

CRUMB AND MOLDED BALE OF CONJUGATED DIENE POLYMER

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a crumb and a bale of a conjugated diene polymer.

Description of the Related Art

In processes for producing conjugated diene polymers by solution polymerization, it is common practice to obtain solid particles (crumb) of a conjugated diene polymer by removing a solvent from a post-polymerization mixture of the conjugated diene polymer and the solvent and then fabricate the particles by compression molding into a rectangular parallelepiped molded article called a bale. For example, Japanese Patent Laid-Open No. 2012-86424 discloses a method of manufacturing bales including producing pellets from melt-kneaded and extruded rubber and compression-molding the rubber pellets. Further, for example, Japanese Patent Laid-Open No. 2008-93954 discloses a bale molding apparatus and bale manufacturing method that can prevent inclusion of metal components in the resulting bales.

SUMMARY OF THE INVENTION

In recent years, there is an increasing trend toward requiring high wear resistance of automobile tires which

are a typical application of conjugated diene polymers. To address this trend, increase in the molecular weight of conjugated diene polymers is strongly needed. In view of these circumstances, the present inventors have investigated problems from which bales can suffer because of the increase in molecular weight. As the molecular weight of a conjugated diene polymer increases, a crumb of the conjugated diene polymer, which is obtained by solvent removal following polymerization for synthesis of the conjugated diene polymer, becomes more prone to detachment from bale surfaces. The crumb may scatter around a molding machine or around a conveyor carrying molded bales during long-time operation, thus causing a working environment problem. Additionally, bales have a tendency to expand soon after molding, and the increase in the molecular weight of the conjugated diene polymer enhances this tendency and may make difficult placement of bales into containers. For bales of conjugated diene polymers having a high molecular weight, therefore, reduction in detachment of particles from the surface of the bales and reduction in expansion ratio of the bales are desired.

It is therefore an object of the present invention to reduce detachment of a crumb of a conjugated diene polymer from the surface of a bale of the conjugated diene polymer and reduce the expansion of the bale.

As a result of intensive investigations aimed at solving the above problems with prior art, the present inventors have found that controlling the specific surface areas of a crumb and a bale of a conjugated diene polymer within given ranges can lead to reduction in detachment of the crumb of the conjugated diene polymer from the surface of the bale and to reduction in expansion of the bale.

That is, the present invention is as follows.

- [1] A crumb of a conjugated diene polymer, the crumb having a specific surface area of $0.7 \text{ m}^2/\text{g}$ to $3.2 \text{ m}^2/\text{g}$.
- [2] The crumb according to [1], wherein the conjugated diene polymer comprises 30 to 90% by mass of a component having a molecular weight of 1,000,000 or more.
- [3] The crumb according to [1] or [2], further comprising 1 to 20 parts by mass of a process oil based on 100 parts by mass of the conjugated diene polymer.
- [4] A bale of a conjugated diene polymer, the bale having a specific surface area of $0.005 \text{ m}^2/\text{g}$ to $0.05 \text{ m}^2/\text{g}$.
- [5] A method of manufacturing a bale, comprising the steps of: producing crumb of a conjugated diene polymer, wherein the crumb has a specific surface area of $0.7 \text{ m}^2/\text{g}$ to $3.2 \text{ m}^2/\text{g}$; and compression-molding the crumb to obtain a bale.
- [6] The method of manufacturing the bale according to [5], further comprising the step of classifying the crumb of the conjugated diene polymer by sieving.

The bale of the present invention is resistant to detachment of the crumb of the conjugated diene polymer from the surface thereof and undergoes little expansion after molding.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, an embodiment of the present invention (hereinafter referred to as "present embodiment") will be described in detail.

The present invention is not limited to the embodiments described below and can be implemented with various modifications falling within the scope of the gist of the present invention.

[Conjugated Diene Polymer]

The monomer serving as a starting material for the conjugated diene polymer used in the present embodiment is not particularly limited and may be any polymerizable conjugated diene compound, examples of which 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. Among these, 1,3-butadiene and isoprene are preferred in view of industrial availability, and 1,3-butadiene is preferred for the purpose of imparting wear resistance, elasticity, and strength to tire treads. One of the above dienes may be used alone, or two or more thereof may be used in combination. If an impurity such as an allene or acetylene is contained in the conjugated

diene compound, the impurity may inhibit a modification reaction of the polymer terminus. Thus, the total content (mass) of such impurities is preferably 200 ppm or less, more preferably 100 ppm or less, and even more preferably 50 ppm or less.

Examples of the allene include, but are not particularly limited to, propadiene and 1,2-butadiene. Examples of the acetylene include, but are not particularly limited to, ethylacetylene and vinylacetylene.

The conjugated diene polymer used in the present embodiment may be a copolymer of a conjugated diene monomer as described above and an aromatic vinyl compound. The aromatic vinyl compound is not particularly limited and may be any monomer copolymerizable with the conjugated diene compound, and examples of the aromatic vinyl compound include styrene, m- or p-methylstyrene, α -methylstyrene, vinylethylbenzene, vinylxylene, vinylnaphthalene, diphenylethylene, and divinylbenzene. Among these, styrene is preferred in view of industrial availability. One of these compounds may be used alone, or two or more thereof may be used in combination.

When the conjugated diene polymer used in the present embodiment is a copolymer, the copolymer may be a random copolymer or a block copolymer.

Examples of the random copolymer include, but are not particularly limited to, butadiene-isoprene random

copolymer, butadiene-styrene random copolymer, isoprene-styrene random copolymer, and butadiene-isoprene-styrene random copolymer. The composition distribution of the monomers in the copolymer chain is not particularly limited, and the copolymer may be, for example, a truly random copolymer having a composition close to a statistically random composition or a tapered (gradient) random copolymer having a gradient composition distribution. The form of the linkage of the conjugated diene, namely the proportion of the 1,4-linkage or 1,2-linkage, may be the same or different among the molecular chains.

Examples of the block copolymer include, but are not particularly limited to, a two-block copolymer consisting of two blocks, a three-block copolymer consisting of three blocks, or a four-block copolymer consisting of four blocks. Denoting by "S" a block consisting of an aromatic vinyl compound such as styrene and denoting by "B" a block consisting of a conjugated diene compound such as butadiene or isoprene and/or a block consisting of a copolymer of the aromatic vinyl compound and the conjugated diene compound, the block copolymer is represented, for example, as S-B two-block copolymer, S-B-S three-block copolymer, or S-B-S-B four-block copolymer.

In the above representations, the boundary between the blocks does not need to be clearly defined. For

example, when the block B consists of a copolymer of the aromatic vinyl compound and the conjugated diene compound, the aromatic vinyl compound in the block B may be present in a uniform distribution or in a tapered distribution. The block B may include a plurality of moieties where the aromatic vinyl compound is present in a uniform distribution and/or a plurality of moieties where the aromatic vinyl compound is present in a tapered distribution. Further, the block B may include a plurality of segments with different contents of the aromatic vinyl compound. When a plurality of blocks S and a plurality of blocks B are present in the copolymer, the structural properties such as the molecular weight and composition may be the same or different for each block S and for each block B.

In the present embodiment, the weight-average molecular weight of the conjugated diene polymer is preferably 300,000 to 2,000,000. The weight-average molecular weight is preferably 800,000 or more in view of the wear resistance of tires and is preferably 1,800,000 or less in view of processability into tires.

