

CROSS-LINKED POLYDIENE AND RUBBER MIX BASED THEREON

Technical field to which the invention relates

The invention relates to the production of synthetic rubbers, used in the production of tyres and tyre components, rubber-based products, golf balls etc. Specifically, the present invention relates to a cross-linked polydiene, characterized by an optimal balance of properties of linear and branched polymers, and consequently, superior processability and superior elastic-hysteresis and physical-mechanical properties. The invention also relates to a method for obtaining a cross-linked polydiene and a rubber compound based on same. The invention, in addition, relates to the application of said rubber compound for the production of rubber-based products, specifically car tyres, as well as to a product based on said rubber compound, specifically, car tyres.

The Prior Art

Rubber compounds for tyres, based on linearly structured polybutadienes, have a number of advantages when compared with compounds produced using branched polybutadienes, specifically: they have enhanced hysteresis properties and reduced rolling resistance, and consequently, reduce fuel consumption when tyres are running.

However, linear polybutadienes result in high viscosity (Mooney viscosity) of rubber compounds, at the same time polymers do not lend themselves well to processing in the rubber mixing process: they do not mix readily with various fillers, they require a longer mixing time and high energy costs. Branched polymers are characterized by relatively low rubber-mix viscosities, a short mixing time and low extrusion temperatures, but the branched structure of the polymer has an adverse effect on the elastic-hysteresis and strength properties of rubber compounds based on same.

In an attempt to achieve a balance between the properties of linear and branched structures, manufacturers of polymers use various modifying agents. Specifically, a modification using various sulphur compounds is widely known. Variations of this modification are described in detail in patents and scientific literature.

Document DE1260794 (publication date 08.02.1968, BAYER AG) describes a method for producing diene elastomers with enhanced properties, specifically enhanced cold flow. According to this patent, diene polymers, following polymerisation, are treated using disulphur dichloride, sulphur dichloride, thionyl chloride, disulphur dibromide or thionyl bromide.

However, the method described in DE1260794 has a number of disadvantages. Specifically, the ionic-coordinate polymerisation process is conducted at low temperatures, necessary for the suppression of undesirable secondary reactions. This is costly in terms of energy consumption. Also, according to this process, aromatic solvents are used, but at the same time stearic acid is used as a stopping agent, despite the fact that stearic acid does not dissolve readily in aromatic solvents and does not dissolve in aliphatic solvents. Sulphur chlorides result in a step-change increase in Mooney viscosity, but intensify gelation, since the modification reaction takes place not only through the active site of the molecule but also results in the formation of cross links. Furthermore, significant dosages of sulphur chlorides are used, which result in localised restructuring of chains, or said sulphur chloride dosages do not fully engage with the reaction. Excess modifying agent is removed during the degassing process, but this leads to equipment corrosion due to the formation of sour gases.

Document EP0707017 (publication date 16.12.1998, BAYER AG) discloses a method for producing polybutadienes, characterized by reduced cold flow and a faint odour. The method is carried out by adiabatic polymerisation of diolefins at temperatures of between -20 and 150°C in inert organic solvents, and in the presence of organometallic mixed neodymium carboxylate-based catalysts, followed by depressurisation in the reaction mix after polymerisation and by post-polymerisation treatment of the reaction mix with disulphur dichloride, sulphur dichloride and/or thionyl chloride.

A disadvantage of this method is the use of stearic acid as the stopping agent. Document EP0707017 also describes the use of significant dosages of sulphur chlorides, which, during an incomplete modification reaction, during the degassing stage, will form hydrochloric acid leading to equipment corrosion.

Document RU2660853 (publication date 10.07.2018, ARLANXEO DEUTSCHLAND GMBH) discloses a method for producing neodymium polybutadiene, according to which method, post-polymerisation modification using sulphur chlorides is carried out, and after which the polymer is mixed together with a plasticizing agent. The resulting polybutadiene contains more than 90 wt.% of 1,4-cis units and less than 1 wt.% 1,2-vinylbutadiene, based on neodymium-catalysed polybutadiene. Moreover, the neodymium-catalysed polybutadiene exhibits a fall in

molar mass of at least 25%, preferably of at least 33%, and more preferably, of at least 50%.

A disadvantage of this method is the use of powdered substances, in solid form, as the plasticizing additive. At the mixing stage this may result in an uneven distribution of plasticator on the rollers, in the volume of rubber. Furthermore, some of the indicated plasticizing additives, when used in a powder form, cause skin and eye irritation.

Document RU2673051 (publication date 21.11.2018, ARLANXEO DEUTSCHLAND GMBH) discloses a vulcanizable composition of rubbers. This composition includes at least one sulphur chloride-modified polybutadiene. According to the patent, the sulphur chloride, prior to being added, can be treated either using a complex ether of carboxylic or fatty acid, or using the carboxylic or fatty acids themselves, and/or a mixture thereof.

Disadvantages of said method are an increased quantity of gel in the polymer, which has a negative effect on the processability of rubber in rubber compounds. Treatment of sulphur chloride using carboxylic acid results in deactivation of the modifying agent, which does not enable the required degree of branching to be achieved and has a negative effect on the physical-mechanical and elastic-hysteresis properties of the product.

Document RU2588136 (publication date 27.06.2016, TRINSEO EUROPE GMBH) proposes a method, according to which a polymer is first modified by adding one or several alkoxysilane compounds and then adding disulphur dichloride, sulphur dichloride, thionyl chloride, disulphur dibromide, thionyl bromide or mixtures of the aforelisted.

Inasmuch as alkoxysilane compounds (tetramethoxysilane and hexamethoxydisilane) are used in this method, there is a high probability that corresponding alcohols, in particular, in the instances described in the embodiments, methanol, will be formed during the water-steam degassing process,. This alcohol has a boiling point which is close to the boiling point of the most frequently used hydrocarbon solvents (hexane-heptane fraction, hexane, cyclohexane). On the scale of an industrial enterprise, the alcohol can, as a result, build up in the solvent, and the presence of the alcohol in the loop, together with the solvent, will either lead to the loss of the active sites of the catalytic complex, or will require additional methods for treating and monitoring the solvent composition. Furthermore, according to

RU2588136 dual modification is used – using expensive oxysilane compounds, sulphur-containing oxysilane compounds, as well as sulphur halides, all of which complicate the monitoring of modification parameters and may result in changes to the cross-linking, changes which degrade the strength and hysteresis properties of the polymer.

The closest in terms of technical essence and the achieved result is the method described in document RU2638960 (publication date 19.12.2017, ARLANXEO DEUTSCHLAND GMBH). According to this method, polymerisation is terminated by adding proton compounds, after which sulphur chlorides are added to the polymerisation product, said sulphur chlorides having been treated, prior to their addition, with a complex ether of fatty acid of plant origin, being an epoxidized soybean oil. Sulphur chlorides are added in the form of a solution in epoxidized soybean oil with a concentration of 37.5-64%. As a result, a high molecular weight polybutadiene is obtained, having a step-change increase in Mooney viscosity, and containing in excess of 95 wt.% of 1,4-cis-units and containing less than 1 wt.% of 1,2-vinyl groups.

