-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 of the following Expression (1):

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

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

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

CLAIMS

1. A method for producing the branched conjugated diene-aromatic vinyl copolymer (C), 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;

wherein the branched conjugated diene-aromatic vinyl copolymer (C) is characterized in that

the branched conjugated diene-aromatic vinyl copolymer (C) is a random copolymer,

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

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

a polystyrene-equiv

alent weight average molecular weight (Mw-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 ((Mw-C)/(Mn-C)) of a weight average molecular weight (Mw-C) to a number average molecular weight (Mn-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 of the following Expression (1):

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

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

2. The method for producing the branched conjugated diene-aromatic vinyl copolymer (C) according to Claim 1, wherein the branched conjugated diene-aromatic vinyl copolymer (C) is 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 of the following Expression (2):

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

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

with a multifunctional modifier having 4 or more functional groups.

3. A method for producing the branched conjugated diene-aromatic vinyl copolymer (C), 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 from 15 minutes to 35 minutes while maintaining the internal temperature at the outlet of the reactor at from 95 to 110°C;

wherein the branched conjugated diene-aromatic vinyl copolymer (C) is characterized in that

the branched conjugated diene-aromatic vinyl copolymer (C) is a random copolymer,

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

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

a polystyrene-equivalent weight average molecular weight (Mw-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 ((Mw-C)/(Mn-C)) of a weight average molecular weight (Mw-C) to a number average molecular weight (Mn-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 of the following Expression (1):

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

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

4. The method for producing the branched conjugated diene-aromatic vinyl copolymer (C) according to Claim 3, wherein the branched conjugated diene-aromatic vinyl copolymer (C) is 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 of the following Expression (2):

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

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

with a multifunctional modifier having 4 or more functional groups.

5. The method for producing the branched conjugated diene-aromatic vinyl copolymer according to Claim 3 or 4, 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.

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 (Mw-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 ((Mw-C)/(Mn-C)) of a weight average molecular weight (Mw-C) to a number average molecular weight (Mn-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):

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

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 (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 ≤ (MSR-I) ≤ {310-(ML-I)}/300 ... (2)~~

where 65 ≤ (ML-I) ≤ 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.

4. A method for producing the branched conjugated diene-aromatic vinyl copolymer (C) according to claim 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 claim 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 claim 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.