In the present embodiment, the conjugated diene polymer preferably contains a high-molecular-weight component in view of the strength and wear resistance of silica-containing vulcanized products. The proportion of a component having a molecular weight of 1,000,000 or more may be used as an exemplary measure related to the

high-molecular-weight component, and the proportion of a component having a molecular weight of 1,000,000 or more is preferably 30 to 95% by mass, more preferably 30 to 90% by mass, and even more preferably 40 to 90% by mass. When the proportion of a component having a molecular weight of 1,000,000 or more is 30% by mass or more, excellent wear resistance is achieved. When the proportion is 95% by mass or less, silica can be well dispersed at mixing of the conjugated diene polymer and silica, and the good dispersion of silica leads to excellent fuel consumption-reducing effect and excellent grip performance of the resulting tire products. When the proportion of the high-molecular-weight component is within the above range, the likelihoods of crumb detachment and bale expansion tend to be high; in this case, therefore, the significance of controlling the specific surface area of the bale within the given range is further increased.

<Polymerization for Synthesis of Conjugated Diene Polymer>

The initiator used for polymerization of the conjugated diene or aromatic vinyl is not particularly limited and may be any anionic polymerization initiator. In view of stability and handleability, for example, alkyl compounds of metals such as aluminum, magnesium, lithium, sodium, and potassium are preferred. Among such compounds, organolithiums are particularly preferred in

view of polymerization efficiency. Examples of the organolithium used as the polymerization initiator include, but are not particularly limited to, organolithiums that are low-molecular-weight compounds or solubilized oligomers. The organolithium is not particularly limited by the form of the linkage between the organic group and lithium, and may be, for example, a compound having a carbon-lithium bond, a compound having a nitrogen-lithium bond, or a compound having a tin-lithium bond.

Examples of the organolithium having a carbon-lithium bond include, but are not particularly limited to, n-butyllithium, sec-butyllithium, tert-butyllithium, n-hexyllithium, benzyllithium, phenyllithium, and stilbenelithium.

Examples of the organolithium having a nitrogen-lithium bond include, but are not particularly limited to, lithium dimethylamide, lithium diethylamide, lithium dipropylamide, lithium di-n-hexylamide, lithium diisopropylamide, lithium hexamethyleneimide, lithium pyrrolidide, lithium piperidide, lithium heptamethyleneimide, and lithium morpholide.

The organolithium used is not limited to the monoorganolithiums mentioned above. A polyfunctional organolithium may be used alone or in combination with a monoorganolithium for polymerization.

Examples of the polyfunctional organolithium include, but are not particularly limited to, 1,4-dilithiobutane, a reaction product of sec-butyllithium and diisopropenylbenzene, 1,3,5-trilithiobenzene, a reaction product of n-butyllithium, 1,3-butadiene, and divinylbenzene, and a reaction product of n-butyllithium and a polyacetylene compound. Further, organolithiums as disclosed in US Patent No. 5,708,092, GB Patent No. 2,241,239, and US Patent No. 5,527,753 can also be used. Preferred as the organolithium are n-butyllithium and sec-butyllithium, in view of industrial availability and ease of control of polymerization reaction.

One organolithium may be used alone, or a mixture of two or more organolithiums may be used.

When an organolithium is actually used for polymerization, the organolithium is used as a solution diluted with a hydrocarbon diluent in order to improve the handleability and the dispersibility in the polymerization solution. Examples of the hydrocarbon diluent include, but are not particularly limited to, C4 to C8 hydrocarbon diluents, which may be cyclic and may contain an unsaturated bond or a branched structure (i.e., the hydrocarbon diluent may be toluene or xylene). C5 or C6 hydrocarbon diluents are preferred because they have a boiling point and vapor pressure which allow easy handling in the manufacturing process. Specifically,

pentane, normal hexane, and cyclohexane are preferably used.

When the organolithium is diluted with a hydrocarbon as described above, the concentration of the organolithium is preferably in the range of 0.01% by mass to 1% by mass and particularly preferably in the range of 0.1% by mass to 0.8% by mass in view of the polymerization initiation efficiency and uniform mixing with the monomer(s).

The polymerization reaction of the conjugated diene compound is preferably carried out in a solvent. Examples of the solvent include, but are not particularly limited to, hydrocarbon solvents such as saturated hydrocarbons and aromatic hydrocarbons. Specifically, for example, mixtures of alicyclic hydrocarbons such as butane, pentane, normal hexane, isohexane, heptane, cyclopentane, cyclohexane, methylcyclopentane, and methylcyclohexane are preferred. One of these hydrocarbons may be used alone, or two or more thereof may be used in combination. In order to reduce the size of the copolymer particles obtained after solvent removal, a mixed solvent containing normal hexane is more preferred. In order to prevent scale formation in the polymerization vessel, a mixed solvent of normal hexane, isohexane, and cyclohexane is particularly preferred. When a mixed solvent is used, the proportion of normal hexane in the mixed solvent is preferably 20 to 80% by

mass, more preferably 30 to 70% by mass, and particularly preferably 40 to 65% by mass. The reason why the proportion of normal hexane is preferably 20% by mass or more is that in this case the residual solvent content after solvent removal can be reduced, and the reason why the proportion of normal hexane is preferably 80% by mass or less is that in this case scale formation in the polymerization vessel can be prevented.

Prior to the polymerization reaction, an allene or acetylene contained as an impurity is preferably treated with an organometal compound, because the pretreatment tends to give a polymer with a high content of active terminal and, when the polymerization is followed by a modification reaction, result in a high degree of modification.

For the polymerization reaction of the conjugated diene compound, a polar compound may be added. The polar compound can be used to allow the aromatic vinyl compound to undergo random copolymerization with the conjugated diene compound, and can also be used as a vinylation agent for controlling the microstructure of the conjugated diene moiety. The polar compound may exert an effect, for example, on improvement in polymerization rate.

Examples of polar compounds that can be used include, but are not particularly limited to: 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, dipiperidinoethan, trimethylamine, triethylamine, pyridine, and quinuclidine; alkali metal alkoxide compounds such as potassium-t-amylate, potassium-t-butylate, sodium-t-butylate, and sodium amylate; and phosphine compounds such as triphenylphosphine. One of these polar compounds may be used alone, or two or more thereof may be used in combination.

The amount of the polar compound used is not particularly limited and may be chosen, for example, depending on the purpose. In general, the amount of the polar compound is preferably 0.01 to 100 moles based on 1 mole of the polymerization initiator. Such a polar compound (vinylation agent) can be used as a regulator for the microstructure of the conjugated diene moiety of the polymer in an amount appropriate for the desired vinyl bond content.

Many polar compounds further exhibit an advantageous randomization effect in the copolymerization of the conjugated diene compound and the aromatic vinyl compound and can be used as an agent for adjustment of the distribution of the aromatic vinyl compound or for adjustment of the styrene block content. A method that

may be used to allow the conjugated diene compound and the aromatic vinyl compound to undergo random polymerization is, for example, a method as disclosed in Japanese Patent Laid-Open No. 59-140211, in which 1,3-butadiene is intermittently added in several portions during polymerization.

The polymerization temperature is not particularly limited and may be any temperature at which the polymerization can take place. In view of the productivity, the polymerization temperature is preferably 0°C or higher. In order to avoid deactivation during the polymerization, the polymerization temperature is preferably 120°C or lower. A polyfunctional aromatic vinyl compound such as divinylbenzene for controlling branching may be used in order to prevent cold flow of the conjugated diene polymer.