Despite the wide range of substances claimed in the document as being capable of terminating the butadiene polymerisation process, the embodiments present only one, stearic acid, which is insoluble in aliphatic solvents and has limited solubility in aromatic solvents, which will complicate dosing in industrial conditions and will reduce the rate of the active chain termination reaction. The rate and effectiveness with which the polymerisation process is stopped by other proton compounds depends on the class of these compounds, the ease of application of same (the ability to dissolve in organic solvents, to form, together with solvents, during treatment, azeotropic mixtures which will have a negative effect when the solvent is used after recycling (reused)). Furthermore, according to the document, many fatty acids and complex ethers of plant origin (both modified and unmodified) can be used, at the rubber modification stage, for treating dithiodichloride, however only the use of epoxidized soybean oil is presented in the embodiments. Based on the materials of RU2638960 it follows that soybean oil is introduced in insufficient amount, in terms of its mole ratio with S_2Cl_2 , despite the fact that the concentration of dithiodichloride in epoxidized soybean oil varies between 37.5 and 64 wt.%. This oil is characterized by the fact that it does not have, or has an insignificant number of, double bonds. And inasmuch as sulphur monochloride is capable of interacting with unsaturated carbon-carbon bonds, it

remains unclear whether the result claimed in RU2638960 will be achieved when unmodified oils with a high percentage of double bonds are used. The interaction of sulphur monochloride with oxirane groups in mild conditions is omitted (the document does not describe the conditions and period of interaction of reagents). Other considerations aside, the application of epoxidized soybean oil will increase the cost of the produced polymer.

Despite the fact that dithiodichloride is introduced in the form of a solution in epoxidized soybean oil, the quantities of this solution are too small to achieve even distribution in the polymerisation mass, which can result in localised cross links.

Disclosure of the invention

The technical aim of the present invention is to improve the elastic-hysteresis properties of rubber compounds while retaining a high degree of physical and mechanical properties of same.

The authors of the present invention discovered that the problem in question can be solved by producing a cross-linked polydiene which is characterized by linearity ratio K_L values in a range from 0.35 to 0.75, defined according to formula (1), and viscosity deformation ratio K_{VD} values in a range from 1.5 to 2.3, defined in accordance with formula (2):

$$K_L = A_1/A_2 \quad (1),$$

where A_1 is the area under the polydiene relaxation curve, at the end of the polymerisation stage, A_2 is the area under the polydiene relaxation curve after the neutralisation stage, Mooney stand. units *sec. (standard units of viscosity, Mooney-seconds);

$$K_{VD} = N_1/\eta' \quad (2),$$

where N_1 is the initial normal variance of stresses,
 η' is the dynamic viscosity of polydiene, kPa×sec, determined on an RPA rheometer at a frequency of 0.1-30 Hz, a deformation angle of 15% and a temperature of 100°C.

The term “cross-linked polydiene”, in the context of the present invention, refers to a polydiene with cross links between linear polymer chains, where said cross links are formed as a result of interaction with individual chemical groups or individual atoms acting as a bridging component. Within the scope of the present invention, cross-

linking results from the treatment of a polymer using a modifying agent, with an interaction mechanism according to which cross-linking takes place not through the active centre, but through dual links between polymer chains. Cross-linking reactions result in an increase in the molecular weight of the polymer due to the formation of cross links between macromolecules. As a result of cross-linking, a widely spaced cross-linked structure is formed in the polymer. Treatment of linear polymers using corresponding cross-linking agents makes it possible to regulate the density of the cross-linking. And so, it has been noted by the authors that when the number of cross links is increased, the plasticity of a polymer decreases, and by contrast, the resilience (elasticity) increases, i.e. the capability for reversible deformations in a highly elastic state. Cross-linking can be achieved, specifically, by using halogen-containing sulphur compounds as modifying agents.

In the context of the present invention, the term “neutralisation stage” refers to the treatment of a solution of cross-linked polydiene using water, specifically softened water with a $\text{pH} > 7$.

One more aim of the present invention is a method for producing a cross-linked polydiene according to the invention, which method includes polymerisation of a conjugated diene in a hydrocarbon solvent, termination of the polymerisation reaction through the introduction of a stopping agent, post-polymerisation treatment using a modifying agent and neutralisation of modifying agent which has not reacted.

The aim of the present invention is also a rubber compound based on the cross-linked polydiene according to the invention.

Another aim of the present invention is a product based on said rubber compound, specifically car tyres.

The present invention, in one other respect thereof, relates to the application of the rubber compound according to the invention, for the production of rubber-based products, specifically car tyres.

The technical result is the obtaining of a cross-linked polydiene, characterized by an optimal balance of properties of linear and branched polymers, consequently the polydiene according to the invention is distinguished by superior processability and superior elastic-hysteresis and physical and mechanical properties; improved handling abilities were also noted, such as improved adherence performance on wet roads (in formulations of rubber compounds for the production of tyres) $\tan \delta$ at 0°C and improved

rolling resistance $\tan\delta$ at 60°C. Moreover, the degree of polydiene cross-linking is stable and unchanged over time during storage of same. Furthermore, the process for producing said polymer is simple and does not require additional expenditure in terms of resources.

The authors of the present invention were able to achieve the aforementioned result by achieving a balance between the linear and branched structure of a polydiene by virtue of a specific density of cross-linking of polymer chains. An evaluation of the density of cross-linking according to the present invention is made based on the value of the linearity ratio K_L , which is determined according to formula (1):

$$K_L = A_1/A_2 \quad (1),$$

where A_1 is the area under the polydiene relaxation curve, at the end of the polymerisation stage, A_2 is the area under the polydiene relaxation curve after the neutralisation stage, Mooney units*sec. (Mooney-seconds viscosity units).

The authors of the present invention noted the following: a polydiene, characterized by K_L linearity ratio values ranging between 0.35 and 0.75, preferably between 0.35 and 0.70, more preferably between 0.40 and 0.65, ideally between 0.40 and 0.60, possesses the best and the optimal, considering all the examined parameters, cross-linking density.

Another significant characteristic of a polymer is its rheological (plasto-elastic) properties, whose value, it is proposed, is determined based on the value of the viscosity deformation ratio K_{VD} . The viscosity deformation ratio K_{VD} makes it possible to characterize the rheological properties of a polymer and assess the processing properties of same, based on the different degree of elasticity, branching and flow of the initial polymer.

The K_{VD} ratio is determined according to formula (2):

$$K_{VD} = N1/\eta' \quad (2),$$

where $N1$ is the initial normal variance in stresses, η' is the dynamic viscosity of the polydiene, kPa×sec., which was measured on an RPA instrument at a frequency of 0.1 - 30 Hz, a deformation angle of 15% and a temperature of 100°C.

It was noted that the higher the K_{VD} value was, the more linear, and consequently the more difficult, the polymer, and rubber compounds based on same, are to process.

It was established that a polydiene characterized by viscosity deformation values K_{VD} in the range 1.5 to 2.3 possesses optimal plasto-elastic properties. According to the present invention the cross-linked polydiene is characterized by K_{VD} values in the range 1.5 to 2.3, preferably 1.58 to 2.1, ideally 1.6 to 2.0. At a viscosity deformation value greater than 2.3, the polymer will be characterized by a high degree of linearity of the polymer chains, and, consequently, the processability of rubber compounds based on said polymer will be poorer. A viscosity deformation value of less than 1.5 indicates excessive cross-linking of the polymer, which is also undesirable for a number of reasons, specifically since that may lead to increased formation of high-molecular-weight gel.

In order to determine the linearity ratio K_L of a polydiene, a Mooney stress relaxation measurement is taken. Stress relaxation is the reaction of rubber or a rubber compound to rapid flow termination or sudden deformation. It is in the form of a reduction in shear stress when the rotor of a viscosimeter suddenly stops rotating. Stress relaxation is the combined manifestation of elastic and viscous properties of a material (GOST R 54552-2011). The area contained within the stress relaxation graph is called the area under the relaxation curve A. For different types of polymer, the area under the relaxation curve is different, moreover, it always reduces in size, as the plastic component in the rubber increases and the elastic component decreases. According to the present invention it is proposed that the area below the relaxation curve be measured 2 seconds after the viscosimeter rotor has stopped, since the elastic component is dominant at the very start of relaxation, when the material is trying to move to an equilibrium state, at the moment the external force (deformation) is removed. Recording the elastic component is fundamentally important since it has the greatest influence on the processability (ease of manufacture) of rubber compounds.

