

**Modified diene elastomer of reduced polydispersity index, and
rubber composition containing same**

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The invention relates to a modified diene elastomer comprising at least 70% by weight of a specific linear diene elastomer functionalized predominantly at the chain end by an alkoxysilane group, optionally partially or completely hydrolysed, bearing a primary, secondary or tertiary amine functional group, and at most 30% by weight of a specific star-branched diene elastomer, the Mooney viscosity of the said modified diene elastomer varying from 30 to 80.

Now that savings in fuel and the need to protect the environment have become a priority, it is desirable to produce mixtures having a hysteresis which is as low as possible in order to be able to process them in the form of rubber compositions which can be used in the manufacture of various semi-finished products participating in the composition of tyre casings, such as, for example, underlayers, sidewalls or treads, and in order to obtain tyres having a reduced rolling resistance.

The reduction in the hysteresis of the mixtures is an ongoing objective which has, however, to be done while retaining the suitability for processing, in the raw state, of the mixtures, while maintaining the resistance to flow of the elastomers.

Many solutions have already been experimented with in order to achieve the objective of a fall in hysteresis. Mention may in particular be made of the modification of the structure of diene polymers and copolymers at the end of polymerization by means of functionalization, coupling or star-branching agents, with the aim of obtaining a good interaction between the polymer thus modified and the filler, whether carbon black or another reinforcing inorganic filler.

In the context of mixtures containing a reinforcing inorganic filler of siliceous type, it has been proposed to use diene copolymers functionalized by alkoxysilane derivatives.

Mention may be made, by way of illustration of this prior art, for example, of United States Patent US-A-5 066 721, which describes a rubber composition comprising a diene polymer functionalized by an alkoxysilane having at least one non-hydrolysable alkoxyl residue as a mixture with silica. Mention may also be made

of Patent Application EP A 0 299 074, which describes functionalized polymers comprising alkoxysilane functional groups at the chain end. These functionalized polymers have been described in the prior art as effective in reducing hysteresis and improving abrasion resistance; however, their properties remain insufficient to allow the processing of these polymers in compositions intended to constitute treads of tyres.

Provision has also been made to combine the functionalization by alkoxysilane functional groups with the functionalization by other functional groups, in particular amine functional groups. Thus, Patent EP 0 992 537 describes a rubber composition which comprises an extended elastomer functionalized at the chain end by an alkoxysilane functional group and bearing, at the other end or along its chain, one or more amine functional groups. Furthermore, provision has also been made to improve the properties of rubber compositions by using elastomers functionalized at the chain end by alkoxysilane functional groups bearing an amine group, whether this is as black, silica or hybrid mixture. Mention may be made, for example, of Patent Application US 2005/0203251, which describes a rubber composition reinforced by silica comprising an elastomer functionalized at the chain end by an alkoxysilane bearing an amine group. Nevertheless, it turns out that the compositions comprising elastomers thus functionalized, whether black, silica or hybrid mixtures, do not always exhibit a processing which is acceptable and a hysteresis which is satisfactory for use as a tyre tread.

It is an ongoing concern of designers of materials intended for the manufacture of tyres to improve the compromise in mechanical and dynamic properties of the rubber compositions for the purpose of improving the performance of the tyre in which they are present, without, however, damaging the stages of its manufacture or the properties of the elastomer. Thus, for example, the improvement in the compromise in properties must not be made to the detriment of the flow of the elastomer, which causes major disadvantages during the transportation and storage of rubbers.

Provision has been made in the past to add elastomers coupled or star-branched using additional coupling or star-branching agents comprising tin or silicon in order to limit the flow. Thus, for example, Patent Application WO 2009/077837 describes elastomers functionalized at each chain end in combination with elastomers which are star-branched, particularly by silicon. However, the combinations

illustrated result in a reinforced rubber composition, the processing/hysteresis compromise of which is not satisfactory for a tyre application. The Applicant Companies have furthermore described, in Patent Application WO 2011/042507, a functionalized diene elastomer composed of a diene elastomer functionalized at a chain end by a silanol functional group and, in a certain proportion, of a coupled or star-branched diene elastomer based on tin. This elastomer confers, on a rubber composition in which it is present, hysteresis and processing properties which are satisfactory and acceptable for tyre use, while exhibiting a significantly improved resistance to flow.

The technical problem which the invention intends to solve is that of further improving the compromise in hysteresis and processing properties of a rubber composition for the purpose of a tyre application, without damaging its manufacture or the properties of the elastomer present in this composition, in particular its resistance to flow.

This aim is achieved in that the inventors have just discovered, surprisingly, during their research studies, that a modified diene elastomer comprising at least 70% by weight, with respect to the total weight of the modified diene elastomer, of a linear diene elastomer functionalized predominantly at a chain end by an alkoxysilane group, optionally partially or completely hydrolysed to give silanol, the alkoxysilane group bearing a primary, secondary or tertiary amine functional group, the alkoxysilane group being connected to the diene elastomer via the silicon atom, the said functionalized diene elastomer exhibiting a polydispersity index before functionalization of less than or equal to 1.6 and more than 0, and up to 30% by weight, with respect to the total weight of the modified diene elastomer, of a star-branched diene elastomer exhibiting a polydispersity index before functionalization of less than or equal to 1.6, the Mooney viscosity of the said modified diene elastomer varying from 30 to 80, confers, on the rubber compositions containing it, an improvement in the raw processing/hysteresis compromise while keeping intact the resistance to flow of the elastomer.

A subject-matter of the invention is thus a modified diene elastomer comprising:

a) at least 70% by weight, with respect to the total weight of the modified diene elastomer, of a linear diene elastomer functionalized predominantly at a chain end by an alkoxysilane group, optionally partially or completely hydrolysed to give

silanol, the alkoxysilane group bearing a primary, secondary or tertiary amine functional group, the alkoxysilane group being connected to the diene elastomer via the silicon atom, the said functionalized diene elastomer exhibiting a polydispersity index before functionalization of less than or equal to 1.6,

5 b) more than 0 and up to 30% by weight, with respect to the total weight of the modified diene elastomer, of a star-branched diene elastomer exhibiting a polydispersity index before star-branching of less than or equal to 1.6,

the Mooney viscosity of the said modified diene elastomer varying from 30 to 80.

10 A further subject-matter of the invention is a reinforced rubber composition based on at least one reinforcing filler and on an elastomer matrix comprising at least the said modified diene elastomer.

 In the present description, unless expressly indicated otherwise, all the percentages (%) shown are % by weight. Furthermore, any interval of values denoted
15 by the expression "between a and b" represents the range of values extending from more than a to less than b (that is to say, limits a and b excluded), whereas any interval of values denoted by the expression "from a to b" means the range of values extending from a up to b (that is to say, including the strict limits a and b).

 The expression "composition based on" should be understood as meaning a
20 composition comprising the mixture and/or the reaction product of the various constituents used, some of these base constituents being capable of reacting, or intended to react, with one another, at least in part, during the various phases of manufacture of the composition, in particular during the crosslinking or vulcanization thereof.

25 In the present patent application, "predominantly" or "predominant", in connection with a compound, is understood to mean that this compound is predominant among the compounds of the same type in the composition, that is to say that it is the one which represents the biggest fraction by weight among the compounds of the same type. Thus, a "predominant" functional entity of a
30 functionalized diene elastomer is that representing the biggest fraction by weight among the functionalized entities constituting the diene elastomer, with respect to the total weight of the functionalized diene elastomer. In a system comprising just one compound of a certain type, the latter is predominant within the meaning of the present invention.

In the present description, the term "modified diene elastomer" is understood to mean a diene elastomer which comprises a group comprising one or more heteroatoms.

5 This group can be located at the linear main elastomer chain end. It will then be said that the diene elastomer is functionalized at the chain end. It is generally an elastomer obtained by reaction of a living elastomer with a functionalization agent, that is to say any at least monofunctional molecule, the functional group being any type of chemical group known by a person skilled in the art to react with a living
10 chain end.

 This group can be located in the linear main elastomer chain. It will then be said that the diene elastomer is coupled or alternatively functionalized in the middle of the chain, in contrast to the position "at the chain end", although the group is not located precisely at the middle of the elastomer chain. It is generally an elastomer
15 obtained by reaction of a living elastomer with a coupling agent, that is to say any at least difunctional molecule, the functional group being any type of chemical group known by a person skilled in the art to react with a living chain end.