The process for the polymerization reaction may be any of a batch process, semi-batch process, and continuous process. A continuous process is preferred because in general this type of process yields a wide molecular weight distribution and is likely to give a high-molecular-weight component.

If necessary, a deactivator, a neutralizer, or another additive may be added to the reaction solution. Examples of the deactivator include, but are not particularly limited to, water and alcohols such as methanol, ethanol, and isopropanol. Examples of the

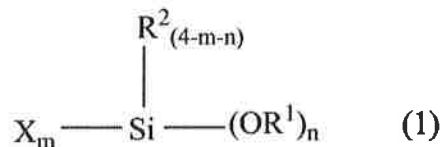
neutralizer include, but are not particularly limited to, carboxylic acids such as stearic acid, oleic acid, and versatic acid, aqueous solutions of inorganic acids, and carbon dioxide gas.

Further, it is preferable to add a rubber stabilizer to the resulting conjugated diene polymer in order to prevent gel formation after polymerization or improve the stability of the polymer during processing. The rubber stabilizer used is not particularly limited and may be a known stabilizer. Preferred examples include antioxidants such as 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.

After the conjugated diene polymer is obtained by the method as described above, the conjugated diene polymer may be modified by reacting a compound having at least one functional group selected from an epoxy group, an alcohol group, an amino group, an isocyanate group, a cyanurate group, a silanol group, and an alkoxy group bonded to silicon, with the active terminal of the conjugated diene polymer. When the polymer is used for a silica-containing composition, it is preferable, in view of silica dispersibility, to carry out the modification with a compound having at least one functional group selected from an epoxy group, a silanol group, and an alkoxy group bonded to silicon.

Examples of the compound having an epoxy group include, but are not particularly limited to: polyglycidyl ethers of polyols, such as ethylene glycol diglycidyl ether and glycerin triglycidyl ether; polyglycidyl ethers of aromatic compounds having two or more phenol groups, such as 4,4'-diglycidyl-bisphenol A; polyepoxy compounds such as 1,4-diglycidylbenzene, 1,3,5-triglycidylbenzene, and polyepoxidized liquid polybutadiene; epoxy group-containing tertiary amines such as 4,4'-diglycidyl-diphenylmethylaniline and 4,4'-diglycidyl-dibenzylmethylaniline; and diglycidylamino compounds such as diglycidylaniline, diglycidyl-o-toluidine, tetraglycidyl-m-xylenediamine, tetraglycidylaminodiphenylmethane, tetraglycidyl-p-phenylenediamine, diglycidylaminomethylcyclohexane, tetraglycidyl-1,3-bisaminomethylcyclohexane, and tetraglycidyl-1,3-bisaminomethylcyclopentane. Among these, polyfunctional compounds having a diglycidylamino group are preferred. The number of epoxy groups in the molecule of the polyfunctional compounds having a diglycidylamino group is two or more, preferably three or more, and more preferably 4 or more.

Examples of the modifier having a silanol group and/or an alkoxyl group bonded to silicon include, but are not particularly limited to, compounds of the following formula (1).

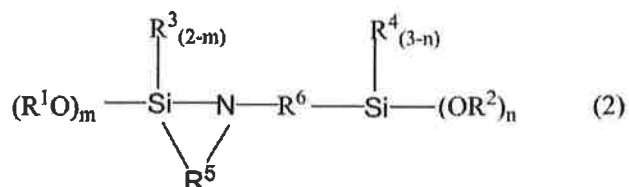


wherein X is any one selected from Cl, Br, and I, R¹ and R² are each independently any one selected from an alkyl group, an aryl group, or a vinyl group, m is an integer of 1 to 4, n is an integer of 1 to 3, and m + n is 2 to 4.

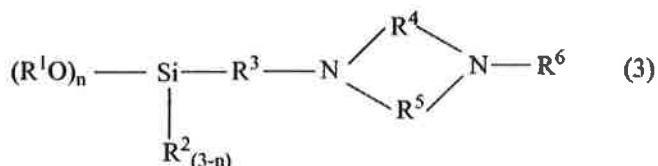
R¹ and R² may be substituted.

Specific examples of the compounds of the formula (1) include, but are not particularly limited to, dimethoxydimethylsilane, diethoxydiethylsilane, triphenoxyvinylsilane, trimethoxyvinylsilane, triethoxyvinylsilane, tri(2-methylbutoxy)ethylsilane, tri(2-methylbutoxy)vinylsilane, triphenoxyphenylsilane, tetraphenoxysilane, tetraethoxysilane, tetramethoxysilane, tetrakis(2-ethylhexyloxy)silane, phenoxydivinylchlorosilane, methoxydiethylchlorosilane, diphenoxymethylchlorosilane, diphenoxyphenyliodosilane, diethoxymethylchlorosilane, dimethoxyethylchlorosilane, triethoxychlorosilane, triphenoxychlorosilane, tris(2-ethylhexyloxy)chlorosilane, phenoxymethyldichlorosilane, methoxyethyldichlorosilane, ethoxymethyldichlorosilane, phenoxyphenyldiiodosilane, phenoxydichlorosilane, dimethoxydichlorosilane, and bis(2-methylbutoxy)dibromosilane.

Further, a compound of the following formula (2) or (3), which has in the molecule a N atom and a plurality of alkoxyethyl groups, is preferably used as the alkoxyethyl group-containing modifier.



wherein R¹ to R⁴ are each independently an alkyl group having 1 to 20 carbon atoms or an aryl group, R⁵ is an alkylene group having 1 to 10 carbon atoms, R⁶ is an alkylene group having 1 to 20 carbon atoms, m is an integer of 1 or 2, and n is an integer of 2 or 3.



wherein R¹ and R² are each independently an alkyl group having 1 to 20 carbon atoms or an aryl group, R³ is an alkylene group having 1 to 20 carbon atoms, R⁴ and R⁵ are each independently a hydrocarbon group having 1 to 6 carbon atoms and forming a ring structure consisting of five or more atoms together with the adjacent two N atoms, R⁶ is a hydrocarbon group having 1 to 20 carbon atoms, a hydrocarbon group having 1 to 20 carbon atoms and substituted with a heteroatom bearing no active hydrogen, or a silyl group substituted with three organic groups, and n is an integer of 2 or 3.

R¹ to R⁶ may be substituted.

Examples of the modifier of the formula (2) include, but are not particularly limited to, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-(4-trimethoxysilylbutyl)-1-aza-2-silacyclohexane, 2,2-dimethoxy-1-(5-trimethoxysilylpentyl)-1-aza-2-silacycloheptane, 2,2-dimethoxy-1-(3-dimethoxymethylsilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-diethoxyethylsilylpropyl)-1-aza-2-silacyclopentane, 2-methoxy-2-methyl-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2-ethoxy-2-ethyl-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, 2-methoxy-2-methyl-1-(3-dimethoxymethylsilylpropyl)-1-aza-2-silacyclopentane, and 2-ethoxy-2-ethyl-1-(3-diethoxyethylsilylpropyl)-1-aza-2-silacyclopentane. Among these, modifiers of the formula (2) wherein m is 2 and n is 3 are preferred in view of reactivity and interactivity between the functional group of the modifier and an inorganic filler such as silica and in view of tensile properties. Specifically, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane and 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane are preferred.

