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PARTICULATE CARBON MATERIAL FROM RENEWABLE RAW MATERIALS

PARTICULATE CARBON MATERIAL FROM RENEWABLE RAW MATERIALS

The present invention relates to a particulate carbon material according to claim 1.

Description

There are many uses for particulate carbon material. One application is as a filler for polymers such as elastomers, thermoplastics or duroplastics. In the production of rubber items from elastomers, fillers are used to influence the technical rubber properties of the cross-linked rubber items, measured, for example, as tensile strength, hardness, rigidity, or tear strength. In addition, the product properties such as rolling resistance, abrasion, and wet skid behaviour are adjusted in this way. The influencing of technical rubber properties by a filler is also referred to as reinforcement.

The currently most common fillers are carbon black and silica. Carbon black is most commonly produced by the pyrolysis of natural gas, petroleum fractions, and/or coal-based oils, wherein significant amounts of carbon dioxide are produced depending on the quality of the carbon black. Precipitated silica is produced from water glass, wherein the production of water glass also produces large amounts of carbon dioxide.

As a result of the scarcity of fossil carbon resources (compare petroleum and coal-derived oils as carbon black raw material), the saving of chemicals (see sulphuric acid in silica precipitation), but above all as a result of avoiding carbon dioxide emissions from fossil sources (see carbonate decomposition in the production of water glass; see combustion of oil or gas in the pre-combustion chamber of carbon black reactors and partial combustion of the carbon black raw material during carbon black formation), there is an increasing need to manufacture industrial products based on renewable raw materials. With renewable raw materials, all carbon comes from atmospheric carbon dioxide. In the energetic utilisation of renewable raw materials, the carbon dioxide balance is largely neutral. In the case of recycling of renewable raw materials, no fossil carbon is released during production and even atmospheric carbon is bound in the carbon-containing material – at least for the duration of the use of the respective product.

A particulate carbon material based on renewable raw materials that can be used as a filler, for example, is described below that has surprisingly good properties when used as a filler in elastomers compared to the conventionally produced fillers carbon black and silica.

The following describes the meaning of terms used herein:

A filler is a particulate solid that is added to an elastomer, thermoplastic, or thermoset.

Depending on the properties of the filler, for example when added to elastomers, the technical rubber properties of a cross-linked (for example, by vulcanisation) rubber mixture are influenced to varying degrees by the addition of the filler, usually together with other additives, before the cross-linking.

A typical filler is silica. Silica essentially means precipitated silica, which is mainly used in rubber articles. There is also pyrogenic silica.

Another typical filler is carbon black. This always refers to carbon black, i.e., a technically targeted carbon black with defined properties. Carbon black is mainly produced via incomplete combustion or pyrolysis. Carbon black here does not mean by-products of combustion as in the case of diesel soot or chimney soot. An example of the production of carbon black is described, for example, in US 2005/100502 A1.

The reinforcing effect of carbon black and/or silica correlates strongly with the primary granule size of the filler. The primary granule size is directly related to the specific surface area.

Against this background, carbon blacks having a low surface area are referred to as inactive carbon blacks, carbon blacks having a medium surface area as semi-active carbon blacks, and carbon blacks having a high surface area are referred to as active carbon blacks, wherein activity here means the degree of reinforcing effect of the respective carbon blacks in the rubber. See also ASTM D 1765. Typically, inactive carbon blacks have BET surface areas < 30 m^2/g, semi-active carbon blacks 30–70 m^2/g, and active carbon blacks 90 to > 150 m^2/g. The importance of the surface area as a guide variable is also made clear by the fact that the first digit of the ASTM carbon blacks reflects the granule size or surface area. In the case of silica, the differentiation is less pronounced. Silicas with a clear reinforcing effect typically have BET surface areas > 100 m^2/g. In the following, filler means a product that achieves at least the performance of an inactive carbon black. A performance that is at least comparable to that of an inactive carbon black is also referred to below as a reinforcing effect. A typical inactive carbon black is N990.

The particle surface consists of the outer and the inner surface. The associated measured variable is the specific surface area of the particulate material. The specific surface can be measured as an outer surface using *statistical thickness surface area*, STSA for short, or as a total surface area from the outer and inner surface using the nitrogen surface according to Brunauer, Emmett, and Teller, BET for short. The difference between the inner and outer surface essentially results from the porosity of the material. In addition to the area surrounding the granules, the inner surface also includes the area present in the pores. A coarse-grained material that has a comparatively small outer (i.e., STSA) surface area can nevertheless have a high total (i.e., BET) surface area (consisting of an outer and inner surface area) if it is highly porous.

Strictly speaking, only the STSA surface area can be used to describe the fineness of a material using specific surface area values. Conversely, the difference "BET surface area minus STSA surface area" is a measure of the porosity of finely divided materials, since it represents the surface area of the pores. The smaller the difference, the less porous the material. In the case of non-porous materials, the BET also describes the fineness well.

The BET surface area and the STSA surface area are determined in accordance with the ASTM D 6556-14 standard. In the present invention, in contrast thereto, the sample preparation/outgassing for the STSA and BET measurement takes place at 150 °C.

The methods and their importance are also described in "Rubber Technology" (Fritz Röthemeier, Franz Sommer, 3rd edition, Carl Hanser Verlag Munich 2013) on page 289 using the example of a classic carbon black. The most important method for determining the specific surface area is the measurement of nitrogen adsorption according to Brunauer, Emmett, and Teller (BET method). First, a sample of the carbon black is heated in a vacuum to remove the substances adsorbed on the surface. After cooling, the sample is charged with nitrogen at the boiling point (77 K) and the adsorbed volume and the associated equilibrium vapour pressure are determined. At low pressures, a monomolecular layer forms first, to which further layers are added as the pressure increases. The specific surface area can be determined by evaluating the adsorption isotherm using the BET method with a nitrogen partial pressure of 0.1 to 0.3. Single-point measurements are sufficient for routine determinations.

Determining the surface area by means of N_2 adsorption results in a larger surface area for microporous carbon blacks since the nitrogen molecules can also penetrate into the pores. This effect can be avoided by using surface-active substances that are larger than the pores (CTAB method) or by determining the N2 adsorption at higher partial pressures (0.2 to 0.5) and further evaluation (STSA method).

STSA method (Statistical Thickness Surface Area): The evaluation uses the same measurement data as with the BET method, but the measurement is carried out at higher partial pressures (0.2 to 0.5). The STSA method is based on what is termed the t-plot evaluation method according to de Boer, later modified by Magee. Here it is assumed that locally the adsorption takes place differently in different stack heights, and then has a statistical thickness. The STSA surface area is also given in m^2/g and is a measure of the "outer" surface area of a carbon black particle, but above all it is a measure of the rubber-active surface area.

When comparing the performance of carbon black or silica in cured rubber articles, given the well-known relationship between surface area and performance, it makes sense to compare fillers of similar surface area. By similar surface area it is meant herein that the BET values of non-porous materials or the STSA values do not differ by more than about 10–20 m^2/g.

Carbon black and silica are made up of primary granules. These geometric units, which do not exist in isolation but are recognisable in pictorial representations, are grown in together into aggregates, wherein the intercrescence takes place through strong chemical bonds. Aggregates can also be combined to form agglomerates, wherein the combination of several aggregates to form agglomerates takes place via weak forces. Agglomerates can be destroyed by dispersal. The degree of aggregate formation is described in an outdated manner by DBP absorption or more recently by oil absorption. Details can be found in ASTM D 2414. One also speaks of the oil absorption number with the abbreviation OAN for English *oil absorption number*. A high DBP or oil absorption value indicates a material with highly branched aggregates. In the case of carbon black in particular, what is termed the structure has a direct influence on its reinforcing effect.

The performance of carbon black or silica in rubber applications is usually determined by measuring rubber parameters. Technical rubber parameters describe certain properties of a rubber composite in the cross-linked, e.g., vulcanised state. In this respect, in this document, rubber articles are to be understood as meaning the finished articles made of rubber after they have been cross-linked or vulcanised. In the present specification, these finished rubber articles are also referred to as rubber parts, moulded bodies, articles made of elastomeric material, or rubber products. The wide variety of rubber parts in the most varied of applications results in a large number of different sizes for describing rubber parts. Depending on the area of application, values of a variable that are stated as positive can also be evaluated elsewhere as negative. The primary rubber parameters are tensile strength (ASTM D 412, DIN 53504), tear strength (DIN 53455) and the stress values at 50%, 100%, 200%, and 300% elongation (DIN 53504), hereinafter referred to as what is termed the 50% modulus, 100% modulus, 200% modulus, or 300% modulus. The hardness (ASTM D 2240), for example, can also play a role. For these quantities, high values, but not too high, are considered positive.