The rate of stress relaxation is linked to the characteristics of the molecular structure of the rubber i.e. it depends on the correlation between the branched and linear components of same and increases with an increase in the number of polymer chains of linear structure. Consequently, we can say that the smaller the area under the relaxation curve, the more linear the polymer. When relaxation time is increased, the contribution of the elastic component decreases and the contribution of the plastic component increases.

Therefore, a decrease in the value of the linearity ratio K_L attests to an improvement in the processability of rubber compounds. However, in order to achieve an optimal balance of properties, a polymer must at the same time possess the properties of both a linear polymer and a branched polymer.

The authors of the present invention have managed to achieve such a balance of properties, having identified the optimal range of linearity ratio values K_L and monitoring the values of same: so, at a value of less than 0.35, the polydiene will be characterized by excessive cross-linking of polymer chains, which may result in increased formation of high-molecular-weight gel; a linearity ratio value exceeding 0.75 indicates excess linearity of the polymer chains, which makes the rubber compounds less easy to process.

The principal process properties, used as a basis for predicting the behaviour of polymers when same are being processed, are plasto-elastic properties. Within the scope of the present invention, for the purposes of evaluating plasto-elastic properties, it is proposed that the viscosity deformation ratio K_{VD} (2) be determined

$$K_{VD} = N1/\eta' \quad (2),$$

where $N1$ is the initial normal variance in stresses, said variance being determined according to formula 3, η' is the polydiene dynamic viscosity, $\text{kPa} \times \text{sec.}$, which was measured on an RPA instrument at a frequency of 0.1-30 Hz, a deformation angle of 15% and a temperature of 100°C.

In turn, the initial normal variance of stresses $N1$ is determined according to formula 3, according to Laun's Rule (Prediction of Elastic Strains of Polymer Melts in Shear and Elongation. H. M. Laun. Journal of Rheology 30, 459, 1986):

$$N1 = 2G'(\omega) \left[1 + \left(\frac{G'(\omega)}{G''(\omega)} \right)^2 \right]^{0.7},$$

where $G'(\omega)$ is the energy storage modulus, kPa ; $G''(\omega)$ is the energy loss modulus, kPa , wherein the aforementioned moduli are measured on an RPA instrument at a frequency of 0.1-30 Hz, a deformation angle of 15% and a temperature of 100°C.

The energy storage modulus G' is the energy which is stored in the structural elements of a rubber sample when subjected to load and which is released when the load is removed.

The energy loss modulus G'' is the energy which, when deformation is applied to the viscous elements of the rubber, cannot be stored in said viscous elements and is dissipated during deformation, therefore G'' energy describes energy dissipation.

Inasmuch as polydienes, having different configurations of molecules (linearity and branching), react differently to deformation at different deformation change frequencies (frequency 0.1-30 Hz, deformation angle 15%), i.e. they exhibit different degrees of elasticity. The test mode using a deformation angle of 15% allows for the initial configuration of molecules to remain unbroken and for a more sensitive and accurate measurement to be taken. Based on the balance between the elastic component G' and the plastic component G'' , it is possible to come to a preliminary conclusion as to the processability of a polymer. Nevertheless, for a more comprehensive and accurate assessment, the viscous properties of the polydienes also need to be considered, specifically the dynamic viscosity value η at different deformation frequencies, said value being correlated to the Mooney viscosity value.

Therefore, the authors of the present invention have established that a polydiene characterized by linearity ratio values K_L in the range from 0.35 to 0.75 and viscosity deformation ratio values K_{VD} in the range from 1.5 to 2.3 is a polydiene which possesses an optimal balance of properties of linear and branched polymers, with all the benefits associated therewith.

The method for obtaining a cross-linked polydiene according to the invention includes the polymerisation of a conjugated diene in a hydrocarbon solvent, termination of the polymerisation reaction through the introduction of a stopping agent, post-polymerisation treatment using a modifying agent and neutralisation of modifying agent which has not reacted.

The method for obtaining cross-linked polydienes can be carried out using any known method. Moreover, post-polymerisation treatment of the polymer using a modifying agent, and having an interaction mechanism whereby cross-linking takes place along dual links between polymer chains, is the most desirable, since cross-linking of the polymer chains makes it possible, without additional effort, to ensure that the values of ratios K_L and K_{VD} correspond to the claimed ranges, and consequently, to also achieve a balance of the properties of branched and linear polymers.

The preferred embodiment of the invention proposes obtaining a neodymium cross-linked polydiene in the way described below:

1) carrying out polymerisation of a conjugated diene in an organic solvent in the presence of a neodymium-based catalyst;

2) termination of the polymerisation process by introducing at least one reactive compound;

3) post-polymerisation modification using at least one modifying agent, to achieve cross-linking of the polymer chains, the modifying agent preferably to be introduced in the form of a 3-20% solution in an organic solvent;

4) neutralisation of unreacted modifying agent, not necessarily by introducing softened water, and then stirring the mixture at a temperature being not lower than the polymerisation temperature;

5) separating out of the polymer.

Catalytic complex

Various ionic-coordinate polymerisation catalytic systems – titanium, cobalt, nickel and neodymium – enable polydienes with differing micro- and macrostructures to be obtained. So, persons skilled in the art know that a titanium polydiene comprises 88-92 wt.% 1,4-cis-units, 2-5 wt.% 1,4-trans-units, 3.5-4.5 wt.% 1,2-units, nickel and cobalt polydienes comprise 95-97 wt.% 1,4-cis-units, 1.2-2.0 wt.% 1,4-trans-units, 1.5-2.5 wt.% 1,2-units, neodymium polydiene comprises 96-99 wt.% 1,4-cis-units, 0.5-2.5 wt.% 1,4-trans-units, 0.5-1, wt.% 1,2-units. Inasmuch as the quantity of 1,4-cis-units in polymers, obtained in different catalytic systems, varies, and modification is carried out specifically on cis-units, when modification is carried out using the same number of modifying agents, the density with which polymer cross links are formed will vary: in a titanium polydiene, the density will be the highest of the four catalytic systems, in a neodymium polydiene, it is the lowest. Furthermore, in the case of nickel or cobalt catalytic systems, the polymers which form are typically more branched than in a titanium catalytic system. A neodymium catalytic system facilitates the formation of highly linear polymers. Modification of polymers obtained in different catalytic systems offers different results – the more branched the polymer, the poorer the strength and hysteresis properties of rubber compounds based on said polymer will be, but at the same time processing of said rubber compounds will be easier.

Currently, the Ziegler-Natta catalytic system is the most widely used system for carrying out polymerisation in industrial manufacturing, said system including (A) neodymium compounds, (B) an organoaluminium compound, (C) optionally, a conjugated diene and (D) a halogen-containing component. These components can be introduced directly into the solution of diene or be used in the form of a preformed catalytic complex. The application of other, lanthanide-based, catalytic systems is possible.

As an alternative to neodymium compounds, other lanthanides can be used, for instance, lanthanum, cerium, praseodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium.

Compounds which contain lanthanides include, but are not limited to, compounds such as: carboxylates, organophosphates, organophosphonates, organophosphonites, carbamates, dithiocarbamates, lanthanide xanthogenates, β -diketonates, halides, oxyhalides, alkoxides.

Polymerisation

Polymerisation of a conjugated diene is carried out in an organic solvent medium, for instance in a hydrocarbon solvent.