 This group can be central, to which n elastomer chains ($n > 2$) are bonded, forming a star-branched structure. It will then be said that the diene elastomer is star-
20 branched. It is generally an elastomer obtained by reaction of a living elastomer with a star-branching agent, that is to say any polyfunctional molecule, the functional group being any type of chemical group known by a person skilled in the art to react with a living chain end.

 A person skilled in the art will understand that a functionalization reaction
25 with an agent comprising more than one functional group which is reactive with regard to the living elastomer results in a mixture of entities functionalized at the chain end and in the middle of the chain, constituting the linear chains of the functionalized elastomer, and also, if appropriate, star-branched entities. Depending on the operating conditions, mainly the molar ratio of the functionalization agent to
30 the living chains, certain entities are predominant in the mixture.

 The term "diene elastomer" should be understood, in a known way, as meaning an (one or more is understood) elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomers (monomers bearing two conjugated or non-conjugated carbon-carbon double bonds). More particularly, the

term "diene elastomer" is understood to mean any homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms or any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic monomers having from 8 to 20 carbon atoms. In the case of copolymers, the latter contain from 20% to 99% by weight of diene units and from 1% to 80% by weight of vinylaromatic units.

The following in particular are suitable as conjugated dienes which can be used in the process in accordance with the invention: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C₁ to C₅ alkyl)-1,3-butenes, such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene or 2-methyl-3-isopropyl-1,3-butadiene, phenyl-1,3-butadiene, 1,3-pentadiene and 2,4-hexadiene, and the like.

The following in particular are suitable as vinylaromatic monomers: styrene, ortho-, meta- or para-methylstyrene, the "vinyltoluene" commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, vinylmesitylene, divinylbenzene and vinylnaphthalene, and the like.

The diene elastomer is preferably selected from the group of highly unsaturated diene elastomers consisting of polybutadienes (BRs), synthetic polyisoprenes (IRs), butadiene copolymers, in particular copolymers of butadiene and of a vinylaromatic monomer, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more particularly butadiene/styrene copolymers (SBRs), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs) and isoprene/butadiene/styrene copolymers (SBIRs). Among these copolymers, butadiene/styrene copolymers (SBRs) are particularly preferred.

The diene elastomer can have any microstructure which depends on the polymerization conditions used. The elastomer can be a block, statistical, sequential or microsequential elastomer, and the like, and can be prepared in dispersion or in solution. When an anionic polymerization is involved, the microstructure of these elastomers can be determined by the presence or absence of a polar agent and the amounts of polar agent employed.

The term "polydispersity index" is understood to mean, within the meaning of the invention, the weight-average molecular weight/number-average molecular weight ratio. The weight-average and number-average molecular weights are measured by size exclusion chromatography.

The term "linear diene elastomer functionalized predominantly at a chain end", i.e. the elastomer a), is understood to mean, according to the invention, the mixture of the linear entities of the functionalized elastomer, namely the linear chains functionalized at a chain end and the linear chains functionalized in the middle of the chain, the former being predominant by weight in this mixture and preferably represents at least 50%, indeed even 70%, by weight of this mixture.

According to a preferred embodiment, the modified diene elastomer according to the invention comprises at least 80% by weight, with respect to the total weight of the modified diene elastomer, of the linear diene elastomer functionalized predominantly at a chain end a).

According to another preferred embodiment, the modified diene elastomer according to the invention comprises at most 20% by weight, with respect to the total weight of the modified diene elastomer, of the star-branched diene elastomer b).

According to a particularly preferred embodiment, the modified diene elastomer according to the invention comprises at least 80% by weight, with respect to the total weight of the modified diene elastomer, of the linear diene elastomer functionalized predominantly at a chain end a) and at most 20% by weight, with respect to the total weight of the modified diene elastomer, of the star-branched diene elastomer b).

According to the invention, in addition to the functional group comprising the silicon atom directly bonded to the elastomer chain (that is to say, the alkoxysilane group), the diene elastomer a) also comprises a primary, secondary or tertiary amine functional group, capable of interacting with a reinforcing filler, this functional group advantageously being borne by the silicon of the alkoxysilane group, directly or via a spacer group. This is understood as not excluding the fact that the alkoxysilane group comprising the silicon atom directly bonded to the elastomer chain interacts favourably with the reinforcing filler.

The term "alkoxysilane group interacting favourably with the reinforcing filler" or "amine functional group capable of interacting with a reinforcing filler" is understood to mean any alkoxysilane group or amine functional group capable of forming, within a rubber composition reinforced by means of a filler, a physical or chemical bond with the said filler. This interaction can be established, for example, via covalent, hydrogen, ionic and/or electrostatic bonds between the said functional group and functional groups present on fillers.

The alkoxy radical of the alkoxysilane group can be of formula $R'O\cdot$, where R' represents a substituted or unsubstituted C_1 - C_{10} , indeed even C_1 - C_8 , alkyl group, preferably a C_1 - C_4 alkyl group, more preferably methyl and ethyl.

5 According to alternative forms of the invention, the alkoxysilane group can comprise two alkoxy radicals. According to other alternative forms, the alkoxysilane group can comprise just one alkoxy radical and an alkyl radical.

According to the latter alternative forms, the alkyl radical of the alkoxysilane group is preferably a linear or branched C_1 - C_{10} , preferably C_1 - C_4 , radical, more preferably a methyl radical.

10 Mention may be made, as secondary or tertiary amine functional group, of amines substituted by C_1 - C_{10} , preferably C_1 - C_4 , alkyl radicals, more preferably a methyl or ethyl radical, or else cyclic amines forming a heterocycle comprising a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms. For example, the methylamino-, dimethylamino-, ethylamino-, diethylamino-,
15 propylamino-, dipropylamino-, butylamino-, dibutylamino-, pentylamino-, dipentylamino-, hexylamino-, dihexylamino- or hexamethyleneamino- groups, preferably the diethylamino- and dimethylamino- groups, are suitable.

Preferably, the functional group capable of interacting with a reinforcing filler of the diene elastomer a) is a tertiary amine functional group, preferably a
20 diethylamine or dimethylamine functional group.

According to an alternative form of the invention, the primary, secondary or tertiary amine functional group is directly bonded to the silicon atom itself directly bonded to the diene elastomer.

25 According to another alternative form of the invention, the primary, secondary or tertiary amine functional group and the silicon atom bonded to the diene elastomer are connected to one another via a spacer group which can be an atom or a group of atoms. The spacer group can be a saturated or unsaturated, cyclic or non-cyclic, linear or branched, divalent C_1 - C_{18} aliphatic hydrocarbon radical or a divalent C_6 - C_{18} aromatic hydrocarbon radical and can comprise one or more aromatic radicals
30 and/or one or more heteroatoms. The hydrocarbon radical can optionally be substituted.

According to a preferred alternative form of the invention, the spacer group is a linear or branched, divalent C_1 - C_{10} aliphatic hydrocarbon radical, more

preferably a linear divalent C₁-C₅ aliphatic hydrocarbon radical and more preferably still the linear divalent C₃ hydrocarbon radical.

5 The different aspects, preferred or nonpreferred, which precede and which relate in particular to the nature of the primary, secondary or tertiary amine functional group, the nature of the spacer group, the nature of the alkoxysilane group and the nature of the diene elastomer can be combined with one another.

According to advantageous alternative forms of the invention, at least one of the four following characteristics is observed and preferably all four:

- the amine functional group capable of interacting with a reinforcing filler is a tertiary amine, more particularly a diethylamino- or dimethylamino- group,
- the spacer group is a linear C₁-C₅ hydrocarbon radical, more preferably still the linear C₃ hydrocarbon radical,
- the functional group comprising the silicon atom is a methoxysilane or ethoxysilane, optionally partially or completely hydrolysed to give silanol,
- 15 - the diene elastomer is a butadiene/styrene copolymer.

The star-branched diene elastomer b) is preferably a tin-based or silicon-based star-branched diene elastomer.

The star-branched diene elastomer b) is preferably a star-branched diene elastomer comprising three or four branches.

20 The linear diene elastomer functionalized predominantly at a chain end a) and the star-branched diene elastomer b) can have, before functionalization and star-branching, the same microstructure or a different microstructure.

Preferably, the linear diene elastomer functionalized predominantly at a chain end a) and the star-branched diene elastomer b) have, before functionalization and star-branching, the same microstructure.

Preferably again, the linear diene elastomer functionalized predominantly at a chain end a) and the star-branched diene elastomer b) have, before functionalization and star-branching, the same microstructure and the same macrostructure.