Another characteristic rubber value is the loss factor tan delta as the quotient of loss modulus E" and storage modulus E' of the elastomer material. A distinction is made between the value of the tan delta in the high temperature range, in particular the tan delta at 60 °C, and the tan delta in the lower temperature range, in particular the tan delta at 0 °C. While the tan delta at 60 °C indicates the rolling friction of a tyre, the tan delta at 0 °C is used to assess a tyre's wet grip. In this context, low values are preferred for the tan delta at 60 °C, and high values for the tan delta at 0 °C. The tan delta values are determined in the course of a dynamic mechanical analysis (*temperature sweep*). In the case described here, the dynamic mechanical analysis (DMA) is carried out with prism-shaped fittings measuring 2×10×35 mm for the temperature variation on an Eplexor 150N Dynamic Mechanical Thermal Spectrometer.

Untreated silica is a filler having polar functional groups that can interfere with cross-linking in sulphur cross-linked systems. The interference with sulphur cross-linking can be based, for example, on the adsorption of vulcanisation adjuvants onto the polar functional groups of the filler surface. In addition, the different surface energies of polymer and filler can, for example, prevent good dispersion of the filler in the polymer, and when the mixture is reheated (e.g., during vulcanisation) can lead to an undesired re-agglomeration of the already dispersed filler particles (what is termed filler flocculation). This is the starting point for adding reagents to the silica. In the simplest case, the polar groups of the silica are reacted with suitable basic composites, as a result of which these groups are deactivated or masked. In this way, the silica as such is activated overall in the function thereof as a reinforcing filler, i.e., the surface chemistry of the silica is adapted to the surface chemistry of the polymer through this activation or masking. Compare with: Fritz Röthemeier, Franz Sommer, 3rd edition, Carl Hanser Verlag Munich 2013 on pages 301–302.

To improve the technical properties of rubber, silica is usually used with coupling agents. Coupling reagents are bifunctional composites that bind to the silica on the one hand and to the rubber on the other hand and can thus create a connection between the silica and the rubber. This is particularly important since silica and rubber are chemically incompatible with one another. A typical coupling agent is bis(triethoxypropylsilyl)tetrasulphide when using silica in rubber.

In the plastics application, adhesion promoters are used, which also ensure a connection between the polymer and another component, which can be another polymer or a filler. In the present specification, a coupling agent is also understood to mean an adhesion promoter.

In the field of powder characterisation, the grain size or grain size distribution is often also specified. This is mainly determined by laser diffraction or sieve analysis. As a rule, either the percentage of the number (Q0 distribution) or the volume (Q3 distribution) of granules of a certain geometric dimension relative to the total amount of granules is stated. The specification is usually in µm. The grain size records the size of the separated granules present under the specific conditions. It depends on the dispersing medium and the quality of the dispersion. The grain size does not differentiate between granules as a result of macroscopic caking, for example due to foreign substances, granules as a result of microscopic agglomeration with insufficient dispersing effort, or granules in the form of isolated aggregates or primary particles. It indicates the dimensions of a body that is limited to the outside, even if it consists of several connected parts. Using the material density (bulk density), the mass distribution can be calculated from the volume distribution.

The morphology of fillers can be fibrous, platelet-like, or spherical. The length-to-diameter ratio can be used as a distinguishing criterion. For this purpose, the dimensions in different spatial directions are determined, for example, by means of electron microscopic measurements (TEM, REM). The aspect ratio, the quotient of the largest and smallest dimensions, is also often spoken of. It can be specified both in the form x:y and in the form of the calculated quotient. As a calculated quotient, a sphere would have an aspect ratio of 1, ellipsoidal structures from around 1.5 to 2 and fibre-like structures over 10.

Conventional carbon black that is produced from raw materials of fossil origin, i.e., based on coal tar, natural gas or crude oil, is referred to below as classic carbon black. In contrast, one speaks of biogenic carbon black if the carbon black was produced from renewable raw materials.

Raw materials of fossil origin are primarily all substances derived from petroleum, such as distillates, distillation residues, or petroleum components processed by cracking processes. Fossil raw materials also include all products that result from the distillation, coking, or liquefaction of lignite, hard coal, or anthracite. Natural gas is also a fossil raw material. What all fossil carbon sources have in common is that their ^{14}C content is below that of renewable raw materials, since they no longer participate in ongoing isotopic exchange.

Renewable raw materials, on the other hand, are all products that are derived from the direct use of plants or animals. If one thinks of the carbon black production process, these can primarily be vegetable oils or animal fats. In the broader sense, and thus in the sense of this document, any biomass is included.

Biomass is all organic matter that is accessible from the use of plants or animals, or that occurs as waste from this use, including derived products and waste produced or separated therefrom. Without imposing any restrictions here, wood, straw, sugar, starch, vegetable oil, leaves, shells, bagasse, empty fruit stalks, fermentation residues, green waste, or organic municipal waste can be named as typical forms of biomass. It is common to refer to organic material that has a faster regeneration time than peat as biomass. In particular, this also includes waste from the industrial use of plants. For example, large quantities of wood are processed in the pulp industry, which produces lignin-containing waste such as black liquor. What all biomasses have in common is that their ^{14}C content is higher than that of fossil raw materials, since they take part in ongoing isotopic exchange.

One type of biomass is lignin, which occurs in some wood processing processes. Lignin is a naturally occurring polymer that can be derived primarily from the building blocks coumaryl, coniferyl, and sinapyl alcohol. Depending on the wood processing process, it accumulates in large quantities as KRAFT lignin, usually dissolved in black liquor, hydrolysis lignin or lignin sulphonate. Depending on the pH value in the respective manufacturing process, the hydrogen atoms in the hydroxyl groups typical of lignin can be partially replaced by metal cations. Lignosulphonate is actually already a chemical derivative of lignin, as it has additional sulphonate groups introduced during processing.

HTC is the abbreviation for hydrothermal carbonisation. This involves the treatment of a substance in the aqueous phase under pressure and at elevated temperature. Due to the increased pressure, it is possible to carry out reactions in liquid water at which the temperature is well above 100 °C, i.e., above the boiling point of water at normal pressure.

According to the prior art, fillers with a reinforcing effect are mainly used to improve the technical rubber properties of rubber articles. The two most widely used fillers for rubber applications are carbon black and silica. Carbon black is obtained almost exclusively from fossil raw materials. Since the product according to the invention is a particulate carbon material that can be used, for example, as a filler and is obtained from renewable raw materials, the classic carbon blacks obtained from fossil raw materials do not belong to the prior art. Silica is a filler that is obtained from inorganic silicon composites. For this reason, silicas are also not part of the prior art.

The object of research activities is the development of alternative fillers from renewable raw materials. The main goal of most of these development efforts is to reproduce the properties of carbon black as well as possible through the refining of renewable raw materials. This applies in particular to the carbon content, which is usually adjusted to more than 90%, but also to the proportion of graphitic carbon. The materials produced in this way are therefore also called bio-based carbon black or *bio-based* carbon black. In most cases, the parallel goal is to provide a filler made from renewable raw materials that can at least partially replace classic carbon blacks. There are also development efforts aimed at using the renewable raw materials directly as fillers after cleaning, fractionating, or crushing them as necessary.

It is known from WO 2010/043562 A1, for example, that carbon black can also be produced from renewable raw materials. As a filler, the carbon black disclosed should above all have an improved modulus in rubber applications with a particularly narrow aggregate size distribution. With regard to their basic properties, the carbon blacks characterised in WO 2010/043562 A1 are within the range of the classic carbon blacks N220 and N375. The carbon black described here is produced in the classic furnace process, wherein natural gas is used in a pre-combustion chamber and fossil carbon is released. The carbon black obtained in this way has an S content of max. 2.5%, a volatile components content according to DIN 53552 of max. 2.5%, and thus an approximate C content of more than 95% carbon.