The solvent used for polymerisation is an organic solvent which is inert in reaction conditions and does not contain active groups capable of interacting with the components of the catalytic system. The following can be used as the solvent, either individually, or in mixtures with one another: hydrocarbon solvents, specifically aliphatic hydrocarbons, and specifically those such as butane, pentane, hexane, heptane, or isomers of the aforelisted; alicyclic hydrocarbons, and specifically cyclopentane, cyclohexane, or isomers of the aforelisted; monoolefins, such as 1-butene, 2-butene, or mixtures thereof; aromatic hydrocarbons, specifically those such as benzene, toluene, xylol.

Conjugated dienes in use include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethylbutadiene, 1-phenyl-1,3-butadiene and 1,3-hexadiene. In the preferred embodiment, 1,3-butadiene and/or isoprene are used.

The polymerisation process, specifically, is conducted in the following way. A monomer is mixed together with the solvent, for example, in the ratio (5-20):(95-80) pts. wt. respectively, the monomer:solvent ratio being preferably (8-17):(92-87) pts. wt., ideally (10-15):(90-85) pts. wt. The polymerisation temperature is most commonly

40-120°C, preferably 50-110°C, ideally 60-100°C, the optimal polymerisation duration is 1.5 to 2 hours. Monomer conversion, in the case of polymerisation in a solution, is typically up to 95-99%. When conversion of at least 95% is achieved, the reaction is stopped. Lowering the polymerisation temperature affects the rate at which the reaction takes place – it slows down, which in some instances can be undesirable. High polymerisation temperatures can lead to degradation of the catalytic complex. Therefore, the conditions for polymerisation are selected individually, in accordance with the specified parameters.

Stopping – termination of the polymerisation reaction

Stopping of the polymerisation process is carried out by introducing at least one reactive short-stop compound to the polymerisation product, said short-stop compound being capable of reacting with the active site of the polymer molecule and of terminating the polymerisation process.

Alcohols, polyols, organic acids and ethers thereof can be used as a stopping agent, specifically including, but not limited to, the use of compounds such as methanol, ethanol, 1-octanol, 2-ethylhexanol, ethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 2-ethylhexanoic acid, lauric acid, oleic acid, versatic acid, methyl stearate, methyl oleate etc. After being introduced into the reaction mass, these compounds react with the active metals of the catalytic complex (Nd, Al), forming corresponding salts which are physically bonded to the macromolecules of the polydiene and which, after being separated out, remain in the rubber composition, acting as a plasticizer and additionally improve the processability of rubber compounds based on said rubbers.

The compounds, which act as a stopping agent, are dissolved in an organic solvent (hexane, cyclohexane, pentane, 2-methyl-pentane, 3-methyl-pentane, 2,3-dimethyl-pentane or mixtures of the aforelisted), preferably in the solvent which is being used for polymerisation. As a rule, stopping agents are used in the form of a solution with a concentration of 5-15 wt.%, preferably 8-12 wt.%. The quantity of stopping agent introduced depends on the number of catalyst components. If insufficient stopping agent is used, a portion of the cross-linking sites will remain active and capable of reacting with the modifying agent, which can lead to excessive cross-linking of polymer chains and to an increase in the quantity of gel.

After a short stop has been applied to the reaction mass, monomer which has not reacted is preferably removed. Specifically, removal of unreacted monomer is carried

out using a method of sparging of the reaction mass with surplus inert gas (helium, nitrogen, argon etc.). The unreacted monomer is able to react with the modifying agent, forming toxic chlorine-containing compounds. Removal of the unreacted monomer is continued until the monomer is completely absent from the egressing gas phase (ideally within no less than 30 minutes). Monitoring of the gas phase composition is carried out using gas chromatography.

Modification

At the end of the stopping process, a modifying agent is introduced into the polymerisation product, said modifying agent being capable of generating cross-linking of polymer chains. Preferably, the modifying agent is a halogen-containing sulphur compound.

For halogen-containing sulphur compounds, it is preferable to use sulphur chlorides and sulphur bromides, and specifically dithiodichloride, sulphur chloride, thionyl chloride, dithiodibromide, sulphur bromide, thionyl bromide. Sulphur halides, used as the modifying agent, contain at least two halogen atoms, and at least one sulphur atom. The preferred embodiment is a modifying agent containing two sulphur atoms and two halogen atoms. The preferred modifying agent is dithiodichloride.

The modifying agent is used in the form of a solution in an organic solvent, preferably the same as that used for polymerisation. In the preferred embodiment the concentration of the solution is between 3 and 20 wt.%. A concentration exceeding 20 wt.% may result in dosage errors and difficulties in monitoring the process. A concentration of modifying agent solution of below 3 wt.% is uneconomic, cost-effective modification requires a greater volume of solution. Furthermore, the indicated concentrations of solutions make it possible to eliminate the occurrence of localised cross-linkages in the polydiene, by virtue of a more even distribution of modifying agent in the reaction volume.

The use of a modifying agent in the form of a solution in a solvent enables the modifying agent to be dosed accurately, and to be better distributed in the polymerisation product. In this way, a uniformly cross-linked polymer is obtained. The use of a modifying agent in its pure form is possible but can lead to poor distribution of the modifying agent in the polymerisation product, to the formation of localised cross-linkages and to the obtaining of a polymer which has a non-uniform structure. The use of a modifying agent in the form of oil-based solutions is also possible, but has

a number of disadvantages compared to use in a solution: a solution of modifying agent in oil must have a sufficiently high concentration, since oil is a plasticizer and it will have an influence on the rheological properties of the polymer (specifically the Mooney viscosity). At the same time, highly concentrated oil-based solutions carry a risk of dosage errors and localised cross-linkages and non-uniformities of the polymer. Furthermore, oil-based solutions have a distinctly higher dynamic viscosity than solutions in hydrocarbon solvents. Another method for increasing the effectiveness with which a modifying agent is distributed is to mix same with a polymer solution in a turbulent mode of operation. This mode of operation is achieved by virtue of a high rotational speed of the mixer.

Dosage of the modifying agent is preferably 0.1-1.0 pts. wt. to 100 pts. wt. of polymer, more preferably 0.2-0.7 pts. wt., ideally 0.25-0.45 pts. wt. According to the present invention, dosage of the modifying agent is calculated in such a way that the modifying agent is supplied in a quantity at which a portion of the polymer chains remain unlinked in the polymer end product.

Monitoring, to assess the extent to which a balance of polydiene properties has been achieved, is carried out based on the linearity ratio K_L values and the viscosity deformation ratio K_{VD} values.

Neutralisation

At the end of the modification process, unreacted modifying agent is neutralised. In the preferred embodiment, softened water (pH of water = 7.5-9.0) is added to the polymerisation product. Despite the fact that only a very limited amount of modifying agent is supplied, a portion of unreacted modifying agent frequently remains in the system. Water, added to the polymerisation product, deactivates the unreacted modifying agent, and in this way stabilises the properties of the obtained polymer. If water is not added to the polymerisation product, then the remaining unreacted modifying agent will, over time, continue to interact with the polymer, and as a result the properties of the polymer will change and will not correspond to the parameters at the monitoring point. As a consequence, predicting and correcting the properties of the polymer will become more difficult.

Preferably, the softened water is added in the ratio of at least 1 pt. wt. of water to 5 pts. wt. of polymerisation product. This quantity is sufficient to deactivate the

modifying agent. The water is mixed with the polymerisation product for approximately 10-120 minutes, preferably 20-80 minutes, ideally 30-60 minutes.

Separating out of the polymer

At the end of the neutralisation process, any suitable antioxidant is introduced into the polymer, the polymer is separated out and dried. Preferably, separating out of the polymer is carried out using a water-steam degassing method, the polymerization product may be preliminarily concentrated prior to degassing.

Production of rubber compounds

The present invention also relates to rubber compounds based on cross-linked polydienes according to the invention. The composition of components of the rubber compound is determined by application, operating conditions and product technical requirements, the production process and other aspects.