Examples of the modifier of the formula (3) include, but are not particularly limited to, 1-[3-

(trialkoxysilyl)-propyl]-4-alkylpiperazine, 1-[3-(alkyldialkoxysilyl)-propyl]-4-alkylpiperazine, 1-[3-(trialkoxysilyl)-propyl]-3-alkylimidazolidine, 1-[3-(alkyldialkoxysilyl)-propyl]-3-alkylimidazolidine, 1-[3-(trialkoxysilyl)-propyl]-3-alkylhexahydropyrimidine, 1-[3-(alkyldialkoxysilyl)-propyl]-3-alkylhexahydropyrimidine, 3-[3-(trialkoxysilyl)-propyl]-1-alkyl-1,2,3,4-tetrahydropyrimidine, and 3-[3-(alkyldialkoxysilyl)-propyl]-1-alkyl-1,2,3,4-tetrahydropyrimidine. Specific examples are listed below.

That is, examples of the modifier of the formula (3) include 1-[3-(triethoxysilyl)-propyl]-4-methylpiperazine, 1-[3-(diethoxyethylsilyl)-propyl]-4-methylpiperazine, 1-[3-(trimethoxysilyl)-propyl]-3-methylimidazolidine, 1-[3-(diethoxyethylsilyl)-propyl]-3-ethylimidazolidine, 1-[3-(triethoxysilyl)-propyl]-3-methylhexahydropyrimidine, 1-[3-(dimethoxymethylsilyl)-propyl]-3-methylhexahydropyrimidine, 3-[3-(tributoxysilyl)-propyl]-1-methyl-1,2,3,4-tetrahydropyrimidine, 3-[3-(dimethoxymethylsilyl)-propyl]-1-ethyl-1,2,3,4-tetrahydropyrimidine, 1-(2-ethoxyethyl)-3-[3-(trimethoxysilyl)-propyl]-imidazolidine, and (2-{3-[3-(trimethoxysilyl)-propyl]-tetrahydropyrimidine-1-yl}-ethyl)dimethylamine. A preferred compound is 1-[3-(triethoxysilyl)-propyl]-4-methylpiperazine.

A crumb of a conjugated diene polymer can be obtained, for example, by removing a solvent from a solution of the conjugated diene polymer.

Examples of the method for solvent removal include, but are not particularly limited to, a steam stripping method as disclosed in International Publication No. WO 2013-080969, a flush evaporation method as disclosed in Japanese Patent Laid-Open No. 6-93014, and a method that accomplishes solvent removal in conjunction with conveyance by means of a twin screw.

A process oil may be added to the conjugated diene polymer to give an oil-extended conjugated diene polymer. Examples of the process oil include, but are not particularly limited to, aromatic, naphthenic, and paraffinic RAE (residual aromatic extracts), MES (mild extracted solvates), and TDAE (treated distilled aromatic extracts), among which TDAE are preferred in view of the moldability and the vulcanization properties of a silica-containing mixture.

The amount of the process oil added is preferably 1 to 50 parts by mass, more preferably 1 to 30 parts by mass, even more preferably 5 to 30 parts by mass, particularly preferably 5 to 20 parts by mass, based on 100 parts by mass of the conjugated diene polymer. When the amount of the process oil added is 1 part by mass or more, the formation of fines can be reduced during control of the specific surface area of the conjugated

diene polymer, and when the amount of the process oil added is 50 parts by mass or less, good solvent removability is achieved.

The process oil may be added prior to solvent removal from the solution of the conjugated diene polymer or may be added by kneading after solvent removal.

The content of residual volatile matter in the conjugated diene polymer crumb obtained after solvent removal is preferably 100 to 10,000 ppm, more preferably 200 to 7,000 ppm, and particularly preferably 500 to 5,000 ppm. A residual volatile matter content of 10,000 ppm or less is preferred in view of working environment because in this case the amount of gas generated during the bale molding step will be small. When the residual volatile matter content is 100 ppm or more, scattering of rubber powder is reduced. The term "residual volatile matter" as used herein refers to, for example, hexane used in the production process of the conjugated diene polymer or water used in the solvent removal step.

The method for adjusting the residual volatile matter content is not particularly limited, and exemplary methods used when the solvent removal is carried out by steam stripping include: adjusting the temperature or amount of the steam brought into contact with the conjugated diene polymer; adding a surfactant to the steam; and adjusting the shape or rotation speed of a rotating blade used for mixing of the steam and the

conjugated diene polymer. Among these methods, adjusting the temperature of the steam is simple and effective. If the residual volatile matter content is more than 10,000 ppm, the content can be adjusted to 10,000 ppm or less by elevating the steam temperature. If the residual solvent content is less than 100 ppm, the content can be adjusted to 100 ppm or more by lowering the steam temperature. When the solvent removal is carried out in conjunction with conveyance by means of a twin screw, a simple and effective method is to adjust the heating temperature of the twin-screw apparatus. If the residual volatile matter content is more than 10,000 ppm, the content can be adjusted to 10,000 ppm or less by elevating the heating temperature. If the residual solvent content is less than 100 ppm, the content can be adjusted to 100 ppm or more by lowering the heating temperature.

The particle size of the conjugated diene polymer crumb obtained after the solvent removal is preferably 0.1 to 20 mm, and, in view of handleability, is preferably 0.5 to 15 mm. When the particle size of the conjugated diene polymer crumb is 0.1 mm or more, the amount of the crumb detached from the molded bale is small, and when the particle size of the conjugated diene polymer crumb is 20 mm or less, the expansion of the bale after bale molding is reduced.

The method for adjusting the particle size of the conjugated diene polymer crumb is categorized into

adjustment carried out in the course of a process in which the polymer solution obtained after polymerization is subjected to solvent removal to produce the crumb and adjustment carried out by processing the produced crumb. Examples of the method used when the adjustment is carried out in the course of the process of solvent removal for production of the crumb include, but are not particularly limited to: adjusting the amount of the process oil to be added to the polymer solution; adjusting the size of the die opening of a dry extruder; and adjusting the conditions of the solvent removal by introduction of the polymer solution into hot water. Examples of the method used in the latter case where the adjustment is carried out by processing the produced crumb include, but are not particularly limited to: classifying the crumb by sieving; and deagglomerating or pulverizing the crumb with a mixer or granulator.

The specific surface area of the conjugated diene polymer crumb of the present embodiment is 0.7 to 3.2 m^2/g and, in view of handleability, is more preferably 1.0 to 3.0 m^2/g . When the specific surface area of the conjugated diene polymer crumb is 0.7 m^2/g or more, each crumb particle can have a large area of adhesion to the neighboring crumb particles in molding of the crumb into a bale, so that the crumb will be resistant to detachment from the bale. When the specific surface area of the conjugated diene polymer crumb is 3.2 m^2/g or less, the

crumb particles are compressed to a high density in molding of the crumb into a bale, and the voids between the crumb particles are reduced, so that the expansion of the bale will be reduced.

Examples of the method for adjusting the specific surface area of the conjugated diene polymer crumb within the above range include, but are not particularly limited to, classifying the conjugated diene polymer crumb by sieving into groups and then adjusting the proportion of the sieved crumb of each group.

The method of manufacturing bales according to the present embodiment comprises the steps of: producing crumb of a conjugated diene polymer, wherein the crumb has a specific surface area of $0.7 \text{ m}^2/\text{g}$ to $3.2 \text{ m}^2/\text{g}$; and compression-molding the crumb to obtain a bale. Preferably, the method of manufacturing bales according to the present embodiment further comprises the step of classifying the crumb of the conjugated diene polymer by sieving.