In WO 2014/096544 A1, a carbon product is claimed which is formed from porous carbon particles with a surface area of more than 500 m^2/g and an average pore volume of less than 1 mL/g, which in turn consist of primary particles, such as aggregates, that have a particle size of less than 250 nm. The carbon product is obtained from hydrothermal carbonisation of bio-material that contains more than 40% carbon on a dry matter basis. Lignin, tannin and betulin, hydrolysis lignin, products from the manufacture of paper, boards, bio-fuel, or brewing products are mentioned as starting materials. The carbon content of the products described in the examples is between 77.31 and 86.44% carbon. The high carbonisation of the material given in the examples means that other elements, such as oxygen and hydrogen in particular, must be depleted. This inevitably leads to the disadvantage that the surface chemistry of the material is depleted, i.e., there are fewer functional groups on the surface. The fewer surface groups have a negative effect on possible mechanisms of attachment to the polymer.

It is also known that renewable raw materials such as lignin or lignin derivatives can be used directly in rubber mixtures, both with and without coupling agents, to influence the technical rubber properties in the cross-linked state.

For example, DE 10 2008 050 966 A1 describes a rubber mixture that contains a lignin derivative, more specifically a lignosulphonic acid derivative, up to alkali metal or alkaline earth metal salts of lignosulphonic acid. The rubber mixture produced using this lignosulphonic acid derivative can also contain carbon black or diatomaceous earth. The application also claims a tyre made from the aforementioned rubber composite. A disadvantage, as the examples disclosed in DE 10 2008 050 966 A1 show, is that the lignin derivatives are always used in addition to 40 phr of carbon black or 80 phr of diatomaceous earth/5 phr of carbon black. The term diatomaceous earth is used in this document for silica. An improvement in the technical rubber parameters is therefore only achieved in combination with the classic fillers.

When using renewable raw materials in rubber mixtures with the help of coupling reagents, the knowledge gained with the use of silica is of particular use.

In the case of silica, it is generally known that fillers with polar functional groups, such as untreated silica, interfere with cross-linking in sulphur-cross-linked systems. At the same time, it is known that this interference can be alleviated by adding suitable reagents such as amines or glycols. The functional groups are blocked or masked. Compare with: Fritz Röthemeier, Franz Sommer, 3rd edition, Carl Hanser Verlag Munich 2013 on pages 301–302.

In the case of reinforcement with silica, it is known that the effect of the silica can be significantly improved by coupling reagents. Functional alkoxysilanes are used, which on the one hand can bind to the silica when mixed with the alkoxysilane group to form an Si-O-Si bond and later bind to the rubber polymer with another function during vulcanisation, possibly with the help of added sulphur. Silica and silicates are suitable as reinforcing light-coloured fillers. By treating the silica with silanes, the mechanical properties and the processing properties are significantly improved (see Fritz Röthemeier, Franz Sommer: Rubber Technology, 3rd edition, Carl Hanser Verlag Munich 2013, pages 112–113, Chapter 2.5.4.3 Fillers).

Similarly, uses of silane as a coupling agent in renewable raw materials that are to be used as fillers are known.

Thus, EP 2 223 928 A1 describes a functionalised lignin, wherein groups contained in the lignin react with functionalising agents, and these reagents can be anhydrides, esters and silanes. Furthermore, a rubber mixture is disclosed, which contains functionalised lignin as a filler, possibly in a mixture with classic carbon black or silica, and optionally a coupling agent for the functionalised lignin or for the silica.

It is also known to produce finely divided materials (which could be used as fillers) by hydrothermal carbonisation (HTC).

Reference is made to WO 2014/122163 A1, which describes a method for producing carbon-enriched biomass material, the biomass material obtained, and the use thereof. The lignocellulose material used is treated at elevated temperature, preferably at a maximum of 120–320 °C, and under partially oxidising conditions, i.e., with a sub-stoichiometric presence of oxygen preferably in the range 0.15–0.45 mol/kg dry lignocellulose material, and after opening of the reactor, solid products are optionally separated from the reaction mixture. The feedstock has a moisture content between 10% and 70% and a size between 0.2 and 100 mm. The pressure applied is between 1 and 100 bar absolute. The reaction time given is 2–500 minutes. Preferably 0.1–1 kg of water or steam/kg of lignocellulose is used. The carbon concentration is increased by 8–25%. The material obtained has a maximum of 45–60% carbon, in addition to 5–8% hydrogen and 35–50% oxygen. The only use given is incineration, specifically in the milled state for dust firing.

Furthermore, a method for obtaining carbonised lignin with a defined grain size distribution from a lignin-containing liquid is known, wherein the lignin-containing liquid is subjected to hydrothermal carbonisation, whereby the lignin is converted into a carbonised lignin, and the carbonised lignin from the carbonised lignin-containing liquid is separated, the lignin-containing liquid is subjected to hydrothermal carbonisation at temperatures in the range from about 150 °C to about 280 °C and the grain size distribution of the carbonised lignin is set by adjusting the H^+ ion concentration in the lignin-containing liquid before and/or during hydrothermal carbonisation. Thus, it is known that by adjusting the H^+ ion concentration of a liquid containing lignin, the distribution of the grain size of the product obtained, i.e., the size of the agglomerates, can be influenced.

WO 2015/018944 A1 also discloses a method for obtaining undissolved carbonised lignin from black liquor.

The object of the invention is to provide a particulate carbon material from renewable raw materials that can be used, for example, as a filler, which, for example, when used in rubber mixtures after cross-linking, shows comparable performance in terms of technical rubber parameters to a classic carbon black having a similar BET/STSA surface area. In addition, the object of the invention is to provide an efficient method with regard to the use of energy and adjuvants, by means of which the material according to the invention can be produced.

This object is achieved by a particulate carbon material having the features of claim 1.

Accordingly, a particulate carbon material made from renewable raw materials, in particular from lignin-containing biomass, is provided with the following features:

- a ^{14}C content, which corresponds to that of renewable raw materials, of greater than 0.20 Bq/g carbon, particularly preferably greater than 0.23 Bq/g carbon, and less than 0.45 Bq/g carbon;

- a carbon content, based on the ash-free dry substance, between 60% by mass and 80% by mass;
- an STSA surface area of at least 5 m^2/g and at most 200 m^2/g; and
- an oil absorption number (OAN) between 50 mL/100 g and 150 mL/100 g.

As mentioned above, the renewable raw material used is preferably lignin-containing biomass and here in particular lignin-containing biomass having a Klason lignin content of more than 80% (the Klason method is used to determine the lignin content, in which the polysaccharides are separated by a two-stage acid hydrolysis and the remaining lignin residue is subsequently weighed as Klason lignin). Lignin is a by-product of woody biomass fractionation processes. During the fractionation processes, the lignin is typically either solubilised and then separated from the insoluble components of the woody biomass (e.g., KRAFT process) or the woody biomass is depolymerised such that the lignin remains predominantly as a solid (e.g., hydrolysis process). Depending on the sort of fractionation process, the lignin is either dissolved in a liquid containing lignin, for example black liquor, or as a solid, which is usually mechanically dewatered. If the lignin is dissolved in a lignin-containing liquid, the lignin can usually be precipitated therefrom, for example using acids or gases with an acidic action, and obtained as a mechanically dehydrated solid (compare, for example, the LignoBoost process).

The ^{14}C content, which corresponds to that of renewable raw materials, distinguishes the present particulate carbon material, which can be used, for example, as a filler in elastomers, thermoplastics or duroplastics, from classic carbon black that is obtained on the basis of fossil raw materials. In the present case, the particulate carbon material has a ^{14}C content of greater than 0.20 Bq/g carbon, particularly preferably greater than 0.23 Bq/g carbon, but less than 0.45 Bq/g carbon in each case.

The ^{14}C content in biomass grown in 1950, i.e., at the beginning of mankind's extensive nuclear weapons tests, was 0.226 Bq/g carbon. It increased to 0.42 Bq/g carbon during the time of nuclear weapons testing and is now returning to about the original level. In 2009, 0.238 Bq/g carbon was measured. To distinguish the carbon material according to the invention from materials with an artificially enriched ^{14}C content, the ^{14}C content in the carbon material according to the invention is at most 0.45 Bq/g of carbon.