The process for producing rubbers includes mixing the rubber, together with ingredients, in specialised mixers, or on rollers, cutting up and cutting to shape of semi-finished rubber products (the shapes and dimensions depend on the planned future use of the produced rubber product, specifically, on the planned method of testing) and vulcanisation of the produced semi-finished products in specialised pieces of equipment (moulding machines, autoclaves, shaper-vulcanisers etc.).

Specifically, in order to assess the properties of the rubber compounds, based on the obtained polydienes, said rubber compounds were obtained according to the model tread rubber compound with silica presented in table 3.

Application of rubber compounds

The present invention also relates to the application of the rubber compound according to the invention, for the purpose of producing various rubber-based products, specifically, car tyres.

Products based on the rubber compounds.

The present invention also relates to a product based on the rubber compound, specifically, to car tyres.

Embodiment of the invention

Embodiments of the present invention will be described below. It is important to clarify that it is not limited solely to the presented embodiments and that it is also possible to achieve the same effect in other embodiments, which are not beyond the scope of the essence of the claimed invention.

The testing methods, used to evaluate the properties of polymers obtained by the claimed method, are described.

1. The degree of monomer conversion was determined using a method by which polymer is precipitated from the polymerisation product. To this end, 50 ml of ethyl alcohol was added to a pre-selected sample of polymerisation product, the precipitated polymer was separated from the remaining liquid phase and the separated-out polymer was dried until a fixed mass was obtained. The degree of monomer conversion was determined as the ratio of the mass of dried rubber to the mass of diene supplied for the reaction.

2. The quantity of monomer in the egressing gas phase was determined by a gas chromatography method, on a Kristall 5000 instrument, using a thermal conductivity detector at an initial temperature of 35-40°C.

3. The microstructure of the polymer chains was determined by infrared (IR) spectroscopy, using an in-house methodology and a multiple ATR (multiple attenuated total reflection) attachment with a ZnSe crystal, recording of the IR spectrum of a sample in the range 4,000 to 600 cm^{-1} with a resolution of 4 cm^{-1} , number of scans = 32. Calibration of the IR-spectrometer was conducted using industry-standard samples of a polydiene microstructure, in which samples the mass percentage of isomer chains was determined based on the NMR spectra ^1H and ^{13}C .

4. The molecular-mass characteristics of the rubbers were determined by a gel-permeation chromatography method using an in-house methodology and a Breeze gel-chromatography unit with a refractive index detector manufactured by the Waters company. The rubber samples were dissolved in freshly distilled tetrahydrofuran, mass concentration of polymer in the solution was 2 mg/ml, universal calibration was according to polystyrene standards. The calculation was performed using the Mark-Kuna-Hauvinka constant for polydiene ($K = 0.000457$, $\alpha = 0.693$). Specified conditions:

- a bank consisting of 4 columns with high resolution (300 mm in length, 7.8 mm in diameter), filled with styragel HR3, HR4, HR5, HR6, enabling polymers with a molecular mass of between 500 and $1 \cdot 10^7$ amu to be analysed;

- solvent – tetrahydrofuran, flow rate – 1 $\text{cm}^3/\text{min}.$;

- temperature of the thermostat in the columns and the refractometer – 300°C.

5. The Mooney viscosity number was determined in accordance with ASTM D 1646.

6. The area under the relaxation curve, measured 2 seconds after the viscosimeter rotor was stopped, was determined in accordance with ASTM D 1646.

5 7. Values of dynamic viscosity, storage modulus and energy losses modulus were determined using an RPA-2000 rheometer manufactured by the company Alpha Technologies, at a deformation amplitude of 15%, a frequency of 0.1-30 Hz and a temperature of 100°C.

Embodiment 1 (according to the prior art)

10 8,500 g of hexane/cyclohexane, 1,300 g of 1,3 butadiene, 21.4 mmol of diisobutylaluminium hydride (DIBAL-H), 1.44 mmol ethylaluminium sesquichloride (EASC) and 1.44 mmol of neodymium versatate (NdV_3) were loaded into a 20-litre volume steel autoclave. Polymerisation was carried out, to which end the mixture was heated during the mixing process, up to 70-75°C for a period of 60 minutes. Butadiene
15 conversion was 98 wt.%. Polymerisation was terminated by adding a dispersion of stearic acid in toluene in the ratio of 0.5 pts. wt. to 100 pts. wt. of polybutadiene.

Mooney viscosity of the obtained polymer was 24 standard Mooney units.

Next, 720 g of polymerisation product was loaded into a 2-litre autoclave, 1.24 g of a 54% solution of dithiodichloride in epoxidized soybean oil (0.7 pts. wt. to 100 pts.
20 wt. of rubber), was added. The mixture was mixed for 15 minutes at 65°C. A sample was taken to determine the degree of dithiodichloride conversion. Dithiodichloride conversion was 94%. The obtained polymer was unloaded from the autoclave and stabilised using the antioxidant Irganox 1520, at a dosage of 0.2 pts. wt. to 100 pts. wt. of polymer. It was separated out using water-steam degassing and dried on rollers. The
25 Mooney viscosity of the modified polymer was 44 standard Mooney units.

Embodiment 2 (according to the prior art): High-viscosity polybutadiene

The same as embodiment 1, differing therefrom in that 21.4 mmol DIBAL-H, 1.44 mmol EASC and 1.31 mmol of NdV_3 were supplied into the reactor. Polymerisation was carried out, to which end the mixture was heated during the mixing process, up to
30 70-75°C, for a period of 60 minutes. Butadiene conversion was 98 wt.%. Polymerisation was terminated by adding a dispersion of stearic acid in toluene, in the ratio of 0.5 pts. wt. to 100 pts. wt. of polybutadiene.

The Mooney viscosity of the obtained polymer was 37 standard Mooney units.

Next, 720 g of polymerisation product was loaded into a 2-litre autoclave, 1.51 g of dithiodichloride was added, said dithiodichloride being in the form of a solution in epoxidized soybean oil containing 54 wt.% of the base material (based on 0.7 pts. wt. per 100 pts. wt. of rubber). The mixture was mixed for 15 minutes at a temperature of 65°C. A sample was taken to determine the degree of dithiodichloride conversion. Dithiodichloride conversion was 94%. The obtained polymer was unloaded from the autoclave and stabilised by adding the antioxidant Irganox 1520 at a dosage rate of 0.2 pts. wt. to 100 pts. wt. of polymer. It was separated out using water-steam degassing and dried on rollers. The Mooney viscosity of the modified polymer was 64 standard Mooney units.

Embodiment 3 (comparative)

Polymerisation of butadiene (hereafter Bd) was carried out in a hydrocarbon solvent in the presence of a catalytic complex, prepared by mixing 1.32 mmol NdV₃ in the form of a solution in a hydrocarbon solvent (nefras), which is a mixture of 70% cyclohexane and 30% C₆-fraction isomers, having a concentration of 0.5 mol/L, 10.56 mmol Bd, 13.2 mmol DIBAL-H, in the form of a solution in nefras, having a concentration of 1.0 mol/L, with the subsequent addition of 1.4 mmol of EASC, in the form of a solution with nefras, having a concentration of 0.5 mol/L. The ratio of components in the catalytic complex was Nd:Bd:DIBAL-H:EASC = 1:8:10:1. The maturation period of the complex was 20 hours at a temperature of 25°C.

Polymerisation was carried out in a 10L-volume reactor, equipped with a stirring device and a jacket for heat removal. 600 g of 1,3-butadiene and 4,810 g of nefras were supplied to the reactor. The temperature of the polymerisation reaction was 75°C, the duration of polymerisation was 120 minutes, monomer conversion was 97% wt.