30 According to a preferred embodiment, the functionalized diene elastomer a) exhibits a polydispersity index before functionalization varying from 1.2 to 1.6 and the star-branched diene elastomer b) exhibits a polydispersity index before star-branching varying from 1.2 to 1.6.

The modified diene elastomer according to the invention can be obtained by means of a process as described below.

The first stage of a process for the preparation of the modified diene elastomer is the anionic polymerization of at least one conjugated diene monomer in the presence of a polymerization initiator.

5 Use may be made, as polymerization initiator, of any known monofunctional anionic initiator. However, an initiator comprising an alkali metal, such as lithium, is preferably used.

10 Organolithium initiators comprising a carbon-lithium bond are suitable in particular. Use will preferably be made of a hydrocarbon organolithium initiator not comprising a heteroatom. Representative compounds are aliphatic organolithium compounds, such as ethyllithium, n-butyllithium (n-BuLi), isobutyllithium, and the like.

15 The polymerization is preferably carried out in the presence of an inert hydrocarbon solvent which can, for example, be an aliphatic or alicyclic hydrocarbon, such as pentane, hexane, heptane, isooctane, cyclohexane or methylenecyclohexane, or an aromatic hydrocarbon, such as benzene, toluene or xylene.

The polymerization can be carried out in a way known per se and in particular continuously. The continuous polymerization can be carried out in a known way in one or more reactors assumed to be perfectly stirred by a person skilled in the art.

20 In the case of the polymerization in several reactors, the number of reactors generally varies from 2 to 15 and preferably from 2 to 9.

The polymerization is generally carried out at a temperature varying from 20°C to 150°C and preferably from 30°C to 120°C.

25 According to a continuous implementation of the process, the polymerization can advantageously be carried out in several reactors by controlling and by balancing the conversion in each reactor. For example, the maintenance in each reactor of an individual degree of conversion within a range of values which depends on the theoretical individual degree of conversion, calculated from the overall degree of conversion at the end of polymerization divided by the number of
30 reactors, can contribute to a reduced polydispersity index of at most 1.6 being obtained. Preferably then, the individual degree of conversion can vary by plus or minus 20% from the overall conversion, with respect to this theoretical value.

It is known that the conversion in each reactor is controlled in particular by the temperature, the residence time, the amount of polar agent and the amount of monomer entering each reactor.

5 The balancing of the conversions in each reactor, as indicated above, makes it possible to minimize the polydispersity index.

According to a continuous implementation of the process, the polymerization in several reactors in series can advantageously be carried out by producing a temperature gradient in the range of temperatures indicated above, so that the temperature in each reactor is greater than or equal to the temperature of the reactor which immediately precedes it, the temperature of the final reactor being
10 strictly greater than the temperature of the first reactor.

According to a continuous implementation of the process, the polymerization in several reactors in series can also advantageously be carried out with additional injections of solvents and/or of monomers in at least one other reactor
15 than the first. These monomers and/or solvents are then purified so that the proportion of the number of dead chains in the stream at the outlet of the final polymerization reactor is less than 30%, preferably less than 10%, of the number of living chains initiated in the first reactor. The term "dead chains" is understood to mean the chains of polymers, the propagation of which has been halted by reaction
20 with impurities and which are no longer reactive at polymerization outlets.

These continuous implementations of the polymerization process in several reactors can be combined with one another.

It is, of course, also possible to add, at the end of polymerization, a transmetallation agent in order to modify the reactivity of the living chain end. The
25 living diene elastomer resulting from the polymerization is subsequently functionalized in order to prepare the modified diene elastomer according to the invention.

According to a first alternative form of the preparation of the modified diene elastomer according to the invention, the linear diene elastomer functionalized
30 predominantly at a chain end a) and the star-branched diene elastomer b) are mixed in the appropriate proportions.

The linear diene elastomer functionalized predominantly at a chain end a) can be obtained by reaction of the living diene elastomer with a functionalization agent capable of introducing, at the polymer chain end, a hydrolysable or non-

hydrolysable alkoxysilane group bearing a primary, secondary or tertiary amine functional group, the alkoxysilane group being connected to the diene elastomer via the silicon atom.

5 The functionalization agent which can be used according to the invention can bear an alkoxysilane functional group, which can be hydrolysed to give a silanol functional group, or a non-hydrolysable alkoxysilane functional group, and a protected or unprotected primary amine functional group, a protected or unprotected secondary amine functional group or a tertiary amine functional group, the two functional groups being directly bonded to one another or being bonded to one another via a spacer
10 group.

The molar ratio of the functionalization agent to the initiator of the living polymer chains is greater than or equal to 0.75, preferably greater than 1.

The functionalization agent can be represented by the following formula (I):



in which:

- R denotes a linear or branched C₁-C₁₀, preferably C₁-C₄, alkyl radical, more preferably a methyl radical,
- 20 - the R' radicals, which are identical to or different from one another, represent a linear or branched C₁-C₁₀, preferably C₁-C₄, alkyl radical, more preferably a methyl or ethyl radical,
- R₂ is a saturated or unsaturated, cyclic or non-cyclic, divalent C₁-C₁₈ aliphatic hydrocarbon group or divalent C₆-C₁₈ aromatic hydrocarbon group, preferably a linear divalent C₁-C₆ aliphatic hydrocarbon group, more
25 preferably the saturated linear divalent C₃ aliphatic hydrocarbon radical,
- R'', which are identical or different, represent a trialkylsilyl radical, the alkyl groups, which are identical or different, having from 1 to 4 carbon atoms, or a linear or branched C₁-C₁₈, preferably C₁-C₄, alkyl radical, more
30 preferably a methyl or ethyl radical, or else the R'' radicals form, with N to which they are bonded, a heterocycle containing a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms,
- x is an integer equal to 2 or 3 and y is an integer equal to 0 or 1, such that x + y = 3.

The different aspects, preferred or nonpreferred, which precede and which relate in particular to the nature of the primary, secondary or tertiary amine functional group, the nature of the spacer group R_2 and the nature of the alkoxy silane group can be combined with one another.

5 Mention may be made, as functionalization agent, of (N,N-dialkylaminopropyl)(alkyl)dialkoxysilanes, (N,N-dialkylaminopropyl)trialkoxysilanes, (N-alkylaminopropyl)(alkyl)dialkoxysilanes and (N-alkylaminopropyl)trialkoxysilanes, the secondary amine functional group of which is protected by a trialkylsilyl group, and (aminopropyl)(alkyl)dialkoxysilanes
10 and (aminopropyl)trialkoxysilanes, the primary amine functional group of which is protected by two trialkylsilyl groups. The alkyl substituents present on the nitrogen atom are linear or branched and advantageously have from 1 to 10 carbon atoms, preferably from 1 to 4, more preferably 1 or 2. For example, the methylamino-, dimethylamino-, ethylamino-, diethylamino-, propylamino-, dipropylamino-,
15 butylamino-, dibutylamino-, pentylamino-, dipentylamino-, hexylamino-, dihexylamino- or hexamethyleneamino- groups, preferably the diethylamino- and dimethylamino- groups, are suitable as alkyl substituents. The alkoxy substituents are linear or branched and generally have from 1 to 10 carbon atoms, indeed even 1 to 8, preferably 1 to 4 and more preferably 1 or 2.

20 Preferably, the functionalization agent can be chosen from (3-N,N-dialkylaminopropyl)(alkyl)dialkoxysilanes and (3-N,N-dialkylaminopropyl)trialkoxysilanes, the alkyl group on the silicon atom being the methyl or ethyl group and the alkoxy group being the methoxy or ethoxy group. More preferably, the functionalization agent is a compound of the (3-N,N-dialkylaminopropyl)(alkyl)dialkoxysilane type.
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 Preferably, the functionalization agent can be chosen from (3-N,N-alkyltrimethylsilylaminopropyl)(alkyl)dialkoxysilanes and (3-N,N-alkyltrimethylsilylaminopropyl)trialkoxysilanes, the alkyl group on the silicon atom being the methyl or ethyl group and the alkoxy group being the methoxy or ethoxy group. More preferably, the functionalization agent is a compound of the (3-N,N-alkyltrimethylsilylaminopropyl)(alkyl)dialkoxysilane type.
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 Preferably, the functionalization agent can be chosen from (3-N,N-bis(trimethylsilyl)aminopropyl)(alkyl)dialkoxysilanes and (3-N,N-bis(trimethylsilyl)aminopropyl)trialkoxysilanes, the alkyl group on the silicon atom

being the methyl or ethyl group and the alkoxy group being the methoxy or ethoxy group. More preferably, the functionalization agent is a compound of the (3-N,N-bis(trimethylsilyl)aminopropyl)(alkyl)dialkoxysilane type.