The particles of the conjugated diene polymer crumb may be closely adhered to each other in compression molding of the crumb, and thus the specific surface area of the bale will be smaller than the specific surface area of the crumb. The adhesion between the crumb particles in compression molding can be adjusted depending on the molecular weight of the conjugated diene polymer, the proportion of the process oil, and the

temperature and pressure during compression. For example, when it is desired to increase the adhesion between the crumb particles and decrease the specific surface area of the bale, it is preferable to decrease the molecular weight of the conjugated diene polymer, increase the proportion of the process oil, and raise both the temperature and pressure during compression.

The specific surface area of the bale of the present embodiment is 0.005 to 0.05 m²/g and, in view of film packaging, is more preferably 0.01 to 0.04 m²/g. The reason why the specific surface area of the bale is preferably 0.005 m²/g or more is that in this case the expansion of the bale is reduced, and the reason why the specific surface area of the bale is preferably is 0.05 m²/g or less is that in this case the detachment of the crumb from the bale is reduced.

The specific surface areas of crumb and bales of conjugated diene polymers can be determined by a BET method. Nitrogen or krypton gas can be used as the adsorbent. When the specific surface area is less than 0.1 m²/g, krypton gas is preferred because the use of this gas yields high measurement accuracy.

The specific surface area of a bale may vary from site to site in the bale. The specific surface area in the central region of the bale has a high correlation with bale expansion and crumb detachment, and thus a sample used for specific surface area measurement is

preferably obtained from the central region of the bale. The "central region" refers to a point at which the sum of the distances from all the faces of the bale is largest.

The crumb used for bale molding may be the crumb obtained after solvent removal as such, as long as the specific surface area of the molded bale will be within the above range. It is preferable, after solvent removal, to classify the crumb by sieving according to particle size and mix the classified crumb particles in appropriate proportions.

If the specific surface area of the bale molded using the crumb obtained after solvent removal as such is beyond the upper limit of the above range, it is recommended to classify the crumb by sieving and increase the proportion of large-size crumb particles while decreasing the proportion of small-size crumb particles. If the specific surface area of the bale molded using the crumb obtained after solvent removal as such is less than the lower limit of the above range, it is recommended to decrease the proportion of large-size crumb particles while increasing the proportion of small-size crumb particles.

For example, assume that in the crumb obtained after solvent removal as such, the weight-average molecular weight of the conjugated diene polymer is 1,000,000 and the proportion of the process oil is 10 parts by mass,

and that the crumb is sieved through metal sieves with opening sizes of 0.5 mm, 3.4 mm, 4.0 mm, 6.7 mm, 8.0 mm, and 9.5 mm. If the mass proportions of the crumb retained on these sieves are 30, 10, 10, 20, 20, and 10 parts by mass respectively and the specific surface area of the bale is 0.004 to 0.0048 m²/g, the bale specific surface area can be adjusted to 0.030 to 0.038 m²/g by decreasing the proportion of the crumb on the 0.5-mm sieve to 10 parts by mass, increasing the proportion of the crumb on the 3.4-mm sieve to 20 parts by mass, and increasing the proportion of the crumb on the 4.0-mm sieve to 20 parts by mass.

The way of classification of the crumb by sieving is not particularly limited and, for example, the classification by sieving can be carried out according to JIS Z 8815:1994 "Test sieving-General requirements". The classification by sieving is done using a plurality of sieves with different opening sizes. In selecting the sieves, it is recommended that a sieve through which even the smallest-size crumb particles cannot pass be selected as the sieve with the smallest opening size and that a sieve having an opening size slightly smaller than the largest-size crumb particles be selected as the sieve with the largest opening size. It is preferable to use at least other three sieves with different opening sizes intermediate between the largest opening size and the

smallest opening size, because in this case the accuracy of control of the bale specific surface area is improved.

The compression pressure during bale molding is preferably 3 to 30 MPa and more preferably 10 to 20 MPa. When the compression pressure during bale molding is 30 MPa or less, the apparatus used can be compactly designed to give good installation efficiency. When the compression pressure during bale molding is 3 MPa or more, high bale moldability can be achieved. High bale moldability tends to lead to smooth surface of the bale, non-occurrence of polymer detachment after the molding step, and reduction in post-molding expansion.

The temperature of the conjugated diene polymer during bale molding is preferably 30 to 120°C and, in view of reduction in residual solvent content and prevention of thermal deterioration, is more preferably 50 to 100°C. The reason why the temperature of the conjugated diene polymer during bale molding is preferably 30°C or higher is that in this case high bale moldability is achieved, and the reason why the temperature of the conjugated diene polymer during bale molding is preferably 120°C or lower is that in this case gel formation caused by thermal deterioration after bale molding is reduced.

With the molecular weight of the conjugated diene polymer and the proportion of the process oil kept constant, the specific surface area of the bale decreases

with increase in the temperature and pressure during bale molding.

The pressure retention time during compression is preferably 3 to 30 seconds and more preferably 5 to 20 seconds. When the pressure retention time during compression is 30 seconds or less, the production efficiency is high, and when the pressure retention time during compression is 5 seconds or more, the moldability is high.

Molded bales may be individually packaged with a resin film to avoid adhesion between the molded bales. The resin of the film is not particularly limited and, for example, PET, polyethylene, or polystyrene can be used.

The resulting bales are placed into containers for transportation. It is preferable that the expansion ratio of the bales, as measured 1 day after molding, be less than 5%, because in this case the placement into the containers can be efficiently accomplished.

A hole may be formed in the resin film in order to prevent water in the bale from forming condensation on the film during transportation.

The conjugated diene polymer may be combined with another rubber material such as natural rubber or with an inorganic material such as silica or carbon and processed into, for example, tires, various types of industrial belts, and footwears.

EXAMPLES

The present invention will be described in more detail by the following examples. The present invention is not limited by the following examples and comparative examples, and other variations are possible without departing from the gist of the invention.

(1) Bonded Styrene Content

100 ml of solution was sampled from the polymerization solution output from the polymerization reaction vessel, and 1 ml of ethanol was added and mixed with the sampled solution to deactivate the active terminal of the polymer molecular chain to obtain a polymer solution. Subsequently, a vacuum dryer was used to remove the solvent from the polymer solution, and thus a solid sample for measurement was prepared. Chloroform was added to the solid sample to give a chloroform solution, and this chloroform solution was subjected to the measurement of the bonded styrene content (% by mass) on the basis of 254-nm UV absorption by the phenyl group of styrene (apparatus: UV-2450, available from Shimadzu Corporation).

(2) Vinyl Bond Content of Butadiene Moiety

A solid sample obtained in the same manner as in (1) was dissolved in 10 mL of carbon disulfide to prepare a solution cell. The solution cell was subjected to the measurement of an infrared spectrum in the range from 600

to 1000 cm^{-1} with an infrared spectrophotometer (available from JASCO Corporation under the product name "FT-IR230"). Using the absorbance obtained as a result of the measurement, the microstructure of the butadiene moiety, i.e., the vinyl bond content (mol%) of the butadiene moiety was determined according to the calculation formula of the method of Hampton (the method described by R.R. Hampton in *Analytical Chemistry* 21,923 (1949)).