The carbon content, based on the ash-free dry matter, is more than 60% by mass and less than 80% by mass, preferably more than 65% by mass and less than 75% by mass, more preferably more than 68% by mass and less than 74% by mass, more preferably more than 70% by mass and less than 73% by mass (carbon content via elemental analysis according to DIN 51732; ash content according to DIN 51719 at 815 °C) distinguishes the present filler particulate carbon material from renewable raw materials used directly as a filler, such as sawdust, etc., which typically have a lower carbon content. Furthermore, the carbon content based on the ash-free dry substance of more than 60% by mass and less than 80% by mass distinguishes the present particulate carbon material from products made from renewable raw materials, for example by fractionation, extraction, distillation, or crystallisation, such as sugar, starch, cellulose, etc., which typically have a lower carbon content based on the ash-free dry substance of 40% by mass to 50% by mass. Furthermore, the present particulate carbon material differs in its preferred embodiment from lignin which was separated by means of a KRAFT process from biomass, which typically has a carbon content based on the ash-free dry matter of 65% by mass.

The carbon content, based on the ash-free dry substance of more than 60% by mass and less than 80% by mass, also distinguishes the present particulate carbon material from classic carbon black that was produced using the usual carbon black production processes or the variants of *bio-based* carbon blacks, which are produced both via the usual carbon black production process but also, for example, via pyrolysis, partial oxidation, carbonisation, or similar processes, which typically have a higher carbon content based on the ash-free dry matter of about 95% and more. Even in the case of highly oxidised carbon black with a content of volatile components at 950 °C according to DIN 53552 of 20% and an additional 2.5% sulphur, the carbon content, based on the ash-free dry matter, is roughly over 88%.

The advantage of the present product's low carbon content compared to carbon black is that the surface functionality originating from the renewable raw materials is partially retained and can be used in the application, for example, via coupling reagents.

The STSA surface area of at least 5 m^2/g and at most 200 m^2/g, preferably between 8 m^2/g and 100 m^2/g further distinguishes the present particulate carbon material from non-porous lignin or non-porous particulate material, which was produced via hydrothermal carbonisation, which usually has BET surface areas of less than 2 m^2/g, wherein the STSA surface areas – usually not measured – are naturally slightly lower.

Furthermore, the present particulate carbon material differs from particulate materials from renewable raw materials that have a high specific BET surface area due to their high porosity, such as pyrolysis coals, coals that were obtained via partial oxidation, coals that were obtained via hydrothermal carbonisation and activated carbons in that the particulate carbon material present is largely non-porous and very finely divided, as detected by the STSA surface.

In a variant of the present particulate carbon material, the STSA surface area has values between 10 m^2/g and 80 m^2/g, preferably between 12 m^2/g and 70 m^2/g, more preferably between 15 m^2/g and 70 m^2/g, particularly preferably between 20 m^2/g and 70 m^2/g.

Advantageously, the BET surface area of the present particulate carbon material differs from the STSA surface area by only a maximum of 20%, preferably a maximum of 15%, more preferably a maximum of 10%. The pore volume of the particulate carbon material is advantageously < 0.1 cm^3/g, more preferably < 0.01 cm^3/g, particularly preferably < 0.005 cm^3/g. This distinguishes the present particulate carbon material from finely divided porous materials such as milled biogenic powdered activated carbon, which in addition to a BET surface area of usually more than 500 m^2/g can also have an STSA surface area of at most 10 m^2/g.

The advantage of the STSA surface area, which is high compared to lignin and HTC carbon, is the high degree of fineness of the product, which enables a high degree of interaction between the product and, for example, polymers. The advantage of the almost non-existent porosity of the present product is that additives and cross-linking chemicals cannot lose their effectiveness by penetrating the pores, for example compared to the use of porous carbon materials.

However, the average size of the primary granules of the particulate carbon material is advantageously limited to a value greater than 8 nm, preferably greater than 10 nm, more preferably greater than 15 nm.

The primary particles of the particulate carbon material advantageously have a heterogeneous size distribution. The smaller particle fraction accordingly has a size of greater than 8 nm, preferably greater than 10 nm, more preferably greater than 15 nm up to a size of 250 nm. The larger particle fraction has sizes above 250 nm.

Advantageously, primary particles have grown into aggregates, as a result of which the size of the primary particles differs from the size of the aggregates. The size of the primary particles is then preferably below 250 nm. In this preferred case, the primary particles are smaller than aggregates, preferably by an average of at least a factor of 2, more preferably by an average of at least a factor of 4. To clarify, it should be added that primary particles can also be present individually in this preferred embodiment and can then theoretically be equated with aggregates. In this preferred embodiment, however, this is only rarely the case, preferably less than 25%, more preferably less than 20%, particularly preferably less than 15%. This applies in particular to primary particles with a size of more than 250 nm.

Since the size of the primary particles and aggregates cannot be determined, or only to an insufficient extent, by measuring the grain size, for example using laser diffraction or sieve analysis, images taken with a scanning electron microscope, for example, can be used to determine these sizes.

The oil absorption number (OAN) between 50 mL/100 g and 150 mL/100 g distinguishes the present particulate carbon materials from carbon materials pulverised, for example, by grinding or steam explosion, which have lower OAN values due to the missing aggregates or those destroyed by the grinding process.

In a further variant of the present particulate carbon material, the OAN value is between 65 mL/100 g and 150 mL/100 g, more preferably between 70 mL/100 g and 130 mL/100 g, moreover more preferably between 75 mL/100 g and 130 mL/100 g, particularly preferably between 80 mL/100 g and 120 mL/100 g. The OAN absorption is determined according to the ASTM D 2414-00 standard.

The advantage of the high oil absorption number compared to carbon products with a lower oil absorption number is the presence of aggregates, which have an advantageous effect on the interactions between the particulate carbon material present and, for example, polymers.

In one variant, the particulate carbon material present has a water content of less than 5% by mass, preferably less than 3% by mass, more preferably less than 2% by mass. The present low water content or the dry state of the carbon material enables its incorporation, for example as a filler in polymers, because the generation of vapour bubbles at high temperatures is avoided. In addition, increased moisture content of the carbon material interferes with the use of coupling reagents.

In a further embodiment, a 15% suspension of the particulate carbon material in distilled water has an electrical conductivity of less than 5 mS/cm, preferably less than 3 mS/cm and particularly preferably less than 2 mS/cm. The electrical conductivity (determined as the conductivity of the measuring probe of the device PCE-PHD1 at 20 °C to 25 °C) is used here as a measure of the ion content or the ion concentration, in particular of ions selected from the group containing Na^+, Ca^{2+}, SO_4^{2-}, CO_3^{2-}, S^{2-}, HS^-. The advantage of the low conductivity is the low proportion of water-soluble ions, which could also separate from the present product when used, for example, in polymers.

Also, one embodiment of the particulate carbon material has a pH of > 6, preferably > 7, more preferably > 8 in a 15% suspension in distilled water. The pH of a 15% suspension of the particulate carbon material in distilled water is preferably less than 10, more preferably less than 9. The advantage of the neutral or slightly basic pH of the present product is, for example, its good compatibility with the other components of the polymer mixture.

It is also advantageous if the particulate carbon material present has a D/G signal ratio in the Raman spectrum between 0.20 and 0.90, preferably between 0.40 and 0.75, more preferably between 0.45 and 0.70 as a measure of the proportion of graphitic carbon.

The area ratio D/G of the D band to the G band in the Raman spectrum can be used as a measure of the proportion of graphitic carbon in the material. The D-band *(disorder band)* is above 1300 cm-1 to about 1360 cm-1 and the G-band *(graphite band)* is about 1580–1590 cm-1. To calculate the D/G area ratio, the integrals of the Raman spectrum over the D band and over the G band are calculated and then related.

The advantage of the specified D/G ratio is that the material can be used in some applications – due to its proportion of graphitic carbon – like a classic carbon black, and moreover – due to its proportion of amorphous carbon and the elements bound to it – other functionalities are available.

In another embodiment, the present particulate carbon material has low solubility in basic solution.