5 The star-branched diene elastomer b) can be obtained in a way known per se by reaction of the living chain end with a star-branching agent, that is to say any polyfunctional molecule, the functional group being any type of chemical group known by a person skilled in the art to react with a living chain end. The molar ratio of the star-branching agent to the initiator of the living polymer chains is less than or equal to 0.4 and preferably varies from 0.15 to 0.4.

10 According to alternative forms of the invention, the star-branching agents are tin-based or silicon-based agents with a functionality of greater than 2 and which can be represented by the formula MR_xX_{4-x} , M represents a Sn or Si atom, x represents an integer with a value from 0 to 2, preferably with a value from 0 to 1, R represents an alkyl radical of 1 to 10 carbon atoms, preferably an alkyl radical having from 1 to 4 carbon atoms, and X is a halogen atom, preferably chlorine. Mention may be made, as examples, of compounds such as tin tetrachloride, methyltin trichloride, dimethyltin dichloride, tetrachlorosilane, methyltrichlorosilane and dimethyldichlorosilane.

20 According to other alternative forms of the invention, the star-branching agent can be a trialkoxysilane bearing a protected primary amine, protected secondary amine or tertiary amine functional group, preferably exhibiting the formula (I) described above in which x has the value 3 and y has the value 0. Thus, the star-branching agent can be chosen from the compounds of trialkoxysilane type described above in the context of the functionalization agent of formula (I), in particular (N,N-dialkylaminopropyl)trialkoxysilanes, (N-alkylaminopropyl)trialkoxysilanes, the secondary amine functional group of which is protected by a trialkylsilyl group, and aminopropyltrialkoxysilanes, the primary amine functional group of which is protected by two trialkylsilyl groups.

30 More preferably then, the star-branching agent can be chosen from (3-N,N-dimethylaminopropyl)trimethoxysilane, (3-N,N-methyltrimethylsilylaminopropyl)trimethoxysilane and (3-N,N-bis(trimethylsilyl)aminopropyl)trimethoxysilane.

The mixing of the two elastomers can be carried out in an inert solvent, for example an aliphatic or alicyclic hydrocarbon, such as pentane, hexane, heptane,

isooctane or cyclohexane, or an aromatic hydrocarbon, such as benzene, toluene or xylene, which can be the same as the polymerization solvent. The mixing will then be carried out at a temperature of between 20°C and 120°C and preferably in the vicinity of 30°C to 110°C.

5 According to a second alternative form of the preparation of the modified diene elastomer according to the invention, the living diene elastomer resulting from the polymerization stage is subjected to the reaction of a star-branching agent and to that of a functionalization agent capable of introducing, at the polymer chain end, a hydrolysable or non-hydrolysable alkoxy silane group bearing a primary, secondary
10 or tertiary amine functional group, the alkoxy silane group being bonded to the diene elastomer via the silicon atom.

 The functionalization agents and the star-branching agents which can be used in the context of this second alternative form can be chosen from those mentioned in the context of the first alternative form. The molar ratio of the
15 functionalization agent to the initiator of the living polymer chains is greater than or equal to 0.75, preferably greater than 1. The molar ratio of the star-branching agent to the initiator of the living polymer chains is predetermined so as to form a content of star-branched diene elastomer of less than or equal to 30% by weight, with respect to the weight of the modified diene elastomer.

20 According to a third alternative form of the preparation of the modified diene elastomer according to the invention, the living diene elastomer resulting from the polymerization stage is subjected to the reaction of a functionalization agent of trialkoxy silane type as described above, capable of introducing, at the polymer chain end, a hydrolysable alkoxy silane group bearing a primary, secondary or tertiary
25 amine functional group, the alkoxy silane group being bonded to the end of the diene elastomer via the silicon atom. On conclusion of the functionalization, the elastomer is subjected to controlled operating conditions which make possible the hydrolysis and the condensation of the chain ends so as to create star-branched elastomers in the desired proportions. Such processes are described in the literature; reference may in particular be made to the document EP 2075278 A1.

30 The functionalization of the living diene elastomer resulting from the polymerization stage can be carried out at a temperature varying from 20°C to 120°C, in the presence, to begin with, of an appropriate amount of a star-branching agent in order to star-branch at most 30% by weight of the living diene elastomer. Then,

subsequently, the remaining living chains of the diene elastomer obtained after the first stage are functionalized by addition of a functionalization agent capable of introducing, at the polymer chain end, the alkoxy silane group bearing a primary, secondary or tertiary amine functional group and reaction with this agent.

5 According to the alternative forms of the invention according to which the functionalization agent bears a protected primary or secondary amine functional group, the synthesis process can be continued by a stage of deprotection of the primary or secondary amine. This stage is carried out after the modification reaction. The chains functionalized by the protected amine group can, by way of example, be
10 reacted with an acid, a base, a fluorinated derivative, such as tetrabutylammonium fluoride, a silver salt, such as silver nitrate, and the like, in order to deprotect this amine functional group. These different methods are described in the work "Protective Groups in Organic Synthesis", T. W. Green and P. G. M. Wuts, Third Edition, 1999. This deprotection stage can have the effect of hydrolysing all or a
15 portion of the hydrolysable alkoxy silane functional groups of the modified diene elastomer in order to convert them into silanol functional groups.

 According to alternative forms of the invention, the synthesis process can comprise a stage of hydrolysis of the hydrolysable alkoxy silane functional groups by addition of an acidic, basic or neutral compound, as described in the document EP 2
20 266 819 A1. The hydrolysable functional groups are then converted in all or in part into silanol functional groups.

 According to alternative forms of the invention, the process can comprise a conventional stage of halting by means, for example, of methanol or water. The process for the synthesis of the modified diene elastomer according to the invention
25 can be continued in a way known per se by the stages of recovery of the modified elastomer.

 According to alternative forms of this process, these stages comprise a stripping stage for the purpose of recovering the elastomer resulting from the prior stages in dry form. This stripping stage can have the effect of hydrolysing all or a
30 portion of the hydrolysable alkoxy silane functional groups of the modified diene elastomer in order to convert them into silanol functional groups. Advantageously, at least 50 mol% to 70 mol% of the functional groups can thus be hydrolysed.

The modified diene elastomer in accordance with the invention exhibits a satisfactory resistance to flow, which induces good behaviour during the storage and transportation of this rubber.

5 The modified diene elastomer according to the invention can be advantageously used, for a tyre application, in a rubber composition reinforced with at least one inorganic filler, such as silica, the raw processing/hysteresis compromise of which it improves. This rubber composition is also the subject-matter of the invention.

10 Thus, as explained above, another subject-matter of the invention is a reinforced rubber composition based on at least one reinforcing filler and on an elastomer matrix comprising at least one modified diene elastomer as described above. It should be understood that the rubber composition can comprise one or more of these modified diene elastomers according to the invention.

15 The reinforced rubber composition according to the invention can be provided in the crosslinked state or in the non-crosslinked, in other words crosslinkable, state.

20 The modified diene elastomer according to the invention can, according to different alternative forms, be used alone in the composition or as a blend with at least one other conventional diene elastomer, whether or not star-branched, coupled or functionalized. Preferably, this other diene elastomer used in the invention is selected from the group of highly unsaturated diene elastomers consisting of polybutadienes (BRs), synthetic polyisoprenes (IRs), natural rubber (NR), butadiene copolymers, isoprene copolymers and the mixtures of these elastomers. Such copolymers are more preferably selected from the group consisting of
25 butadiene/styrene copolymers (SBRs), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs) and isoprene/butadiene/styrene copolymers (SBIRs). It is also possible to envisage a blend with any synthetic elastomer other than a diene elastomer, indeed even with any polymer other than an elastomer, for example a thermoplastic polymer.

30 When the conventional elastomer used as a blend is natural rubber and/or one or more diene polymers, such as, for example, polybutadienes, polyisoprenes or butadiene/styrene or butadiene/styrene/isoprene copolymers, this elastomer or these elastomers, modified or unmodified, can then be present at from 1 to 70 parts by weight per 100 parts of modified diene elastomer according to the invention.

It should be noted that the improvement in the properties of the composition according to the invention will be greater as the proportion of the elastomer(s) different from the modified diene elastomers of the invention in this composition becomes lower.