(3) Molecular Weight and Molecular Weight Distribution

GPC employing a column packed with a filler of polystyrene gel was used to measure chromatograms of the sample and standard polystyrene. A calibration curve was created from the measurement result of standard polystyrene, and the molecular weight and molecular weight distribution of the sample were calculated based on the calibration curve. The eluent used was tetrahydrofuran (THF). For the measurement, 10 mg of the sample was dissolved in 20 ml of THF, and the resulting solution was injected into the 200 μl column. The measurement was conducted using HLC 8020 of Tosoh Corporation (detector: RI) at an oven temperature of 40°C and a THF flow rate of 1.0 ml/min.

(4) Measurement of Specific Surface Area

The specific surface area was determined by a BET method. Specifically, the sample was devolatilized under vacuum at 25°C for 8 hours, after which adsorption-

desorption isotherm was measured using krypton gas to determine the specific surface area.

For the measurement on bales, a portion of the central region equally distant from all the faces of the rectangular parallelepiped body was used as the measurement sample.

(5) Bale Expansion Ratio

The bale expansion ratio was determined using the following equation (1) from the bale volume (V_0) m^3 immediately after molding and the bale volume (V_1) m^3 at 1 day after molding.

$$\text{Bale expansion ratio (\%)} = 100 \times \{(V_1) - V_0\} / (V_0) \dots$$

(1)

In view of the efficiency of placement of bales into metal containers, the bale expansion ratio is preferably less than 5%.

(6) Test of Crumb Detachment

A bale dropping test was conducted, and the amount of the conjugated diene polymer crumb detached from the molded bale was determined. Specifically, the bale was dropped vertically on a concrete floor from a height of 100 cm, and the amount of the conjugated diene polymer crumb detached from the bale was measured. The amount of the conjugated diene polymer crumb detached is preferably small because this means that the amount of the polymer crumb to be detached from the bale after the molding step in the actual manufacturing process will also be small.

The amount of the conjugated diene polymer crumb detached is preferably less than 0.2% by mass based on the whole amount of the bale.

(Production Example 1 of Solution of Oil-Extended Conjugated Diene Polymer A)

Two 10 L reactors ($L/D = 4$, where L/D represents the ratio of the length (L) of the reactor to the diameter (D) of the reactor) equipped with a stirrer with four paddles were arranged in series, and the first reactor was used as a polymerization reactor while the second reactor was used as a modification reactor. 1,3-Butadiene, styrene, and n-hexane, from which impurities such as water were removed beforehand, were delivered at rates of 22.0 g/min, 7.1 g/min, and 144 g/min, respectively, to mix them together. Further, for impurity deactivating treatment, n-butyllithium (treatment n-butyllithium) was added at a rate of 0.10 mmol/min using a static mixer immediately before the mixture entered the polymerization reactor. After that, the mixture was continuously supplied to the bottom of the polymerization reactor. Further, as a polar substance, 2,2-bis(2-oxolanyl)propane, was supplied to the bottom of the polymerization reactor at a rate of 0.040 g/min while as a polymerization initiator, n-butyllithium, was supplied to the bottom of the polymerization reactor at a rate of 0.180 mmol/min, and the polymerization reaction was allowed to continue with

the inside temperature at the outlet of the reactor being maintained at 90°C. The polymerization solution output from the first reactor for polymerization was directly supplied to the second reactor for modification.

The temperature of the modification reactor was maintained at 85°C, and tetraglycidyl-1,3-bisaminomethylcyclohexane was added as a modifier through the bottom of the modification reactor at a rate of 0.35 mmol/min to cause a modification reaction, in consequence of which a solution of conjugated diene polymer A was output from the modification reactor. TDAE oil (VIVATEC 500) was added to the solution to obtain a solution of oil-extended conjugated diene polymer A.

Analysis of the conjugated diene polymer A revealed that the bonded styrene content was 24% by mass, the bonded butadiene content was 76% by mass, the vinyl bond content in butadiene was 65 mol%, the weight-average molecular weight (Mw) was 1,050,000, and the proportion of a component having a molecular weight of 1,000,000 or more was 45% by mass.

(Production Example 2 of Solution of Oil-Extended Conjugated Diene Polymer B)

A solution of conjugated diene polymer B was obtained in the same manner as in Production Example 1 of the solution of oil-extended conjugated diene polymer A, except that 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane was used as a modifier instead of

tetraglycidyl-1,3-bisaminomethylcyclohexane. A desired amount of TDAE oil (VIVATEC 500) was added to the solution output from the outlet of the reactor, and thus a solution of oil-extended conjugated diene polymer B was obtained.

Analysis of the conjugated diene polymer B revealed that the bonded styrene content was 24% by mass, the bonded butadiene content was 76% by mass, the vinyl bond content in butadiene was 65 mol%, the weight-average molecular weight (Mw) was 1,300,000, and the proportion of a component having a molecular weight of 1,000,000 or more was 70% by mass.

[Production Example 1 of Conjugated Diene Polymer Crumb]

The solution of conjugated diene polymer was continuously supplied to a twin-screw extruder with a screw diameter of 50 mm and L/D of 10, at a rate of 5 kg per hour through the inlet port of the extruder. A heat carrier oil at 180°C was supplied to the jacket of the twin-screw extruder to heat the solution of conjugated diene polymer. The vent port was connected to a vacuum pump through a pipe to maintain the internal pressure of the extruder at 100 torr. The solvent of the conjugated diene polymer solution was removed in the extruder. The conjugated diene polymer obtained by solvent removal was discharged as particles (crumb) into a tank connected to the discharge port of the twin-screw extruder.

[Production Example 2 of Conjugated Diene Polymer Crumb]

5 L of hot water at 80°C was placed in a 10 L container and, under stirring with a paddle stirrer, the solution of conjugated diene polymer was added dropwise at a rate of 100 g per minute for 30 minutes. After the dropwise addition, the stirring was continued for another 30 minutes to accomplish solvent removal. The conjugated diene polymer crumb formed in the hot water was dried to obtain conjugated diene polymer crumb.

[Method of Preparation of Crumb for Bale Molding]

The preparation was carried out according to "JIS Z 8815:1994 "Test sieving-General requirements". The crumb as obtained after solvent removal was sieved through metal sieves having a diameter of 200 mm and opening sizes of 0.5 mm, 3.4 mm, 4.0 mm, 6.7 mm, 8.0 mm, and 9.5 mm, and the conjugated diene polymer crumb retained on each metal sieve was separately collected. For example, the crumb retained on the metal sieve with an opening size of 4.0 mm was crumb that passed through the metal sieve with an opening size of 6.7 mm but failed to pass through the 4.0-mm metal sieve, and this crumb will be referred to as "4.0-mm crumb". Likewise, the crumb retained on the other metal sieves will be referred to as "0.5-mm crumb", "3.4-mm crumb", "6.7-mm crumb", "8.0-mm crumb", and "9.5-mm crumb". The crumb particles separately collected by sieving were homogeneously mixed in appropriate proportions to prepare crumb for bale molding.

[Bale Manufacturing Method]

The crumb prepared by the above method was heated to 60°C and filled into a rectangular parallelepiped container whose dimensions were a length of 420 mm, a width of 210 mm, and a depth of 400 mm, and the crumb was compressed by applying a pressure of 3.5 MPa for 10 seconds using a cylinder.