Accordingly, the present particulate carbon material advantageously has a high resistance to bases. In the present case, high resistance to bases means that less than 40%, preferably less than 30%, particularly preferably less than 15%, in particular less than 10% of the particulate carbon material present goes into solution. The procedure for determining the base resistance is preferably as follows:

- weigh out solid, dry particulate carbon material previously washed twice with five times the weight of distilled water each time;
- suspend in distilled water so that the dry matter content is 5%,
- increase the pH value of the distilled water to a value of around 9 by adding caustic soda,
- increase the temperature of the pH-adjusted suspension of carbon material present and distilled water to about 80 °C,
- stir for a period of 2 hours under the above conditions,
- after cooling the suspension to room temperature, repeat the process beginning with the step of adjusting the pH value until the pH value again corresponds to about 9 after cooling the suspension to room temperature,
- centrifuge the suspension for 15 minutes at 9000 rpm,
- separate the liquid phase and dry the remaining solid residue and
- weigh of the dried residue.

The percent base resistance is determined by dividing the dry matter of the weighed residue by the dry matter of the weighed particulate carbon material and multiplying by 100. The percent solubility of the particulate carbon material is determined by subtracting the base resistance from 100.

In this respect, the particulate carbon material according to the invention differs from lignin in that its resistance to bases is significantly increased. This has the advantage that the particulate carbon material present, for example in the case of use as a filler in rubber products or plastic products, cannot easily be washed out of the rubber product or plastic product upon contact with water.

Advantageously, the particulate carbon material of the present invention has a surface chemistry comparable to silica. By having a surface chemistry comparable to silica it is meant that the carbon material present has high OH group density. In particular, the oxygen content of the present ash-free particulate carbon material is between 20% by mass and 30% by mass, preferably between 20% by mass and 25% by mass.

In this respect, the present particulate carbon material differs from carbon black, which is obtained from renewable raw materials, for example, through intensive carbonisation (pyrolysis, oxidation, hydrothermal carbonisation, etc.) in that the functional groups of the renewable raw materials used to produce the present particulate carbon material are largely not separated by the thermal treatment, but continue to be available for binding to polymers or coupling reagents.

The ash content of the particulate carbon material, based on the dry substance, is preferably at least 1% by mass but less than 8% by mass, more preferably at least 2% by mass and less than 6% by mass, more preferably at least 3% by mass and less than 6% by mass, in particular at least 4% by mass and less than 6% by mass (ash content according to DIN 51719 at 815 °C).

In a further variant of the present particulate carbon material, the D90 of the Q3 distribution of the grain size (as a measure of the size of the granules present separately under the specific conditions) is less than 30 µm, preferably less than 20 µm, more preferably less than 15 µm, more preferably less than 10 µm, in particular less than 5 µm.

In a further variant of the present particulate carbon material, the D99 of the Q3 distribution of the grain size is less than 30 µm, preferably less than 20 µm, more preferably less than 15 µm, more preferably less than 10 µm, in particular less than 5 µm.

In a further variant of the present particulate carbon material, the D99 of the Q3 distribution of the grain size is more than 1 µm, preferably more than 2 µm.

The advantage of the maximum values of the Q3 distribution of the grain size given above is that when used in polymers, for example, the present particulate carbon material does not cause any defects due to the maximum size of the separated granules present which, for example, lead to premature tearing or breaking of the polymer or to lead to surface defects during extrusion.

The average ball diameter determined with the help of the STSA surface, assuming a material density (bulk density) of 1500 kg/m^3, is advantageously at least 2 times, preferably at least 3 times, more preferably at least 4 times, in particular at least 6 times smaller than the mean diameter (D50) of the separated granules measured over the Q3 distribution of grain size. The average ball diameter is calculated using the following formulas:

1. STSA surface area = sphere surface area/(sphere volume* material density)
2. sphere surface area = PI* average sphere diameter^2
3. sphere volume = 1/6* PI* average sphere diameter^3

Inserting expressions 2 and 3 into 1 results in the following relationship:

average ball diameter = 6/(STSA surface area* material density)

The grain size distribution of the particulate carbon material is measured in a 10% suspension with distilled water by means of laser diffraction. Before and/or during the measurement of the grain size distribution, the sample to be measured is dispersed with ultrasound until a grain size distribution that is stable over several measurements is obtained.

The STSA surface of the present particulate carbon material is preferably largely independent of its Q3 distribution of the grain size. and characterises the fineness of the primary granules.

In a preferred embodiment, the present particulate carbon material has

- a ^{14}C content, which corresponds to that of renewable raw materials, of greater than 0.20 Bq/g carbon, particularly preferably greater than 0.23 Bq/g carbon, but less than 0.45 Bq/g carbon in each case;
- a carbon content, based on the ash-free dry substance, between 60% by mass and 80% by mass;
- an STSA surface area of at least 5 m^2/g and at most 200 m^2/g;
- an Oil Absorption Number (OAN) between 50 mL/100 g and 150 mL/100 g; and
- a D90 of the Q3 grain size distribution of less than 20 µm, preferably less than 15 µm.

Advantageously, the present particulate carbon material has a shape that largely corresponds to the shape of classical carbon black. A form of the present particulate carbon material that is comparable to classic carbon black is given, for example, by the fact that the particulate carbon material

- consists of less porous primary particles,
- several of which have grown into aggregates, and
- these in turn are at least partially agglomerated.

In this respect, the present particulate carbon material, which can be used as a filler among other things, differs from fillers according to the prior art, which are obtained, for example, by grinding renewable raw materials in that the filler has a clear structure which is comparable to the structure of classic carbon blacks. The shape can be determined, for example, by REM images.

The particulate carbon material replaceable as filler preferably has a non-fibrous morphology, by which is meant that the aspect ratio is less than 10, preferably less than 5.

In another preferred embodiment, the present particulate carbon material has

- a ^{14}C content, which corresponds to that of renewable raw materials, of greater than 0.20 Bq/g carbon, particularly preferably greater than 0.23 Bq/g carbon, but less than 0.45 Bq/g carbon in each case;
- a carbon content, based on the ash-free dry substance, of more than 60% by mass and less than 80% by mass;
- an STSA of at least 5 m^2/g and at most 200 m^2/g;
- an OAN of 50 mL/100 g–150 mL/100 g;
- a surface chemistry comparable to silica; and
- a form that largely corresponds to the form of classic carbon black.

By advantageously combining the properties of a classical carbon black in terms of its shape with those of silica in terms of its surface chemistry, this preferred embodiment of the present particulate carbon material has a similar potential for interactions between filler and polymer as a classical carbon black and makes possible that this interaction potential is additionally supplemented via a mechanism similar to that of silica, for example through coupling reagents.

The particulate carbon material can be used, for example, as a filler or reinforcing filler. The particulate carbon material according to the invention can be used, for example, in rubber and rubber mixtures or plastic.

Another object of the disclosure are polymer mixtures, which are characterised in that they contain at least one polymer and at least one particulate carbon material according to the invention. Polymers can be thermoplastics, duroplastics, or elastomers.

A list of polymers is given, for example, in WO 2010/043562 A1 from page 10, line 20 to page 12, line 36, into which the particulate carbon material according to the invention can be introduced. Preferred polymers are selected from a list of the following plastics or rubbers: polyester, polyethylene, polypropylene, polyester carbonates, polyamides, polyimides, polyesteramides, polyetherimides, polyurethanes, polyvinyl alcohols, polyvinyl acetates, polyvinyl chlorides, polymethacrylates, polystyrenes, styrene maleic anhydride, polycaprolactones, poly(butylene terephthalate)s, polyepoxides; cellulose products such as cellulose acetate or cellulose nitrate, vulcanised fibre, poly(lactic acid), polyhydroxyalkanoates, chitin, casein, gelatine; formaldehyde resins such as melamine-formaldehyde resin, urea-formaldehyde resin, melamine-phenolic resins, phenol-formaldehyde resins; silicone polymers, natural rubber, styrene butadiene copolymers, polybutadiene, polyisoprene, isobutylene isoprene copolymers, ethylene propylene diene copolymers, acrylonitrile butadiene copolymers, chloroprene, fluorine rubber, or acrylic rubber, and mixtures thereof.

Another object of the disclosure are rubber mixtures, which are characterised in that they contain at least one rubber and at least one particulate carbon material according to the invention.

The particulate carbon material can be used in amounts of 10% by mass to 150% by mass, preferably 20% by mass to 120% by mass, more preferably 40% by mass to 100% by mass, particularly preferably 50% by mass to 80% by mass, based on the mass of the rubber used, are used.

The rubber mixture preferably contains at least the particulate carbon material according to the invention and, in addition, naturally occurring mineral, siliceous, chalky or calcareous fillers.