At the second stage, a branching agent, stannic chloride, was supplied to the reactor, said stannic chloride being in the form of a solution in nefras, having a concentration of 0.85 mol/L (based on 0.3 pts. wt. per 100 pts. wt. of Bd). The modification process was carried out, with constant mixing, for a period of 30 minutes at a temperature of 75-80°C, after which the antioxidant Irganox 1520 was introduced at a dosage of 0.2 pts. wt. to 100 parts. wt. of polymer and was mixed using an IKA overhead stirrer for a period of 30 minutes. It was separated out of the solution using water-steam degassing and dried on rollers at 70-80°C. The characteristics of the obtained polymer are presented in table 1.

Embodiment 4 (according to the invention)

Polymerisation of Bd was carried out in a hydrocarbon solvent in the presence of a catalytic complex prepared by mixing 1.32 mmol NdV_3 , in the form of a solution in nefras, which is a mixture of 70% cyclohexane and 30% C_6 -fraction isomers, said
 5 solution having a concentration of 0.5 mol/L, 10.56 mmol Bd, 13.2 mmol DIBAL-H, in the form of a solution in nefras, having a concentration of 1.0 mol/L, and subsequently adding 1.4 mmol EASC in the form of a solution in nefras, having a concentration of 0.5 mol/L. The ratio of components in the catalytic complex was Nd: Bd: DIBAL-H:EASC= 1 : 8: 10 : 1. The maturation period of the complex was 20 hours at a
 10 temperature of 25°C.

Polymerisation was carried out in a 10 L volume reactor equipped with a stirring device and a jacket for heat removal. 600 g of Bd and 4,810 g of nefras were supplied to the reactor. The temperature of the polymerisation reaction was 75°C, the duration of polymerisation was 120 minutes, monomer conversion was 97% wt.

15 Polymerisation was terminated by adding 37.0 g of a 10% solution of palmitic acid in nefras (based on 0.84 pts. wt. per 100 pts. wt. of Bd). It was stirred for a period of 20 minutes, after which 1.5 kg of polymerisation product (the control sample) was drawn off from the equipment, the polymer was separated out from the solution using water degassing and dried on rollers at 70-80°C. The remaining polymerisation product
 20 was purged with nitrogen for a period of 30 minutes, after which 17.2 g of a 5% solution of S_2Cl_2 in hexane (based on 0.2 pts. wt. per 100 pts. wt. of butadiene) was added to the remainder, stirred for 30 minutes at 75°C and then cooled down to 30°C. It was unloaded from the autoclave, 2 kg of water and 0.2 pts. wt. of the antioxidant Irganox 1520 were added and mixed together for 30 minutes. The polymer was separated out
 25 from the solution using water-steam degassing and dried on rollers at 70-80°C. The characteristics of the obtained polymer are presented in table 1.

Embodiment 5 (according to the invention)

The same as embodiment 4, differing therefrom in that: isoprene was used as the monomer; and the polymerisation process was terminated by adding 9.6 g of isopropyl
 30 alcohol, in the form of a 10% solution in hexane; 15.3 g of dithiodibromide, in the form of an 8% solution in hexane (based on 0.28 pts. wt. per 100 pts. wt. monomer) was used as the modifying agent.

Embodiment 6 (according to the invention)

The same as embodiment 4, differing therefrom in that: isoprene was used as the monomer; 1.42 mmol of praseodymium versatate, in the form of a solution in nefras, having a concentration of 0.5 mol/L, was used as the lanthanoid; 10 g of
5 2-ethylhexanoate acid, in the form of a 15% solution in nefras (based on 0.34 pts. wt. per 100 pts. wt. isoprene), was used as the stopping agent; the selected modifying agent was dithiodichloride, 18.1 g thereof, in the form of an 8% solution in hexane (based on 0.33 pts. wt. per 100 pts. wt. monomer).

Embodiment 7 (according to the invention)

10 The same as embodiment 4, differing therefrom in that: piperylene was used as the monomer; 1.45 mmol of neodymium naphthenate, in the form of a solution in nefras, having a concentration of 0.6 mol/L, was used as the lanthanoid; 46.5 g of palmitic acid, in the form of a 10% solution in nefras (based on 1.06 pts. wt. per 100 pts. wt. monomer), was used as the stopping agent; the selected modifying agent was thionyl
15 chloride, 22 g thereof, in the form of a 5% solution in hexane (based on 0.25 pts. wt. per 100 pts. wt. monomer).

Embodiment 8 (according to the invention)

The same as embodiment 4, differing therefrom in that: 1.5 mmol of neodymium 2-ethylhexanoate, in the form of a solution in nefras, having a concentration of
20 0.22 mol/L, was used as the lanthanoid; 57.1 g of oleic acid, in the form of a 15% solution in nefras (based on 1.3 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the selected modifying agent was dithiodichloride, 14.6 g thereof, in the form of a 3% solution in hexane (based on 0.1 pts. wt. per 100 pts. wt. Bd).

Embodiment 9 (according to the invention)

25 The same as embodiment 4, differing therefrom in that: isoprene was used as the monomer: 1.35 mmol of neodymium 2-ethylhexyl phosphate, in the form of a solution in nefras, having a concentration of 0.62 mol/L, was used as the lanthanoid; 21.3 g of octyl alcohol, in the form of a 12% solution in nefras (based on 0.58 pts. wt. per 100 pts. wt. isoprene) was used as the stopping agent; the selected modifying agent was
30 dithiodichloride, 13.5 g thereof, in the form of an 11% solution in hexane (based on 0.34 pts. wt. per 100 pts. wt. monomer)

Embodiment 10 (according to the invention)

The same as embodiment 4, differing therefrom in that: piperylene was used as the monomer; 1.35 mmol of neodymium 2-ethylhexyl phosphate, in the form of a solution in nefras, having a concentration of 0.62 mol/L, was used as the lanthanoid;
 5 78.5 g of lauric acid, in the form of a 5% solution (based on 0.9 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the selected modifying agent was dithiodibromide, 12 g thereof, in the form of an 11% solution in hexane (0.3 pts. wt. per 100 pts. wt. Bd).

Embodiment 11 (according to the invention)

10 The same as embodiment 4, differing therefrom in that: 18.4 g of versatic acid, in the form of a 15% solution in nefras (based on 0.63 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the selected modifying agent was dithiodibromide, 13 g thereof, in the form of a 17% solution in hexane (based on 0.5 pts. wt. per 100 pts. wt. Bd).

15 Embodiment 12 (according to the invention)

The same as embodiment 4, differing therefrom in that: 30 g of oleic acid, in the form of a 15% solution in nefras (based on 1 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the modifying agent was thionyl chloride, 8.8 g thereof, in the form of a 20% solution in hexane (based on 0.4 pts. wt. per 100 pts. wt. Bd).

20 Embodiment 13 (according to the invention)

The same as embodiment 4, differing therefrom in that: 8.8 g of 1,4-butanediol, in the form of a 10% solution in nefras (based on 0.2 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the selected modifying agent was dithiodichloride, 13.1 g thereof, in the form of a 15% solution in hexane (based on 0.45 pts. wt. per 100 pts. wt. Bd).
 25 Bd).

Embodiment 14 (according to the invention)

The same as embodiment 8, differing therefrom in that: 75.3 g of methyl stearate, in the form of an 8% solution in nefras (based on 1.4 pts. wt. per 100 pts. wt. Bd) was used as the stopping agent; the selected modifying agent was 17.5 g of dithiodibromide
 30 in the form of an 8% solution in hexane (based on 0.32 pts. wt. per 100 pts. wt. Bd).

Embodiment 15 (according to the invention)

The same as embodiment 4, differing therefrom in that: 1.85 mmol of gadolinium versatate, in the form of a solution in nefras, having a concentration of 0.4 mol/L, was

used as the lanthanoid; 45 g of 2-ethylhexanoate acid, in the form of an 8% solution in nefras (based on 0.82 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the selected modifying agent was dithiodichloride, 11.7 g thereof, in the form of a 15% solution in hexane (based on 0.4 pts. wt. per 100 pts. wt. Bd).