[Example 1]

The solution of oil-extended conjugated diene polymer A was subjected to solvent removal according to Production Example 1 for crumb, to thereby obtain crumb. The amount of the TDAE oil added was 20 parts by mass based on 100 parts by mass of the conjugated diene polymer. Crumb to be used for bale molding was formulated and prepared according to the above crumb particle size control method. As for the mixing proportions, 0.5-mm crumb accounted for 10% by mass, 3.4-mm crumb accounted for 20% by mass, 4.0-mm crumb accounted for 20% by mass, 6.7-mm crumb accounted for 20% by mass, 8.0-mm crumb accounted for 20% by mass, and 9.5-mm crumb accounted for 10% by mass. The specific surface area of the crumb for bale molding was 1.72 m²/g. The prepared crumb for bale molding was used to carry out the above bale manufacturing method to obtain a rectangular parallelepiped bale weighing 6 kg. The dimensions of the obtained bale were a length of 420 mm, a width of 210 mm, and a height of 88 mm. The central region of the bale

was cut out, and the specific surface area of this region was measured and found to be $0.020 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.60 g , which corresponded to 0.010% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured, and the expansion ratio was determined to be 3.3% .

[Example 2]

A rectangular parallelepiped bale weighing 6 kg was obtained in the same manner as in Example 1, except that the amount of the TDAE oil added was 10 parts by mass based on 100 parts by mass of the conjugated diene polymer. The specific surface area of the crumb for bale molding was $1.77 \text{ m}^2/\text{g}$. The dimensions of the molded bale were a length of 420 mm , a width of 210 mm , and a height of 90 mm . The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.037 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.96 g , which corresponded to 0.016% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured, and the expansion ratio was determined to be less than 1% .

[Example 3]

A rectangular parallelepiped bale weighing 6 kg was obtained in the same manner as in Example 1, except that solvent removal was conducted according to Production Example 2 for crumb. The specific surface area of the crumb for bale molding was $1.84 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 88 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.019 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.582 g, which corresponded to 0.0097% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be 3.5%.

[Example 4]

A rectangular parallelepiped bale weighing 6 kg was obtained in the same manner as in Example 3, except that the amount of the TDAE oil added was 10 parts by mass based on 100 parts by mass of the conjugated diene polymer. The specific surface area of the crumb for bale molding was $1.70 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 90 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.041 \text{ m}^2/\text{g}$. The bale surface

was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 1.02 g, which corresponded to 0.017% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Example 5]

A rectangular parallelepiped bale weighing 6 kg was obtained in the same manner as in Example 1, except that the solution of oil-extended conjugated diene polymer B was used instead of the solution of oil-extended conjugated diene polymer A and that the amount of the TDAE oil added was 15 parts by mass based on 100 parts by mass of the conjugated diene polymer. The specific surface area of the crumb for bale molding was $1.76 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 90 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.025 \text{ m}^2/\text{g}$. The bale surface was smooth, and none of the conjugated diene polymer crumb was detached in the dropping test. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Example 6]

A rectangular parallelepiped bale weighing 6 kg was obtained in the same manner as in Example 5, except that solvent removal was conducted according to Production Example 2 for crumb and that the mixing proportions in the crumb for bale molding were adjusted so that 0.5-mm crumb accounted for 15% by mass, 3.4-mm crumb accounted for 25% by mass, 4.0-mm crumb accounted for 10% by mass, 6.7-mm crumb accounted for 10% by mass, 8.0-mm crumb accounted for 20% by mass, and 9.5-mm crumb accounted for 20% by mass. The specific surface area of the crumb for bale molding was $2.90 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 90 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.042 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.72 g, which corresponded to 0.012% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Example 7]

A rectangular parallelepiped bale weighing 6 kg was obtained in the same manner as in Example 6, except that the solution of oil-extended conjugated diene polymer A was used and that solvent removal was conducted according

to Production Example 1 for crumb. The specific surface area of the crumb for bale molding was $2.73 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 90 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.045 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.72 g, which corresponded to 0.012% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Example 8]

Crumb was obtained by using the solution of oil-extended conjugated diene polymer A and conducting solvent removal according to Production Example 1 for crumb. The amount of the TDAE oil added was 5 parts by mass based on 100 parts by mass of the conjugated diene polymer. Except for this, a rectangular parallelepiped bale weighing 6 kg was obtained in the same as in Example 1. The specific surface area of the crumb for bale molding was $1.75 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 90 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.018 \text{ m}^2/\text{g}$. The bale surface

was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.78 g, which corresponded to 0.013% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Example 9]

Crumb was obtained by using the solution of oil-extended conjugated diene polymer A and conducting solvent removal according to Production Example 2 for crumb. The amount of the TDAE oil added was 5 parts by mass based on 100 parts by mass of the conjugated diene polymer. Except for these, a rectangular parallelepiped bale weighing 6 kg was obtained in the same as in Example 1. The specific surface area of the crumb for bale molding was $1.82 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 90 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.025 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 0.60 g, which corresponded to 0.010% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from

which the expansion ratio was determined to be less than 1%.

[Comparative Example 1]

Crumb was obtained by subjecting the solution of oil-extended conjugated diene polymer A to solvent removal according to Production Example 1 for crumb. The amount of the TDAE oil added was 10 parts by mass based on 100 parts by mass of the conjugated diene polymer. Sieving of the crumb revealed that 0.5-mm crumb accounted for 19% by mass, 3.4-mm crumb accounted for 37% by mass, 4.0-mm crumb accounted for 22% by mass, 6.7-mm crumb accounted for 12% by mass, 8.0-mm crumb accounted for 6% by mass, and 9.5-mm crumb accounted for 4% by mass. Bale molding was carried out without adjusting the crumb proportions, and thus a rectangular parallelepiped bale weighing 6 kg was obtained. The specific surface area of the crumb for bale molding was $3.46 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 92 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.056 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 1.32 g, which corresponded to 0.022% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its

volume, from which the expansion ratio was determined to be less than 1%.

[Comparative Example 2]

Crumb was obtained in the same manner as in comparative Example 1, except that the amount of the TDAE oil added was 10 parts by mass based on 100 parts by mass of the conjugated diene polymer. Sieving of the crumb revealed that 0.5-mm crumb accounted for 28% by mass, 3.4-mm crumb accounted for 35% by mass, 4.0-mm crumb accounted for 13% by mass, 6.7-mm crumb accounted for 9% by mass, 8.0-mm crumb accounted for 9% by mass, and 9.5-mm crumb accounted for 6% by mass. Bale molding was carried out without adjusting the crumb proportions, and thus a rectangular parallelepiped bale weighing 6 kg was obtained. The specific surface area of the crumb for bale molding was $4.40 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 92 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.071 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 1.86 g, which corresponded to 0.031% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Comparative Example 3]

Crumb was obtained in the same manner as in Comparative Example 2, except that solvent removal was conducted according to Production Example 2 for crumb. Sieving of the crumb revealed that 0.5-mm crumb accounted for 27% by mass, 3.4-mm crumb accounted for 33% by mass, 4.0-mm crumb accounted for 15% by mass, 6.7-mm crumb accounted for 15% by mass, 8-mm crumb accounted for 5% by mass, and 9.5-mm crumb accounted for 5% by mass. Bale molding was carried out without adjusting the crumb proportions, and thus a rectangular parallelepiped bale weighing 6 kg was obtained. The specific surface area of the crumb for bale molding was $4.25 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 92 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.068 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 1.74 g, which corresponded to 0.029% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Comparative Example 4]