The rubber mixture preferably contains the particulate carbon material according to the invention and a coupling agent, preferably an organosilane. The organosilanes can be, for example, bis(trialkoxysilylalkyl) oligo- or polysulphide, for example bis(triethoxysilylpropyl) disulphide, or bis(triethoxysilylpropyl) tetrasulphide, mercaptosilanes, aminosilanes, silanes with unsaturated hydrocarbon groups, for example vinylsilanes. Finally, silanes with large saturated hydrocarbon groups, for example dodecyltriethoxysilane, can also act as coupling agents, wherein however van der Waals forces rather than covalent bonds ensure a certain coupling to the polymer.

The organosilane is preferably used in amounts of 2% by mass to 16% by mass, more preferably 4% by mass to 14% by mass, particularly preferably 6% by mass to 12% by mass, based on the mass of the particulate carbon material used.

When using an organosilane together with an expression of the particulate carbon material according to the invention with an STSA surface that is comparable to that of a non-active carbon black, selected rubber-technical characteristics are preferably achieved in the cross-linked state of the rubber compound, which are comparable to those that can be achieved when using a semi-active carbon black or a silica together with an organosilane.

When using an organosilane together with the particulate carbon material according to the invention, selected technical rubber characteristics are preferably not only achieved in the cross-linked state of the rubber compound, but also exceeded, which are achieved when using a carbon black with an STSA surface comparable to that of the particulate carbon material.

In a further preferred variant, the rubber mixture contains the particulate carbon material according to the invention and a reagent which masks the functional groups, preferably an organosilane, an amine, or a glycol. In this context, the amine used can be, for example, triethanolamine, hexamethylenetetramine, di-o-tolylguanidine, or diphenylguanidine. Ethylene glycol, tetraethylene glycol or poly(ethylene glycol) can be used as the glycol. The organosilane can be a trialkoxysilylalkylsilane, for example triethoxymethylsilane, triethoxyethylsilane or triethoxypropylsilane. The reagents mentioned are not capable of being incorporated into the cross-linking via sulphur bridges. However, they react with the surface of the carbon material according to the invention by consuming the functional groups, so that they have less of an adverse effect on the sulphur cross-linking. Thus, the triethoxyalkylsilanes do not act like a coupling agent. In addition to avoiding a disruption of sulphur cross-linking, such silanes act as compatibilisers, which adapt the surface energy of the filler particles to that of the polymer matrix, and thus lead to significantly improved dispersibility.

Preferably, carbon black in a rubber compound can be substituted up to 100% by the particulate carbon material present and, despite this, can achieve in the cross-linked state a performance comparable to that of the carbon black with regard to selected technical rubber characteristics.

Furthermore, silica in a rubber compound can preferably be substituted up to 100% by the particulate carbon material present and still achieve a comparable performance in the cross-linked state as with the silica with regard to selected rubber characteristics, wherein an organosilane is preferably used.

Preferred rubber characteristics are the 50% modulus and 200% modulus determined in a tensile test. High values for the 50% modulus and 200% modulus are preferred.

Another preferred rubber-related characteristic is the loss factor tan delta (quotient of loss modulus E" and storage modulus E' of the elastomer material) at temperatures between 40 °C, preferably 50 °C, more preferably 60 °C and 100 °C determined in a dynamic mechanical analysis (*temperature sweep*). This parameter is a common predictor value for rolling friction in the tyre industry. Low values for the tan delta in the specified temperature range are preferred, more preferably the tan delta reduction is at least 10% compared to the carbon black reference, very particularly preferably the tan delta reduction is at least 15% compared to the carbon black reference. An additional preferred rubber-related characteristic is the loss factor tan delta at 0 °C determined in a dynamic mechanical analysis (*temperature sweep*). This characteristic value is a common predictor value for wet grip in the tyre industry, wherein high values are preferred for tan delta 0 °C, while the tan delta increase is more preferably at least 10% compared to the carbon black reference.

In a preferred embodiment, the rubber mixture also contains carbon blacks, preferably semi-active carbon blacks or active carbon blacks, in addition to the particulate carbon material.

This rubber mixture preferably contains at least the particulate carbon material, at least one carbon black, preferably a semi-active carbon black or an active carbon black, and naturally occurring mineral, siliceous, chalky, or calcareous fillers.

This rubber mixture preferably contains at least the particulate carbon material, at least one carbon black, preferably a semi-active carbon black or an active carbon black and naturally occurring mineral, siliceous, chalky, or calcareous fillers and at least one organosilane.

The advantage of the simultaneous use of the particulate carbon material together with a carbon black is that certain technical rubber characteristics of the vulcanised rubber compound can be improved.

In another embodiment, the rubber mixture preferably contains, in addition to the particulate carbon material according to the invention, also silicas, preferably precipitated and pyrogenic silicas, and can also contain naturally occurring, mineral, siliceous, chalky, or calcareous fillers and an organosilane.

In addition to natural rubber (NR), synthetic rubbers are also suitable for the production of the rubber mixtures disclosed herein. Preferred synthetic rubbers are described, for example, by W. Hofmann, Rubber Technology, Genter Verlag, Stuttgart 1980 or in WO 2010/043562 from page 15, line 4 to page 15, line 24. Further preferred synthetic rubbers are also given in the following list: styrene butadiene copolymers (SBR), polybutadiene (BR), polyisoprene, isobutylene isoprene copolymers, ethylene propylene diene copolymers, acrylonitrile butadiene copolymers (NBR), chloroprene, fluorine rubber, or acrylic rubber, and mixtures from it.

The rubber mixtures disclosed herein may contain other rubber adjuvants such as reaction accelerators, ageing inhibitors, heat stabilisers, light stabilisers, ozone protection agents, processing aids, plasticisers, tackifiers, blowing agents, dyes, pigments, waxes, extenders, organic acids, retarders, metal oxides, and activators such as diphenylguanidine, triethanolamine, poly(ethylene glycol), alkoxyl-terminated poly(ethylene glycol) or hexanetriol, which are well known in the rubber industry.

Sulphur, organic sulphur donors, or free-radical generators can serve as cross-linking agents. The rubber mixtures disclosed herein can also contain vulcanisation accelerators.

The blending of the rubbers with the particulate carbon material, optionally carbon blacks, optionally silicas, optionally rubber adjuvants, and optionally organosilanes, can be carried out in customary mixing units, such as roll mills, internal mixers, and mixing extruders. Such rubber mixtures are usually prepared in an internal mixer, with the rubbers, wherein the particulate carbon material, any carbon blacks, any silica, any rubber adjuvants and any organosilanes are first mixed in at from 100 °C to 170 °C in one or more successive thermomechanical mixing stages. The order in which the individual components are added and the time at which they are added can have a decisive effect on the mixture properties obtained. The rubber mixture thus obtained is then mixed with the cross-linking chemicals, usually in an internal mixer or on a rolling mill at 40–120 °C, and processed into what is termed the raw mixture for the subsequent process steps, such as shaping and vulcanisation.

The rubber mixtures disclosed herein can be vulcanised at temperatures of from 80 °C to 200 °C, preferably from 130 °C to 180 °C, optionally under a pressure of from 10 to 200 bar.

The rubber mixtures disclosed herein are suitable for the production of rubber articles, i.e., articles made from the fully cross-linked or vulcanised elastomers, what are termed mouldings, for example for the production of pneumatic tyres, tyre treads, tyre sidewalls, cable jackets, hoses, drive belts, conveyor belts, roller coverings, tyres, shoe soles, buffers, sealing rings, profiles, and damping elements.

Another object of the disclosure are plastic mixtures, which are characterised in that they contain at least one plastic and at least one particulate carbon according to the invention. In this context, plastic means a thermoplastic or duroplast.

The particulate carbon material can be used in amounts of 10% by mass to 150% by mass, preferably 20% by mass to 120% by mass, more preferably 30% by mass to 100% by mass, based on the mass of the used plastic, are used.

The plastic mixture preferably contains the particulate carbon material according to the invention and an adhesion promoter or a coupling agent.

The adhesion promoter is preferably based on the use of maleic anhydride or other organic acids, preferably unsaturated carboxylic acids. For example, silanes, preferably with particularly large hydrocarbon radicals, for example triethoxydodecylsilane, can also be used as adhesion promoters.