5 Embodiment 16 (according to the invention)

The same as embodiment 4, differing therefrom in that: 14.3 g of 1,4-butanediol, in the form of a 5% solution in nefras (based on 0.16 pts. wt. per 100 pts. wt. Bd), was used as the stopping agent; the selected modifying agent was thionyl chloride, 13.1 g thereof, in the form of a 5% solution in hexane (based on 0.15 pts. wt. per 100 pts. wt. Bd).

10 Embodiment 17 (according to the invention): High-viscosity polybutadiene

The same as embodiment 4, differing therefrom in that Bd polymerisation was carried out in a hydrocarbon solvent in the presence of a catalytic complex, prepared using: 1.15 mmol NdV₃, in the form of a solution in nefras, having a concentration of 0.5 mol/L; 9.2 mmol Bd; 11.5 mmol DIBAL-H, in the form of a solution in nefras having a concentration of 1 mol/L; and the subsequent addition of 1.15 mmol of EASC, in the form of a solution in nefras, having a concentration of 0.5 mol/L. The ratio of components in the catalytic complex was Nd : Bd : DIBAL-H : EASC= 1 : 8: 10 : 1. 74.1 g of lauric acid, in the form of a 5% solution in nefras (based on 0.85 pts. wt. per 100 pts. wt. Bd) was used as the stopping agent, the selected modifying agent was dithiodichloride, 12 g thereof, in the form of an 11% solution in hexane (based on 0.3 pts. wt. per 100 pts. wt. Bd).

Table 1: Formulation and properties of polydienes

Components	Embodiment ref. number					
	1 According to the prior art	2 According to the prior art	3 Comparative	4	5	6
Catalytic system	NdV ₃	NdV ₃	NdV ₃	NdV ₃	NdV ₃	PrV ₃
Diene	butadiene	butadiene	butadiene	butadiene	isoprene	isoprene
Stopping agent	Stearic acid	Stearic acid	Not used	Palmitic acid	Isopropyl alcohol	2-Ethylhexanoate acid
Dosage of stopping agent, pts. wt.	0.5	0.5	-	0.84	0.22	0.34
Modifying agent	S ₂ Cl ₂ +ESBO 54%	S ₂ Cl ₂ +ESBO 54%	SnCl ₄	S ₂ Cl ₂	S ₂ Br ₂	S ₂ Cl ₂
Dosage of modifying agent, pts. wt.	0.70	0.70	0.30	0.20	0.28	0.33
Polymer properties before and after modification						
Mooney viscosity ML ₁₊₄ (100°C), Mooney std. units Before/after	24/44	37/64	36/47	38/43	35/43	30/42
M _w /M _n Before/after	2.35/2.64	2.37/2.48	2.35/2.42	2.41/2.49	2.30/2.46	2.10/2.33
1,4- <i>cis</i> , % Before/after	97.4/97.4	97.2/97.3	96.6/96.7	97.3/97.3	97.4/97.4	97.0/97.0
K _L	0.84	0.76	0.81	0.57	0.55	0.52
K _{VD}	2.52	2.25	2.45	1.81	1.76	1.71

Table 1 (continued)

Components	Embodiment ref. number					
	7	8	9	10	11	12
Catalytic system	NdNph ₃	NdEh ₃	NdP ₃	NdP ₃	NdV ₃	NdV ₃
Diene	piperylene	butadiene	isoprene	piperylene	butadiene	butadiene
Stopping agent	Palmitic acid	Oleic acid	Octyl alcohol	Lauric acid	Versatic acid	Oleic acid
Dosage of stopping agent, pts. wt.	1.06	1.3	0.58	0.9	0.63	1.00
Modifying agent	SOCl ₂	S ₂ Cl ₂	S ₂ Cl ₂	S ₂ Br ₂	S ₂ Br ₂	SOCl ₂
Dosage of modifying agent, pts. wt.	0.25	0.10	0.34	0.30	0.50	0.40
Polymer properties before and after modification						
Mooney viscosity ML ₁₊₄ (100°C), Mooney std. units Before/after	38/47	38/41	32/46	34/44	32/43	31/44
M _w /M _n Before/after	2.35/2.46	2.33/3.35	2.28/2.49	2.26/2.45	2.22/2.46	2.21/2.29
1,4- <i>cis</i> , % Before/after	97.0/97.0	97.2/97.2	97.1/97.1	97.1/97.1	97.0/97.0	97.2/97.2
K _L	0.56	0.75	0.48	0.55	0.42	0.40
K _{VD}	1.76	2.30	1.64	1.74	1.60	1.58

Table 1 (continued)

Components	Embodiment ref. number				
	13	14	15	16	17
Catalytic system	NdP ₃	NdEh ₃	GdV ₃	NdV ₃	NdV ₃
Diene	butadiene	butadiene	butadiene	butadiene	butadiene
Stopping agent	1,4-butanediol	Methyl stearate	2-ethylhexanoate acid	1,4-butanediol	Lauric acid
Dosage of stopping agent, pts. wt.	0.20	1.40	0.82	0.16	0.85
Modifying agent	SOCl ₂	S ₂ Br ₂	S ₂ Cl ₂	SOCl ₂	S ₂ Cl ₂
Dosage of modifying agent, pts. wt.	0.45	0.32	0.40	0.15	0.50
Polymer properties before and after modification					
Mooney viscosity ML ₁₊₄ (100°C), Mooney std. units Before/after	31/45	35/42	31/41	36/43	40/65
M _w /M _n Before/after	2.28/2.49	2.34/2.39	2.39/2.50	2.44/2.55	2.37/2.48
1,4- <i>cis</i> , % Before/after	97.2/97.2	97.5/97.5	97.3/97.3	97.7/97.9	97.6/97.6
K _L	0.42	0.62	0.46	0.69	0.35
K _{VD}	1.62	1.96	1.68	2.03	1.50

ESBO – epoxidized soybean oil; NdP₃ – neodymium tris-[bis-(2-ethylhexyl)phosphate]; NdV₃ – neodymium neodecanoate;

NdEh₃ – neodymium tris-[(2-ethyl) hexanoate]; GdV₃ – gadolinium versatate; PrV₃ – praseodymium versatate; GdEh₃ –

5 gadolinium tris-[(2-ethyl) hexanoate]; NdNph₃ – neodymium naphthenate

Samples of the polymer obtained according to embodiments №1, 2, 3, 7, 9, 11 and 17, were tested in simulated rubber compounds according to the formulation presented in table 2. The properties of the obtained rubber compounds are presented in tables 3 and 4.