Crumb was obtained in the same manner as in Comparative Example 1, except that the solution of oil-

extended conjugated diene polymer B was used instead of the solution of oil-extended conjugated diene polymer A and that the amount of the TDAE oil added was 15 parts by mass based on 100 parts by mass of the conjugated diene polymer. Sieving of the crumb revealed that 0.5-mm crumb accounted for 23% by mass, 3.4-mm crumb accounted for 32% by mass, 4.0-mm crumb accounted for 18% by mass, 6.7-mm crumb accounted for 13% by mass, 8-mm crumb accounted for 8% by mass, and 9.5-mm crumb accounted for 6% by mass. Bale molding was carried out without adjusting the crumb proportions, and thus a rectangular parallelepiped bale weighing 6 kg was obtained. The specific surface area of the crumb for bale molding was $3.81 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 92 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.063 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 1.26 g, which corresponded to 0.021% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Comparative Example 5]

Crumb was obtained in the same manner as in Comparative Example 4, except that solvent removal was

conducted according to Production Example 2 for crumb. Sieving of the crumb revealed that 0.5-mm crumb accounted for 22% by mass, 3.4-mm crumb accounted for 35% by mass, 4.0-mm crumb accounted for 16% by mass, 6.7-mm crumb accounted for 12% by mass, 8.0-mm crumb accounted for 9% by mass, and 9.5-mm crumb accounted for 6% by mass. Bale molding was carried out without adjusting the crumb proportions, and thus a rectangular parallelepiped bale weighing 6 kg was obtained. The specific surface area of the crumb for bale molding was $3.71 \text{ m}^2/\text{g}$, and the dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 92 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.061 \text{ m}^2/\text{g}$. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 1.50 g, which corresponded to 0.025% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

[Comparative Example 6]

Crumb was obtained by subjecting the solution of oil-extended conjugated diene polymer A to solvent removal according to Production Example 1 for crumb. The amount of the TDAE oil added was 15 parts by mass based on 100 parts by mass of the conjugated diene polymer.

Crumb to be used for bale molding was formulated and prepared according to the above crumb particle size control method. As for the mixing proportions, 9.5-mm crumb accounted for 100% by mass. The specific surface area of the crumb for bale molding was $0.50 \text{ m}^2/\text{g}$. A rectangular parallelepiped bale weighing 6 kg was obtained according to the above bale manufacturing method. The dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 87 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be $0.004 \text{ m}^2/\text{g}$. The bale surface was smooth, and none of the conjugated diene polymer crumb was detached in the dropping test. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be 6.7%.

[Comparative Example 7]

Crumb was obtained by subjecting the solution of oil-extended conjugated diene polymer A to solvent removal according to Production Example 1 for crumb. The amount of the TDAE oil added was 5 parts by mass based on 100 parts by mass of the conjugated diene polymer. The crumb was classified by sieving, and the crumb proportions were adjusted to give a crumb particle size distribution identical to that in Comparative Example 1. The crumb with such a particle size distribution was used for bale molding, by which a rectangular parallelepiped

bale weighing 6 kg was obtained. The dimensions of the molded bale were a length of 420 mm, a width of 210 mm, and a height of 87 mm. The central region of the bale was cut out, and the specific surface area of this region was measured and found to be 0.065 m²/g. The bale surface was smooth, and the amount of the conjugated diene polymer crumb detached in the dropping test was 2.70 g, which corresponded to 0.045% by mass based on the whole amount of the bale. After 1 day, all the dimensions of the bale were measured to determine its volume, from which the expansion ratio was determined to be less than 1%.

The evaluation results of the molding crumb and bales obtained in Examples and Comparative Examples above are shown in Tables 1 and 2.

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9
Crumb for molding	Conjugated diene polymer	A	A	A	A	B	B	A	A	A
	TDAE proportion [parts by mass]	20	10	20	10	15	15	15	5	5
	Production Example	1	1	2	2	1	2	1	1	2
	0.5 mm	10	10	10	10	10	15	15	10	10
	3.4 mm	20	20	20	20	20	25	25	20	20
	4.0 mm	20	20	20	20	20	10	10	20	20
	6.7 mm	20	20	20	20	20	10	10	20	20
	8.0 mm	20	20	20	20	20	20	20	20	20
	9.5 mm	10	10	10	10	10	20	20	10	10
	Specific surface area [m ² /g]	1.72	1.77	1.84	1.70	1.76	2.90	2.73	1.75	1.82
Evaluation result of bale	Specific surface area [m ² /g]	0.020	0.037	0.019	0.041	0.025	0.042	0.045	0.018	0.025
	Expansion ratio after 1 day [vol%]	3.3	Less than 1%	3.5	Less than 1%	Less than 1%	Less than 1%	Less than 1%	Less than 1%	Less than 1%
	Amount of crumb detached in dropping test based on whole amount of bale [% by mass]	0.010	0.016	0.0097	0.017	None	0.012	0.012	0.013	0.01

[Table 2]

	Conjugated diene polymer	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
	TDAE proportion [parts by mass]	20	10	10	15	15	15	5
Crumb for molding	Production Example	1	1	2	1	2	1	1
	0.5 mm	19	28	27	23	22	0	19
	3.4 mm	37	35	33	32	35	0	37
	4.0 mm	22	13	15	18	16	0	22
	6.7 mm	12	9	15	13	12	0	12
	8.0 mm	6	9	5	8	9	0	6
	9.5 mm	4	6	5	6	6	100	4
	Specific surface area [m ² /g]	3.46	4.40	4.25	3.81	3.71	0.5	3.62
	Specific surface area [m ² /g]	0.056	0.071	0.068	0.063	0.061	0.004	0.065
	Expansion ratio after 1 day [vol%]	Less than 1%	Less than 1%	Less than 1%	Less than 1%	Less than 1%	6.7	Less than 1%
Evaluation result of bale	Amount of crumb detached in dropping test based on whole amount of bale [% by mass]	0.022	0.031	0.029	0.021	0.025	None	0.045

Claims

What is claimed is:

1. A crumb for forming a bale, which is of a conjugated diene polymer, wherein the crumb has a specific surface area of $0.7 \text{ m}^2/\text{g}$ to $3.2 \text{ m}^2/\text{g}$, and the conjugated diene polymer is a random copolymer of an aromatic vinyl compound and a conjugated diene compound, and a component that does not pass through a sieve with an aperture size of 4.0 mm is comprised at least 20 % by mass of the whole crumb.
2. The crumb for forming a bale according to claim 1, wherein the conjugated diene polymer contains 30 to 90 % by mass of a component having a molecular weight of 1 million or more.
3. The crumb for forming a bale according to claim 1 or 2, which contains 1 to 20 parts by mass of process oil with respect to 100 parts by mass of the conjugated diene polymer.
4. A bale of a conjugated diene polymer, wherein the bale has a specific surface area of $0.005 \text{ m}^2/\text{g}$ to $0.05 \text{ m}^2/\text{g}$, wherein the conjugated diene polymer is a random copolymer of an aromatic vinyl compound and a conjugated diene compound.

5. A method for producing a bale by preparing a crumb of a conjugated diene polymer, wherein the crumb has a specific surface area of $0.7 \text{ m}^2/\text{g}$ to $3.2 \text{ m}^2/\text{g}$, and compression molding the crumb, wherein the conjugated diene polymer is a random copolymer of an aromatic vinyl compound and a conjugated diene compound, and the crumb is a random copolymer, and a component that does not pass through a sieve with an aperture size of 4.0 mm is comprised at least 20 % by mass of the whole crumb.
6. The method for producing a bale according to claim 5, further comprising a step of sieving the crumb of the conjugated diene polymer.