5 Thus, preferably, the elastomer matrix predominantly comprises by weight the modified diene elastomer according to the invention.

More preferably, the elastomer matrix is composed solely of the modified diene elastomer according to the invention.

10 The rubber composition of the invention comprises, besides at least one elastomer matrix as described above, at least one reinforcing filler.

Use may be made of any type of reinforcing filler known for its abilities to reinforce a rubber composition which can be used in the manufacture of tyre treads, for example carbon black, a reinforcing inorganic filler, such as silica, with which is combined, in a known way, a coupling agent, or also a mixture of these two types of
15 filler.

All carbon blacks, used individually or in the form of mixtures, in particular blacks of the HAF, ISAF or SAF type, conventionally used in the treads of tyres ("tyre-grade" blacks) are suitable as carbon blacks. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series (ASTM grades), such as, for example, the N115, N134, N234, N326, N330, N339,
20 N347 or N375 blacks.

"Reinforcing inorganic filler" should be understood, in the present patent application, by definition, as any inorganic or mineral filler, whatever its colour and its origin (natural or synthetic), capable of reinforcing by itself alone, without means
25 other than an intermediate coupling agent, a rubber composition intended for the manufacture of tyres; such a filler is generally characterized, in a known way, by the presence of hydroxyl (–OH) groups at its surface.

Mineral fillers of the siliceous type, in particular silica (SiO₂), or of the aluminous type, in particular alumina (Al₂O₃), are especially suitable as reinforcing
30 inorganic fillers. The silica used can be any reinforcing silica known to a person skilled in the art, in particular any precipitated or fumed silica exhibiting a BET specific surface and a CTAB specific surface both of less than 450 m²/g, preferably from 30 to 400 m²/g and in particular between 60 and 300 m²/g. Mention will also be made of mineral fillers of the aluminous type, in particular alumina (Al₂O₃) or

aluminium (oxide) hydroxides, or also reinforcing titanium oxides, for example described in US 6 610 261 and US 6 747 087. Also suitable as reinforcing fillers are reinforcing fillers of another nature, in particular carbon black, provided that these reinforcing fillers are covered with a siliceous layer or else comprise, at their surface,
5 functional sites, in particular hydroxyl sites, requiring the use of a coupling agent in order to establish the bond between the filler and the elastomer. By way of example, mention may be made, for example, of carbon blacks for tyres, such as described, for example, in patent documents WO 96/37547 and WO 99/28380.

The physical state in which the reinforcing inorganic filler is provided is not
10 important, whether it is in the form of a powder, of micropearls, of granules, of beads or any other appropriate densified form. Of course, the term "reinforcing inorganic filler" is also understood to mean mixtures of different reinforcing fillers, in particular of highly dispersible siliceous fillers as described above.

Preferably, the content of total reinforcing filler (carbon black and/or other
15 reinforcing filler, such as silica) is between 10 and 200 phr, more preferably between 30 and 150 phr and more preferably still between 70 and 130 phr, the optimum being, in a known way, different according to the specific applications targeted.

According to an alternative form of the invention, the reinforcing filler is
20 predominantly other than carbon black, that is to say that it comprises more than 50% by weight, of the total weight of the reinforcing filler(s), of one or more fillers other than carbon black, in particular a reinforcing inorganic filler, such as silica, indeed even it consists exclusively of such a filler.

According to this alternative form, when carbon black is also present, it can
25 be used at a content of less than 20 phr, more preferably of less than 10 phr (for example between 0.5 and 20 phr, in particular from 1 to 10 phr).

According to another alternative form of the invention, use is made of a reinforcing filler predominantly comprising carbon black and optionally silica or another inorganic filler.

When the reinforcing filler comprises a filler requiring the use of a coupling
30 agent in order to establish the bond between the filler and the elastomer, the rubber composition according to the invention in addition conventionally comprises an agent capable of effectively providing this bond. When silica is present in the composition as reinforcing filler, use may be made, as coupling agents, of organosilanes, in

particular alkoxysilane polysulfides or mercaptosilanes, or else of at least bifunctional polyorganosiloxanes.

Such a coupling agent should not be confused with the coupling agent used for the synthesis of the modified diene elastomer described above.

5 In the composition according to the invention, the content of coupling agent is advantageously less than 20 phr, it being understood that it is generally desirable to use as little of it as possible. Its content is preferably between 0.5 and 12 phr. The presence of the coupling agent depends on the presence of the reinforcing inorganic filler. Its content is easily adjusted by a person skilled in the art according to the
10 content of this filler; it is typically of the order of 0.5% to 15% by weight, with respect to the amount of reinforcing inorganic filler other than carbon black.

 The rubber composition according to the invention can also comprise, in addition to the coupling agents, coupling activators, agents for covering the fillers or more generally processing aids capable, in a known way, by virtue of an
15 improvement in the dispersion of the filler in the rubber matrix and of a lowering of the viscosity of the composition, of improving its ability to be processed in the raw state, these agents being, for example, hydrolysable silanes, such as alkylalkoxysilanes, polyols, polyethers, primary, secondary or tertiary amines, or hydroxylated or hydrolysable polyorganosiloxanes.

20 The rubber compositions in accordance with the invention can also contain reinforcing organic fillers which can replace all or a portion of the carbon blacks or of the other reinforcing inorganic fillers described above. Mention may be made, as examples of reinforcing organic fillers, of functionalized polyvinyl organic fillers, such as described in Applications WO-A-2006/069792, WO-A-2006/069793, WO-A-
25 2008/003434 and WO-A-2008/003435.

 The rubber composition according to the invention can also comprise all or a portion of the usual additives generally used in elastomer compositions intended for the manufacture of tyres, such as, for example, pigments, non-reinforcing fillers, protective agents, such as antiozone waxes, chemical antiozonants or antioxidants,
30 antifatigue agents, plasticizing agents, reinforcing or plasticizing resins, methylene acceptors (for example, phenolic novolak resin) or methylene donors (for example, HMT or H3M), such as described, for example, in Application WO 02/10269, a crosslinking system based either on sulfur or on sulfur donors and/or on peroxide and/or on bismaleimides, vulcanization accelerators or vulcanization activators.

The composition is manufactured in appropriate mixers, using two successive phases of preparation well known to a person skilled in the art: a first phase of thermomechanical working or kneading ("non-productive" phase) at high temperature, up to a maximum temperature of between 110°C and 190°C, preferably
5 between 130°C and 180°C, followed by a second phase of mechanical working ("productive" phase) down to a lower temperature, typically of less than 110°C, for example between 40°C and 100°C, during which finishing phase the crosslinking system is incorporated.

The process for the preparation of a composition according to the invention
10 generally comprises:

- (i) the implementation, at a maximum temperature of between 130°C and 180°C, of a first step of thermomechanical working of the constituents of the composition comprising the modified diene elastomer according to the invention and a reinforcing filler, with the exception of a crosslinking system, then
15
- (ii) the implementation, at a temperature lower than the said maximum temperature of the said first step, of a second step of mechanical working during which the said crosslinking system is incorporated.

This process can also comprise, prior to the implementation of the abovementioned stages (i) and (ii), the stages of the preparation of the modified diene elastomer according to the process described above.
20

Another subject-matter of the invention is a semi-finished article made of rubber for a tyre, comprising a rubber composition according to the invention, which is crosslinkable or crosslinked, or consisting of such a composition.

The final composition thus obtained can subsequently be calendered, for example in the form of a sheet or of a plaque, or also extruded, for example in order to form a rubber profiled element which can be used as semi-finished product made of rubber intended for the tyre.
25

Due to the improved hysteresis/raw processing compromise while maintaining the resistance to flow of the elastomer which characterizes a reinforced rubber composition according to the invention, it should be noted that such a
30 composition can constitute any semi-finished product of the tyre and very particularly the tread, reducing in particular its rolling resistance.

A final subject-matter of the invention is thus a tyre comprising a semi-finished article according to the invention, in particular a tread.

The abovementioned characteristics of the present invention, and also others, will be better understood on reading the following description of several implementational examples of the invention, given by way of illustration and without limitation.

5

Examples

Measurements and tests used

10

Size exclusion chromatography

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The SEC (Size Exclusion Chromatography) technique makes it possible to separate macromolecules in solution according to their size through columns filled with a porous gel. The macromolecules are separated according to their hydrodynamic volume, the bulkiest being eluted first.

20

Without being an absolute method, SEC makes it possible to comprehend the distribution of the molar masses of a polymer. The various number-average molar masses (M_n) and weight-average molar masses (M_w) can be determined from commercial standards and the polydispersity index ($PI = M_w/M_n$) can be calculated via a "Moore" calibration.