5 Table 2: Rubber compound formulation (tyre tread)

Ingredients	Quantity - pts. wt. per 100 pts. wt. of rubber
Butadiene-styrene rubber	60.00
Butadiene rubber	40.00
Silicon oxide Zeosil 1165 MP	72.00
Silane SI75	7.50
Norman 346 oil	16.50
Stearic acid	1.50
Wax	1.50
Zinc oxide	2.00
6PPD anti-ageing agent	1.50
TMQ anti-ageing agent	1.50
TBBS accelerator	1.50
MBTS accelerator	1.55
Sulphur	1.20
PVI anti-scorching agent	0.25

6PPD – N-(1,3-dimethylbutyl)-N'-phenyl-1,4-benzenediamine

TMQ – 2,2,4-trimethyl-1,2-dihydroxyquinoline

TBBS – N-tert-butyl-2-benzothiazole sulphenamide

10 MBTS – dibenzothiazole disulphide

PVI – N-cyclohexyl(thio)phthalimide

Table 3: Properties of rubber compounds, based on rubbers with a standard Mooney viscosity

Description of the parameter	Sample ref. number				
	1	3	7	9	11
1 st mixing stage					
Mooney viscosity ML1+4 (100°C) of the rubber compound, Mooney std. units	37.9	46.1	48.3	36.2	36.4
Area under the relaxation curve A, Mooney std. units * sec.	561	767	789	558	552
2 nd mixing stage					
Mooney viscosity ML1+4 (100°C) of the rubber compound, Mooney std. units	37.3	48.4	49.1	36.1	35.5
Area under the relaxation curve A, Mooney std. units * sec.	480	491	804	507	479
3 rd mixing stage					
Mooney viscosity ML1+4 (100°C) of the rubber compound, Mooney std. units	55.4	58.9	54.2	53.7	52.1
Area under the relaxation curve A, Mooney std. units * sec.	658	650	626	619	595
Physical and mechanical properties					
M ₃₀₀ , MPa	9.5	9.6	9.7	9.6	9.8
Nominal breaking strength, MPa	19.0	19.7	19.8	19.7	20.0
Wear capacity, mm ³	50	49	47	47	46
Elastic-hysteresis properties: tg δ [RPA 2000:60°C, 10 Hz, 10%]	0.141	0.145	0.137	0.137	0.132
Elastic-hysteresis properties of vulcanizates (DMA: between -70°C and +70°C, deformation 1%, 10 Hz, 7 N loading, heating rate 2.5 K/min.)					
0°C	0.314	0.318	0.353	0.342	0.340
+60°C	0.131	0.136	0.126	0.124	0.121

Table 4: Properties of rubber compounds based on high-viscosity rubbers

Description of the parameter	Sample ref. number	
	1	17
1 st mixing stage		
Mooney viscosity ML1+4 (100°C) of the rubber compound, Mooney standard units	53.1	52
Area under the relaxation curve A, Mooney std. units * sec.	1247	1167
2 nd mixing stage		
Mooney viscosity ML1+4 (100°C) of the rubber compound, Mooney std. units	47.2	46.8
Area under the relaxation curve A, Mooney std. units * sec.	975	968
3 rd mixing stage		
Mooney viscosity ML1+4 (100°C) of the rubber compound, Mooney standard units	73.8	71
Area under the relaxation curve A, Mooney std. units * sec.	1120	1060
Physical and mechanical properties		
M ₃₀₀ , MPa	9.8	9.7
Nominal breaking strength, MPa	20.3	20.2
Wear capacity, mm ³	44	43
Elastic-hysteresis properties: tg δ [RPA 2000: 60°C, 10 Hz, 10%]	0.147	0.143
Elastic-hysteresis properties of vulcanizates (DMA: between -70°C and +70°C, deformation 1%, 10 Hz, 7 N loading, heating rate 2.5 K/min.)		
0°C	0.241	0.260
+60°C	0.134	0.129

Table 5: Changes in polydiene properties during storage

Parameter	Embodiment ref. number*				
	1	4	9	14	17
Ageing at 100°C over 24 hours					
Mooney viscosity ML ₁₊₄ (100°C), Mooney std. units	47.2	43.7	46.7	42.3	65.6
K _L	0.78	0.54	0.47	0.57	0.32
K _{VD}	2.43	1.78	1.62	1.95	1.48
Ageing at 160°C over 72 hours					
Mooney viscosity ML ₁₊₄ (100°C), Mooney std. units	53.4	45.1	47.9	43.4	66.9
K _L	0.62	0.48	0.44	0.54	0.28
K _{VD}	2.01	1.73	1.59	1.93	1.45

5 * numbering of embodiments corresponds to the numbering in table 1

As can be seen from Table 1, the step-change in Mooney viscosity of the polydiene according to the invention increases in direct proportion to the increase in the dosage of modifying agent. At the same time, there is a noticeable change (increase) in the degree of cross-linking of the polymer chains, said cross-linking being characterized

by a reduction in the values of the linearity ratio K_L and the viscosity deformation ratio K_{VD} .

It is important to recognise the fact that comparing the properties of rubber compounds which are based on rubbers with a standard Mooney viscosity, being in the range of 39 to 49 std. units, with rubber compounds which are based on high-viscosity rubbers, having a Mooney viscosity in the range of 59 to 69 std. units, would be incorrect, which is why, for the purposes of evaluating properties, samples of polymers with relatively similar Mooney viscosity values were examined.

Considering the results of testing rubber compounds which were based on polydienes obtained according to the invention and which are characterized by K_L ratios in the range of 0.35 and 0.75 and K_{VD} ratios in the range of 1.5 to 2.3 (table 1), it was noted that the samples according to the invention have superior processability and elastic-hysteresis and physical and mechanical properties, as well as improved handling properties, improved grip performance on wet roads and improved rolling resistance were specifically noted. The aforementioned improvements were noted both for samples with standard Mooney viscosity (table 3) as well as high viscosity (table 4).

Moreover, it is obvious from table 5 that the degree of cross-linking of the polydiene according to the invention is stable and remains virtually unchanged during storage of the polymer.

In this way, monitoring of conformity to the linearity and viscosity deformation ratios proposed by the invention makes it possible to obtain polydienes with optimal processability and rheological (plasto-elastic) properties.

CLAIMS

1. Cross-linked polydiene, characterized by linearity ratio values K_L in a range of between 0.35 and 0.75, determined according to formula (1), and viscosity deformation
5 values K_{VD} in a range between 1.5 and 2.3, determined according to formula (2):

$$K_L = A_1/A_2 \quad (1),$$

where A_1 is the area under the relaxation curve of the polydiene at the end of the polymerisation stage, A_2 is the area under the relaxation curve of the polydiene after the neutralisation stage, Mooney standard viscosity units*s;

10 $K_{VD} = N_1/\eta' \quad (2),$

where N_1 is the normal variance in stresses,

η' is the dynamic viscosity of the polydiene, kPa*s, determined on an RPA rheometer at a frequency of 0.1-30 Hz, a deformation angle of 15% and a temperature of 100°C.

15 2. Cross-linked polydiene according to Claim 1, characterized by linearity ratio values K_L in a range between 0.35 and 0.70, preferably between 0.40 and 0.65 and ideally between 0.40 and 0.60.

20 3. Cross-linked polydiene according to Claim 1, characterized by viscosity deformation values K_{VD} in a range between 1.58 and 2.1, preferably between 1.6 and 2.0.

4. Cross-linked polydiene according to Claim 1, catalysed using lanthanide compounds, specifically neodymium compounds.

25 5. Cross-linked polydiene according to Claim 1, which is a polybutadiene or a polyisoprene.

30 6. Method for obtaining a cross-linked polydiene according to any of Claims 1-5, which method includes: the polymerisation of a conjugated diene in a hydrocarbon solvent; termination of the polymerisation reaction through the introduction of a

stopping agent; post-polymerisation treatment with a modifying agent and neutralisation of unreacted modifying agent.

5 7. Method according to Claim 6, characterized in that the neutralisation of unreacted modifying agent is carried out by introducing softened water.

10 8. Method according to Claim 6, characterized in that the modifying agent is selected from compounds which are capable of producing cross-linking of polymer chains, preferably the modifying agent is a halogen-containing sulphur compound.

9. Method according to Claim 6, characterized in that the modifying agent is applied in the form of a solution in an organic solvent.

15 10. Method according to Claim 9, characterized in that the concentration of the modifying-agent solution is between 3 and 20 wt.%.

11. Rubber compound based on the cross-linked polydiene according to any of Claims 1-5.

20 12. Application of the rubber compound according to Claim 11 for the production of rubber-based products.

13. Product based on the rubber compound according to Claim 11.

25 14. Product according to Claim 13 which is car tyres.