The adhesion promoter is preferably used in amounts of 2% by mass to 16% by mass, more preferably 4% by mass to 14% by mass, particularly preferably 6% by mass to 12% by mass, based on the mass of the plastic used.

Plastics can be, for example, polyethylene (PE), polypropylene (PP), poly(vinyl acetate) (PVA) or thermoplastic elastomers (TPE). The plastic mixtures according to the invention are preferably used for the production of cables, pipes, fibres, films, in particular agricultural films, technical plastics, and injection moulded articles.

The present particulate carbon material is produced in a method disclosed herein which, in particular, enables the STSA surface area and the OAN value to be adjusted to the range specified above.

Herein is disclosed a multi-stage, in particular four-stage process for hydrothermal treatment, in particular carbonisation of renewable raw materials, in particular renewable raw materials with a proportion of more than 80% Klason lignin, where

- in a first step, a liquid containing the renewable raw material is provided,
- which, in a second step, undergoes a hydrothermal treatment at a temperature between 150 °C and 250 °C,
- in a third step, the solid present after the hydrothermal treatment is largely separated from the liquid, and
- the residual moisture of the solid is largely removed in a fourth step by drying, whereby a particulate carbon material is obtained,

wherein the STSA surface area and the OAN value of the particulate carbon material obtained in the fourth step are controlled by the mutual matching of

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material,
- the pH value of the liquid containing the renewable raw material,
- the concentration of inorganic ions in the liquid containing the renewable raw material,

- the temperature of the hydrothermal treatment, and
- the residence time in the hydrothermal treatment,

and thus an STSA surface area of at least 5 m^2/g and a maximum of 200 m^2/g, and an OAN value of at least 50 mL/100 g and a maximum of 150 mL/100 g, are set.

Instead of the concentration of the inorganic ions in the liquid containing the renewable raw material, the conductance of the liquid containing the renewable raw material is preferably used.

Due to the mutual coordination of pH, conductivity, and the proportion of organic dry matter as well as the temperature and the residence time in the hydrothermal treatment, conditions are passed through during the hydrothermal treatment which lead to the extraction of the particulate carbon material present. In particular, pH and conductivity change during the hydrothermal treatment and only in the course of the process create the conditions that produce the present particulate carbon material.

Preferably, the STSA surface area and the OAN value of the particulate carbon material obtained in the fourth step are controlled by the mutual matching of

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material,
- the pH value of the liquid containing the renewable raw material,
- the concentration of inorganic ions in the liquid containing the renewable raw material,
- the temperature of the hydrothermal treatment, and
- the residence time in the hydrothermal treatment,

and the desired STSA surface is thereby adjusted in that at a desired increase in the STSA surface

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material is reduced and/or
- the pH value of the liquid containing the renewable raw material is increased and/or
- the concentration of inorganic ions in the liquid containing the renewable raw material is reduced.

The desired STSA surface area is also preferably set by increasing the temperature of the hydrothermal treatment and/or lengthening the residence time in the hydrothermal treatment when there is a desired increase in the STSA surface area.

Preferably, with a desired increase in the STSA surface area, the temperature of the hydrothermal treatment is increased and/or the residence time in the hydrothermal treatment is increased if the yield of dry particulate carbon material is very low, preferably less than 10%, furthermore preferably less than 20%, moreover more preferably less than 30%, particularly preferably less than 40%, each based on the dry matter of the renewable raw material.

Preferably, the STSA surface area and the OAN value of the particulate carbon material obtained in the fourth step are controlled by the mutual matching of

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material,
- the pH value of the liquid containing the renewable raw material,
- the concentration of inorganic ions in the liquid containing the renewable raw material,
- the temperature of the hydrothermal treatment, and
- the residence time in the hydrothermal treatment,

and the desired STSA surface is adjusted in that at a desired reduction in the STSA surface

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material is increased and/or
- the pH of the liquid containing the renewable raw material is lowered and/or
- the concentration of inorganic ions in the liquid containing the renewable raw material is increased.

The desired STSA surface area is also preferably set by lowering the temperature of the hydrothermal treatment and/or shortening the residence time in the hydrothermal treatment when the STSA surface area is reduced.

Temperature and residence time do not only mean the maximum temperature that is maintained over a specific residence time, but also the temperature-time profile that is run through in the second step. If no temperature-time profile is given below, the temperature means the maximum temperature that is maintained over a specific residence time. In the following, temperature and residence time are also jointly referred to as process conditions.

The present method offers the advantage over the prior art that the formation of the desired finely divided particles is not already completed in the first step, but conditions which lead to the formation of the particulate carbon material with the corresponding STSA surface and OAN value are brought about only during the hydrothermal treatment in the second step. Only by carrying out such a process is it possible to bring about particle formation and a reaction at the same time, which ultimately leads to a particulate carbon material that differs from the renewable raw material used, for example with regard to its carbon content or its resistance to bases.

The present method has the particular advantage that due to the preferred setting and mutual coordination,

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material,
- the pH value of the liquid containing the renewable raw material,
- the concentration of inorganic ions in the liquid containing the renewable raw material,
- the temperature of the hydrothermal treatment, and
- the residence time in the hydrothermal treatment,

the polymerisation of the renewable raw material in the second step is largely suppressed or limited to such an extent that a particulate carbon with a corresponding STSA surface area and OAN value is obtained, and via the grain size distribution, i.e., the size distribution of the agglomerates or the present granules which separate out under certain conditions can also directly influence the size of the primary granules, which is detected by the STSA surface. In addition, the build-up of porosity in the material is suppressed, which is evidenced by a small difference between the STSA surface area and the BET surface area of the particulate carbon material.

Preferably for the adjustment and mutual coordination of

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material,
- the pH value of the liquid containing the renewable raw material,
- the concentration of inorganic ions in the liquid containing the renewable raw material,
- the temperature of the hydrothermal treatment, and
- the residence time in the hydrothermal treatment,

one or more of the following metrics is used:

- specific gravity of the liquid containing the renewable raw material after the second step;
- conductivity of the liquid containing the renewable raw material after the second step;
- pH value of the liquid containing the renewable raw material after the second step;

- difference in pH of the liquid containing the renewable raw material before and after the second step;
- difference in conductivity of the liquid containing the renewable raw material before and after the second step;

Advantageously, the STSA surface area and the OAN value of the carbon particulate obtained in the fourth step are controlled to become favourable through the adjustment of

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material, which is preferably between 5% by mass and 40% by mass, more preferably between 10% by mass and 20% by mass,
- the pH of the liquid containing the renewable raw material at 20 °C to 25 °C preferably to a value ≥ 7, more preferably ≥ 8, particularly preferably ≥ 8.5, furthermore preferably ≤ 11,
- the concentration of inorganic ions in the liquid containing the renewable raw material preferably to a value between 10 mS/cm and 200 mS/cm, preferably between 10 and 150 mS/cm, more preferably between 10 and 50 mS/cm, moreover preferably between 10 and 40 mS/cm, particularly preferably between 10 mS/cm and 25 mS/cm (determined as the conductance of the measuring probe of the PCE-PHD1 at 20 °C to 25 °C),
- the temperature of the hydrothermal treatment preferably to a maximum value between 200 °C and 250 °C, preferably to a maximum value between 210 and 245 °C, and/or
- the residence time in the hydrothermal treatment preferably between 1 minute and 6 hours, preferably between 30 minutes and 4 hours, particularly preferably between 1 hour and 3 hours,

and thus set an STSA surface between 5 m^2/g and 200 m^2/g and an OAN value between 50 mL/100 g and 150 mL/100 g.

In the first step, the renewable raw material is advantageously completely dissolved in the liquid containing the renewable raw material. Alternatively, the renewable raw material is not completely dissolved in the liquid containing the renewable raw material in the first step, wherein however

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material,
- the pH value of the liquid containing the renewable raw material and

- the concentration of inorganic ions in the liquid containing the renewable raw material

are set in such a way that the renewable raw material initially completely dissolves due to the temperature increase during the hydrothermal treatment in the second step, before the solid that can be separated in the third step is formed in the second step.

The advantage of the complete solution of the renewable raw material in the liquid containing the renewable raw material is that a solid-solid transition is suppressed and the solid that can be separated in the third step is formed completely from the solution, i.e., a transition from the solution to the solid takes place.