25

There is no specific treatment of the polymer sample before analysis. The latter is simply dissolved in the elution solvent at a concentration of approximately 1 g.l⁻¹. The solution is then filtered through a filter with a porosity of 0.45 μ m before injection.

30

The apparatus used is a Waters Alliance chromatographic line. The elution solvent is either tetrahydrofuran or tetrahydrofuran + 1 vol% of diisopropylamine + 1 vol% of triethylamine, the flow rate is 1 ml.min⁻¹, the temperature of the system is 35°C and the analytical time is 30 min. A set of two Waters columns with the Styragel HT6E trade name is used. The volume of the solution of the polymer sample injected is 100 μ l. The detector is a Waters 2410 differential refractometer and the software for making use of the chromatographic data is the Waters Empower system.

The calculated average molar masses are relative to a calibration curve produced for SBRs having the following microstructure: 25% by weight (with respect to the weight of the polymer) of units of styrene type, 23% by weight (with respect to

the butadiene part) of units of 1,2- type and 50% by weight (with respect to the butadiene part) of units of trans-1,4- type.

5 Mooney viscosity

For the polymers and rubber compositions, the Mooney viscosities $ML_{(1+4)}100^{\circ}C$ are measured according to Standard ASTM D-1646.

10 Use is made of an oscillating consistometer as described in Standard ASTM D-1646. The Mooney plasticity measurement is carried out according to the following principle: the elastomer or the composition in the raw state (i.e., before curing) is moulded in a cylindrical chamber heated to $100^{\circ}C$. After preheating for one minute, the rotor rotates within the test specimen at 2 revolutions/minute and the working torque for maintaining this movement after rotating for 4 minutes is
15 measured. The Mooney plasticity $ML_{(1+4)}$ is expressed in "Mooney unit" (MU, with 1 MU = 0.83 N.m).

The difference between the Mooney viscosity of the composition and the Mooney viscosity of the elastomer makes it possible to measure the raw processability or processing. The smaller this difference, the better the raw
20 processing.

Differential calorimetry

25 The glass transition temperatures (T_g) of the elastomers are determined using a differential scanning calorimeter.

Near-infrared (NIR) spectroscopy

30 The microstructure of the elastomers is characterized by the near-infrared (NIR) spectroscopy technique.

Near-infrared spectroscopy (NIR) is used to quantitatively determine the content by weight of styrene in the elastomer and also its microstructure (relative distribution of the 1,2-, trans-1,4- and cis-1,4- butadiene units). The principle of the

method is based on the Beer-Lambert law generalized for a multicomponent system. As the method is indirect, it involves a multivariate calibration [Vilmin, F., Dussap, C. and Coste, N., Applied Spectroscopy, 2006, 60, 619-29] performed using standard elastomers having a composition determined by ^{13}C NMR. The styrene content and the microstructure are then calculated from the NIR spectrum of an elastomer film having a thickness of approximately 730 μm . The spectrum is acquired in transmission mode between 4000 and 6200 cm^{-1} with a resolution of 2 cm^{-1} using a Brüker Tensor 37 Fourier-transform near-infrared spectrometer equipped with an InGaAs detector cooled by the Peltier effect.

Intrinsic viscosity

The intrinsic viscosity of the elastomers at 25°C is determined from a 0.1 g.dl $^{-1}$ solution of elastomer in toluene, according to the following principle:

The intrinsic viscosity is determined by the measurement of the flow time t of the polymer solution and of the flow time t_0 of the toluene in a capillary tube.

The flow time of the toluene and the flow time of the 0.1 g.dl $^{-1}$ polymer solution are measured in an Ubbelohde tube (diameter of the capillary 0.46 mm, capacity from 18 to 22 ml) placed in a bath thermostatically controlled at $25 \pm 0.1^\circ\text{C}$.

The intrinsic viscosity is obtained by the following relationship:

$$\eta_{inh} = \frac{1}{C} \ln \left[\frac{(t)}{(t_0)} \right]$$

with:

C : concentration of the solution of polymer in toluene in g.dl $^{-1}$,

t : flow time of the solution of polymer in toluene in seconds,

t_0 : flow time of the toluene in seconds,

η_{inh} : intrinsic viscosity expressed in dl.g $^{-1}$.

Cold flow (CF $_{(1+6)}$ 100°C)

It is a matter of measuring the weight of elastomer extruded through a calibrated die over a given time (6 hours) and under fixed conditions ($T = 100^\circ\text{C}$).

The die has a diameter of 6.35 mm and a thickness of 0.5 mm and is located at the bottom and at the centre of a hollowed-out cylindrical dish with a diameter of 52 mm.

40 $\pm$ 4 g of elastomer, formed beforehand into a pellet (thickness of 2 cm and diameter of 52 mm), are placed in this device. A calibrated piston weighing 1 kg ($\pm$ 5 g) is positioned on the elastomer pellet. The assembly is subsequently placed in an oven at 100°C $\pm$ 0.5°C.

As the conditions are not stabilized during the first hour in the oven, the product extruded at $t = 1$ hour is cut off and then discarded.

The measurement is subsequently continued for 6 hours $\pm$ 5 min, during which the product is left in the oven. On conclusion of the 6 hours, the sample of product extruded is cut off and then weighed. The result of the measurement is the weight of elastomer weighed. The lower this result, the more resistant the elastomer is to cold flow.

15

Nuclear Magnetic Resonance (NMR)

¹H NMR makes it possible to quantify the methyl groups borne by the silicon (SiCH₃) by integration of the corresponding signal, located around $\delta = 0$ ppm. The samples are dissolved in carbon disulfide (CS₂). 100 μ l of deuterated cyclohexane (C₆D₁₂) are added for the lock signal. The NMR analyses are carried out on a Bruker 500 MHz spectrometer equipped with a 5 mm BBIZ "broad band" probe. For the quantitative ¹H NMR experiment, the sequence uses a 30° pulse and a repetition time of 2 seconds.

25

Dynamic properties

The dynamic properties and in particular $\tan \delta$ max are measured on a viscosity analyser (Metravib VA4000) according to Standard ASTM D 5992-96. The response of a sample of vulcanized composition (cylindrical test specimen with a thickness of 2 mm and a cross section of 79 mm²), subjected to a simple alternating sinusoidal shear stress, at a frequency of 10 Hz, under standard temperature conditions (40°C) according to Standard ASTM D 1349-99, is recorded. A strain

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amplitude sweep is carried out from 0.1% to 50% peak-to-peak (outward cycle) and then from 50% to 0.1% peak-to-peak (return cycle). The result more particularly made use of is the loss factor $\tan \delta$. For the return cycle, the maximum value of $\tan \delta$ observed, denoted $\tan \delta_{\max}$, is indicated. This value is representative of the hysteresis of the material and in the present case of the rolling resistance: the smaller the value of $\tan \delta_{\max}$, the lower the rolling resistance. In the examples, the results of the dynamic properties are given in base 100. The higher this number expressed in base 100, the lower the hysteresis.

Preparation of the polymers

Preparation of the polymer A: SBR aminoalkoxysilane-functional at the chain end according to the invention

Methylcyclohexane, butadiene, styrene and tetrahydrofurfuryl ethyl ether are continuously introduced into three stirred continuous fed 14-l reactors arranged in series, assumed to be perfectly stirred according to a person skilled in the art, according to the following proportions: butadiene flow rate by weight = 1.854 kg.h^{-1} (1.023 kg.h^{-1} of which are injected at the line inlet, 0.408 kg.h^{-1} of which are injected between the first and the second reactor after having been purified on alumina columns and 0.423 kg.h^{-1} of which are injected between the second and the third reactor after having been purified on alumina columns), styrene flow rate by weight = 0.916 kg.h^{-1} , total concentration by weight of monomer = 12.5 wt.%, tetrahydrofurfuryl ethyl ether flow rate by weight = 108 g/h.

n-Butyllithium (n-BuLi) is introduced in a sufficient amount in order to neutralize the protic impurities introduced by the different constituents present in the line inlet. 470 μmol of n-BuLi per 100 g of monomer are introduced at the inlet of the reactor.

The different flow rates are calculated in order for the mean residence time in each reactor to be 30 min. The three reactors in series are respectively maintained at the following temperatures: 50°C, 60.8°C and 85°C.

A sample of polymer solution is withdrawn at the outlet of the polymerization reactor. The polymer is subsequently subjected to an antioxidizing

treatment with addition of 0.4 phr of 2,2'-methylenebis(4-methyl-6-(tert-butyl)phenol) and 0.2 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The polymer thus treated is separated from its solution by a steam stripping operation and then dried on an open mill at 100°C. The "initial" intrinsic viscosity measured is 1.76 dl.g⁻¹. The number-average molar mass M_n , determined by the SEC technique, is 133 000 g.mol⁻¹ and the polydispersity index PI is 1.39.

At the outlet of the third polymerization reactor, 28 µmol per 100 g of monomer of tin tetrachloride in solution in methylcyclohexane are added to the solution of living polymer ($\text{SnCl}_4/\text{Li} = 0.06$, i.e. 24% of star) and then 800 µmol per 100 g of monomer of (3-N,N-dimethylaminopropyl)dimethoxymethylsilane (1.7 eq. /Li) in solution in methylcyclohexane are added.

The polymer is subsequently subjected to an antioxidizing treatment with addition of 0.4 phr of 2,2'-methylenebis(4-methyl-6-(tert-butyl)phenol) and 0.2 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

The polymer thus treated is separated from its solution by a steam stripping operation and then dried on an open mill at 100°C.

The "final" intrinsic viscosity measured is 1.94 dl.g⁻¹. The jump in viscosity, defined as the ratio of the said "final" viscosity to the said "initial" viscosity, is in this instance 1.10.

The Mooney viscosity of this polymer A is 54.

The number-average molar mass M_n , determined by the SEC technique, is 147 000 g.mol⁻¹ and the polydispersity index PI is 1.46.

The microstructure of this polymer is determined by the NIR method. The content of 1,2- units is 25%, with respect to the butadiene units. The content by weight of styrene is 27.5%.

The glass transition temperature of this polymer is -48.2°C.

The content of (CH₃)Si functional group, determined by ¹H NMR, for the polymer A is 4.6 mmol.kg⁻¹, i.e. 76% of functional chains.

The cold flow CF₍₁₊₆₎100°C of the polymer is 2.1.

Preparation of the polymer B: SBR aminoalkoxysilane-functional at the chain end - Counterexample 1

Methylcyclohexane, butadiene, styrene and tetrahydrofurfuryl ethyl ether are continuously introduced according to the following proportions: butadiene flow rate by weight = 1.379 kg.h^{-1} , styrene flow rate by weight = 0.617 kg.h^{-1} , concentration by weight of monomer = 12.5 wt.%, 60 ppm of tetrahydrofurfuryl ethyl ether, into a stirred continuous fed 14-l reactor, assumed to be perfectly stirred according to a person skilled in the art. n-Butyllithium (n-BuLi) is introduced in a sufficient amount in order to neutralize the protic impurities introduced by the different constituents present in the line inlet. 645 μmol of n-BuLi per 100 g of monomer are introduced at the inlet of the reactor.

The different flow rates are calculated in order for the mean residence time in the reactor to be 40 min. The temperature is maintained at 90°C .

A sample of polymer solution is withdrawn at the outlet of the polymerization reactor. The polymer is subsequently subjected to an antioxidizing treatment with addition of 0.4 phr of 2,2'-methylenebis(4-methyl-6-(tert-butyl)phenol) and 0.2 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The polymer thus treated is separated from its solution by a steam stripping operation and then dried on an open mill at 100°C . The "initial" intrinsic viscosity measured is 2.02 dl.g^{-1} . The number-average molar mass M_n , determined by the SEC technique, is $160\,600 \text{ g.mol}^{-1}$ and the polydispersity index PI is 1.90.

At the outlet of the polymerization reactor, 39 μmol per 100 g of monomer of tin tetrachloride in solution in methylcyclohexane are added to the solution of living polymer ($\text{SnCl}_4/\text{Li} = 0.06$, i.e. 24% of star) and then 1070 μmol per 100 g of monomer of (3-N,N-dimethylaminopropyl)dimethoxymethylsilane (1.7 eq. /Li) in solution in methylcyclohexane are added.

The polymer is subsequently subjected to an antioxidizing treatment with addition of 0.4 phr of 2,2'-methylenebis(4-methyl-6-(tert-butyl)phenol) and 0.2 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

The polymer thus treated is separated from its solution by a steam stripping operation and then dried on an open mill at 100°C .

The "final" intrinsic viscosity measured is 2.12 dl.g^{-1} . The jump in viscosity, defined as the ratio of the said "final" viscosity to the said "initial" viscosity, is in this instance 1.05.

The Mooney viscosity of this polymer B is 75.

The number-average molar mass M_n , determined by the SEC technique, is 175 000 g.mol⁻¹ and the polydispersity index PI is 2.05.

The microstructure of this polymer is determined by the NIR method. The content of 1,2- units is 24.5%, with respect to the butadiene units. The content by weight of styrene is 27.5%.

The glass transition temperature of this polymer is - 48°C.

The content of (CH₃)Si functional group, determined by ¹H NMR, for the polymer B is 3.8 mmol.kg⁻¹, i.e. 76% of functional chains.

The cold flow CF₍₁₊₆₎100°C of the polymer is 1.9.

Preparation of the polymer C: SBR aminoalkoxysilane-functional at the chain end - Counterexample 2

Methylcyclohexane, butadiene, styrene and tetrahydrofurfuryl ethyl ether are continuously introduced into three stirred continuously fed 14-l reactors arranged in series, assumed to be perfectly stirred according to a person skilled in the art, according to the following proportions: butadiene flow rate by weight = 1.854 kg.h⁻¹ (1.023 kg.h⁻¹ of which are injected at the inlet of the first reactor, 0.408 kg.h⁻¹ of which are injected between the first and the second reactor after having been purified on alumina columns and 0.423 kg.h⁻¹ of which are injected between the second and the third reactor after having been purified on alumina columns), styrene flow rate by weight = 0.916 kg.h⁻¹, total concentration by weight of monomer in the second reactor = 12.5 wt.%, tetrahydrofurfuryl ethyl ether flow rate by weight = 108 g/h.

n-Butyllithium (n-BuLi) is introduced in a sufficient amount in order to neutralize the protic impurities introduced by the different constituents present at the inlet of the first reactor. 412 μmol of n-BuLi per 100 g of monomer are introduced at the inlet of the first reactor.

The different flow rates are calculated in order for the mean residence time in the final reactor to be 30 min. The three reactors in series are respectively maintained at the following temperatures: 50°C for the first and 60.8°C for the second and 85°C for the third.

A sample of polymer solution is withdrawn at the outlet of the third polymerization reactor. The polymer thus obtained is subsequently subjected to an antioxidizing treatment with addition of 0.4 phr of 2,2'-methylenebis(4-methyl-6-

(tert-butyl)phenol) and 0.2 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. The polymer thus treated is subsequently separated from its solution by a steam stripping operation and then dried on an open mill at 100°C. The "initial" intrinsic viscosity measured is 2.07 dl.g⁻¹. The number-average molar mass M_n , determined by the SEC technique, is 171 400 g.mol⁻¹ and the polydispersity index PI is 1.4.

At the outlet of the polymerization reactor, 25 µmol per 100 g of monomer of tin tetrachloride in solution in methylcyclohexane are added to the solution of living polymer ($\text{SnCl}_4/\text{Li} = 0.06$, i.e. 24% of star) and then 700 µmol per 100 g of monomer of (3-N,N-dimethylaminopropyl)dimethoxymethylsilane (1.7 eq. /Li) in solution in methylcyclohexane are added.

The polymer is subsequently subjected to an antioxidizing treatment with addition of 0.4 phr of 2,2'-methylenebis(4-methyl-6-(tert-butyl)phenol) and 0.2 phr of N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine.

The polymer thus treated is separated from its solution by a steam stripping operation and then dried on an open mill at 100°C.

The "final" intrinsic viscosity measured is 2.40 dl.g⁻¹. The jump in viscosity, defined as the ratio of the said "final" viscosity to the said "initial" viscosity, is in this instance 1.16.

The Mooney viscosity of this polymer C is 87.

The number-average molar mass M_n , determined by the SEC technique, is 188 700 g.mol⁻¹ and the polydispersity index PI is 1.47.

The microstructure of this polymer is determined by the NIR method. The content of 1,2- units is 24.5%, with respect to the butadiene units. The content by weight of styrene is 27.5%.

The glass transition temperature of this polymer is -48°C.

The content of (CH₃)Si functional group, determined by ¹H NMR, for the polymer C is 3.6 mmol.kg⁻¹, i.e. 76% of functional chains.

The cold flow CF₍₁₊₆₎100°C of the polymer is 1.2.

Comparative examples of rubber compositions

Three compositions given in Table 1 below are compared. The composition of Example 1 is in accordance with the invention. The compositions of

Counterexamples 1 and 2 are comparative compositions not in accordance with the invention.

The formulations are expressed in percentage by weight per 100 parts by weight of elastomer (phr).

5

Table 1

	Ex. 1	Counterex. 1	Counterex. 2
Polymer A	80	0	0
Polymer B	0	80	0
Polymer C	0	0	80
Nd-BR ML44 (*)	20	20	20
Silica (1)	73	73	73
N234	3	3	3
MES Oil (2)	6	6	6
Resin (3)	20	20	20
Coupling agent (4)	6	6	6
ZnO	1	1	1
Stearic acid	2	2	2
Antioxidant (5)	2	2	2
Antiozone wax C32ST (6)	1.6	1.6	1.6
Diphenylguanidine	1.3	1.3	1.3
Sulfur	1	1	1
Sulfenamide (7)	1.6	1.6	1.6

(*) cis-1,4-Polybutadiene obtained by polymerization catalysed by neodymium; Mooney elastomer = 44

(1) Silica, Zeosil 1165MP from Rhodia

(2) Catenex® SBR from Shell

10

- (3) Polylimonene
- (4) Si69 from Degussa
- (5) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
- (6) Antiozone from Repsol
- 5 (7) N-Cyclohexyl-2-benzothiazolesulfenamide

The following procedure is used for the tests which follow:

10 Each of the compositions is produced, in a first step, by thermomechanical working and then, in a second finishing step, by mechanical working.

The elastomer, two-thirds of the silica, the coupling agent, the diphenylguanidine and the carbon black are introduced into a laboratory internal mixer of "Banbury" type which has a capacity of 400 cm³, which is 72% filled and which has an initial temperature of 90°C.

15 The thermomechanical working is carried out by means of blades, the mean speed of which is 50 rev/min and the temperature of which is 90°C.

After one minute, the final one-third of the silica, the antioxidant, the stearic acid, the antiozone wax, the MES oil and the resin are introduced, still under thermomechanical working.

20 After two minutes, the zinc oxide is introduced, the speed of the blades being 50 rev/min.

The thermomechanical working is carried out for a further two minutes, up to a maximum dropping temperature of approximately 160°C.

25 The mixture thus obtained is recovered and cooled and then, in an external mixer (homofinisher), the sulfur and the sulfenamide are added at 30°C, the combined mixture being further mixed for a time of 3 to 4 minutes (second step of mechanical working).

30 The compositions thus obtained are subsequently calendered, either in the form of plaques (with a thickness ranging from 2 to 3 mm) or thin sheets of rubber, for the measurement of their physical or mechanical properties, or in the form of profiled elements which can be used directly, after cutting and/or assembling to the desired dimensions, for example as semi-finished products for tyres, in particular for treads.

Crosslinking is carried out at 150°C for 40 min.

The results are presented in Table 2.

Table 2

5

Rubber results (Tan δ max 40°C, ML₍₁₊₄₎100°C composition, Cold flow):

	Example 1	Counterexample 1	Counterexample 2
	A	B	C
ML ₍₁₊₄₎ 100°C elastomer	54	75	83
Tan δ max 40°C	105	105	103
ML ₍₁₊₄₎ 100°C composition	86	122	121
ML ₍₁₊₄₎ 100°C composition - ML ₍₁₊₄₎ 100°C elastomer	32	47	38
Cold flow (g/6 h)	2.1	1.9	1.3

10 The results presented in Table 2 show an equivalent hysteresis of the composition 1 according to the invention in comparison with that of the composition of Counterexample 1 (polymer B having a high polydispersity index before functionalization and star-branching) and with that of the composition of Counterexample 2 (polymer C having a high Mooney viscosity).

15 The processability of the composition 1 according to the invention is better than that of the compositions of Counterexamples 1 and 2.

 Finally, the resistance to flow of the composition 1 remains satisfactory, in comparison with that of the compositions of Counterexamples 1 and 2, indeed even of the same order as that of the composition of Counterexample 1.

20 Thus, the results presented in Table 2 demonstrate an improvement in the hysteresis/raw processing compromise of the composition containing the polymer according to the invention, while maintaining the resistance to flow of the elastomer.

CLAIMS

1. Modified diene elastomer comprising:

a) at least 70% by weight, with respect to the total weight of the modified diene elastomer, of a linear diene elastomer functionalized predominantly at a chain end by an alkoxysilane group, optionally partially or completely hydrolysed to give silanol, the alkoxysilane group bearing a primary, secondary or tertiary amine functional group, the alkoxysilane group being connected to the diene elastomer via the silicon atom, the said functionalized diene elastomer exhibiting a polydispersity index before functionalization of less than or equal to 1.6,

b) more than 0 and up to 30% by weight, with respect to the total weight of the modified diene elastomer, of a star-branched diene elastomer exhibiting a polydispersity index before star-branching of less than or equal to 1.6,

the Mooney viscosity of the said modified diene elastomer varying from 30 to 80.

2. Modified diene elastomer according to Claim 1, characterized in that the linear diene elastomer a) functionalized predominantly at a chain end by an alkoxysilane group, optionally partially or completely hydrolysed to give silanol, bears a tertiary amine functional group, preferably a diethylamine or dimethylamine functional group.

3. Modified diene elastomer according to Claim 1 or 2, characterized in that the primary, secondary or tertiary amine functional group of the diene elastomer a) and the silicon atom bonded to the elastomer are connected to one another via a spacer group defined as being a saturated or unsaturated, cyclic or non-cyclic, linear or branched, divalent C₁-C₁₈ aliphatic hydrocarbon radical or a divalent C₆-C₁₈ aromatic hydrocarbon radical, the said spacer group optionally comprising one or more aromatic radicals and/or one or more heteroatoms.

4. Modified diene elastomer according to Claim 3, characterized in that the spacer group of the diene elastomer a) is a linear divalent C₁-C₅ aliphatic hydrocarbon radical, preferably the linear C₃ aliphatic radical.

5. Modified diene elastomer according to any one of Claims 1 to 4, characterized in that the alkoxysilane group is a methoxysilane or ethoxysilane group, optionally partially or completely hydrolysed to give silanol.

6. Modified diene elastomer according to any one of Claims 1 to 5, characterized in that it comprises at least 80% by weight, with respect to the total weight of the modified diene elastomer, of the linear diene elastomer functionalized predominantly at a chain end a).

5 7. Modified diene elastomer according to any one of Claims 1 to 6, characterized in that it comprises at most 20% by weight, with respect to the total weight of the modified diene elastomer, of the star-branched diene elastomer b).

8. Elastomer according to any one of the preceding claims, characterized in that the star-branched diene elastomer is a tin-based or silicon-based star-branched elastomer.

10 9. Modified diene elastomer according to any one of the preceding claims, characterized in that the star-branched diene elastomer b) is a star-branched diene elastomer comprising three or four branches.

15 10. Modified diene elastomer according to any one of the preceding claims, characterized in that the diene elastomer is a copolymer of butadiene and of a vinylaromatic monomer, preferably a butadiene/styrene copolymer.

11. Modified diene elastomer according to any one of the preceding claims, characterized in that the diene elastomers a) and b) have, before functionalization and star-branching, the same microstructure and the same macrostructure.

20 12. Modified diene elastomer according to any one of the preceding claims, characterized in that the functionalized diene elastomer a) exhibits a polydispersity index before functionalization varying from 1.2 to 1.6 and the star-branched diene elastomer b) exhibits a polydispersity index before star-branching varying from 1.2 to 1.6.

25 13. Reinforced rubber composition based on at least one reinforcing filler and on an elastomer matrix comprising at least one modified diene elastomer as defined in any one of Claims 1 to 12.

30 14. Composition according to Claim 13, characterized in that the reinforcing filler(s) comprise(s) more than 50% by weight, with respect to the total weight of the reinforcing filler(s), of reinforcing inorganic filler, such as silica.

15. Semi-finished article made of rubber for a tyre, characterized in that it comprises a crosslinkable or crosslinked rubber composition according to Claim 13 or 14.

16. Semi-finished article according to Claim 15, characterized in that the said article is a tread.

17. Tyre, characterized in that it comprises a semi-finished article as defined in Claim 15 or 16.