The process is advantageously operated continuously, wherein the process conditions of the hydrothermal treatment are kept constant in the second step and the pH value and conductivity of the liquid containing the renewable raw material are continuously adjusted in the first step to compensate fluctuations in the quality of the renewable raw material.

This procedure has the advantage that the significantly more complex adjustment of the process conditions in the second step can be avoided.

In a special variant of the method, the temperature and the residence time in the second step are adjusted in such a way that, to achieve an STSA surface area between 5 m^2/g and 200 m^2/g and an OAN value between 50 mL/100 g and 150 mL/100 g,

- a slightly higher concentration of inorganic ions is required than was initially present after adjusting the organic dry matter content of the renewable raw material contained in the liquid and adjusting the pH value, and
- subsequently, the concentration of inorganic ions can be increased further by adding salts until reaching the concentration of inorganic ions that matches the process conditions of the second stage, measured via the conductance.

This procedure has the advantage that the conductance can be used to fine-tune the quality of the liquid containing the renewable raw material, since this can be measured much more easily and reliably than the pH value.

The concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material, the pH value of the liquid containing the renewable raw material, and/or the concentration of inorganic ions in the liquid containing the renewable raw material are advantageously adjusted in the first step.

Alternatively, advantageously, the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material, the pH value of the liquid containing the renewable raw material, and/or the concentration of inorganic ions in the liquid containing the renewable raw material are adjusted in the first step and in the second step.

Alternatively, advantageously, the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material, the pH value of the liquid containing the renewable raw material, and/or the concentration of inorganic ions in the liquid containing the renewable raw material are adjusted in the second step.

In the embodiments in which the adjustment of the concentration of the organic dry matter of the renewable resource in the liquid containing the renewable resource, the pH value of the liquid containing the renewable resource, and/or the concentration of inorganic ions in the liquid containing the renewable resource also takes place in the second step, the renewable raw material is advantageously completely dissolved in the liquid containing the renewable raw material in the first step, and the formation of the desired finely divided particles is prevented during the hydrothermal treatment in the second step not only by the selected process conditions but also by an increase in the concentration the organic dry matter of the renewable raw material in the liquid containing the renewable raw material, a lowering of the pH value of the liquid containing the renewable raw material, or an increase in the concentration of inorganic ions in the liquid containing the renewable raw material.

The advantage of such a method is that the conditions which lead to the formation of the desired finely divided particles can be brought about in a targeted manner in the second step, thereby increasing the stability of the method and possibly reducing the residence time in the second step.

In addition, after completion of the formation of the desired finely divided particles in the second step, it is advantageous to lower the concentration of the organic dry matter in the liquid containing the particulate carbon material, to increase the pH value of the liquid containing the particulate carbon material, or to lower the concentration of inorganic ions induced in the liquid containing the particulate carbon material. This is advantageously done in the second step, or at the latest in the third step.

This procedure ensures that after the formation of the desired finely divided material has been completed, no further solids are formed, for example, during the cooling phase at the end of the second step, or through an increase in the concentration of the organic dry matter in the liquid containing the particulate carbon material, for example by evaporation in the third step.

During the hydrothermal treatment, the pressure corresponds at least to the saturated vapour pressure of the liquid containing the renewable raw material.

In a preferred embodiment

- the concentration of organic dry matter in a liquid containing lignin in the first step is between 10% by mass and 20% by mass,
- the pH of the liquid containing lignin in the first step is more than 8.5 and less than 10.5,
- the concentration of the inorganic ions in the liquid containing lignin in the first step is such that the conductivity is between 10 mS/cm and 25 mS/cm,
- the maximum temperature of the hydrothermal treatment in the second step between 210 °C and 240 °C, and
- the residence time of the liquid containing lignin in the hydrothermal treatment in the second step is between 120 and 240 minutes, whereby
- the STSA surface area of the particulate carbon material thus produced, measured after dewatering in the third step and drying in the fourth step, has a value between 5 m^2/g and 50 m^2/g and an OAN value between 50 mL/100 g and 100 mL/100 g.

The method disclosed herein can further include washing after dehydration in the third step or pulverisation after drying in the fourth step.

The drying in the fourth step is preferably carried out at temperatures below the softening point of the particulate carbon material, preferably at temperatures below 150 °C, more preferably at temperatures below 130 °C.

Advantageously, the D90 of the Q3 distribution of the grain size of the particulate carbon material after drying in the fourth step is adjusted by pulverisation to a value of less than 30 µm, preferably less than 20 µm, more preferably less than 15 µm, particularly preferably less than 10 µm.

The process manages in particular without the addition of a copolymerisable compound or a polymerisation initiator and without a fermentation of the biomass.

The process operates in the liquid phase, wherein it always operates below the critical point of water.

The present invention will now be explained with reference to exemplary embodiments. In the figures:

Figure 1	shows a diagram of the stress-strain curve in the tensile test as an example of the rubber-technical characteristics of cross-linked rubber articles made of SBR with the particulate carbon material according to the invention and of the associated reference.

Figure 2	shows a diagram of the curves of the loss factor tan delta (logarithmic scaling) as a function of the temperature on fully cross-linked articles made of SBR with the particulate carbon material according to the invention or on the reference with N660
Figure 3	shows a diagram of the stress-strain curve in the tensile test as a comparison of the technical rubber values of cross-linked rubber articles made of SBR, which are provided with untreated lignin, with the particulate carbon material according to the invention but without a coupling agent and with the particulate carbon material and coupling agent according to the invention.
Figure 4	shows a diagram of the stress-strain curve in the tensile test as a comparison of the technical rubber values of cross-linked rubber articles made of SBR, with the particulate carbon material according to the invention but without any further additive, and are provided with the particulate carbon material according to the invention and a reagent for masking the functional groups and with the particulate carbon material and a coupling agent.
Figure 5	shows a diagram of the stress-strain curve in the tensile test as a comparison of the technical rubber values of articles made of elastomer material mixtures based on natural rubber and butadiene rubber NR/BR and the particulate carbon material, each with different mixing procedures and from the reference.
Figure 6	shows a diagram of the stress-strain curve in the tensile test as a comparison of the rubber-technical characteristics of cross-linked rubber articles made of NBR, which are provided with the particulate carbon material according to the invention without a coupling agent and of the reference.

In the working examples, the method disclosed herein for obtaining the particulate carbon material according to the invention, its properties and its performance in the cross-linked rubber are described.

Examples 1–11 for preparing the particulate carbon material from lignin

In the first step, a liquid containing the renewable raw material is provided.

First, water (1) and lignin (2) are mixed and a lignin-containing liquid is prepared with a set content of organic dry matter (3).

The lignin is then completely dissolved in the lignin-containing liquid. For this purpose, the pH is adjusted to the desired value (7) by adding a base or an acid (6). The preparation of the solution is supported by intensive mixing at a suitable temperature (4) for a sufficient time (5). A certain concentration of inorganic ions, which can be measured as conductivity (9), is adjusted by the added base or acid and by salts, which are additionally added (8) and/or also come from the ash content of the lignin. The composition and properties of the lignin-containing liquid thus prepared are listed in Table 1,

Example	1		2		3	4	5	6		7	8		9
-	mL	Sort	Sort	g	%	°C	h	Additive	g	-	Additive	g	mS/cm
1	10200	Distilled water	Lignin 1	1800	14.1	80	2	NaOH	107.25	10.1	_	0.0	15.1
2	10200	Distilled water	Lignin 1	1800	14.1	80	2	NaOH	128.40	10.3	_	0.0	17.5
3	10200	Distilled water	Lignin 2	1800	14.2	80	2	NaOH	111.60	10.2	_	0.0	18.1
4	10200	Distilled water	Lignin 2	1800	14.2	80	2	NaOH	111.60	10.2	_	0.0	20.1
6	3854	Ludwigsfelde tap water	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	_	0.0	15.9
7	3854	Ludwigsfelde tap water	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	_	0.0	15.9
8	3854	Ludwigsfelde tap water	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	_	0.0	15.9
9	3854	Ludwigsfelde tap water	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	_	0.0	15.9
10	3854	Ludwigsfelde tap water	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	_	0.0	15.9
11	48.23	Distilled water	Lignin 1	20.9	14.1	80	2	NaOH	0.44	9.8	_	0.0	17.7

Table 1

The composition of the lignin used is given in Table 2.

	Lignin 1	**Lignin 2**	**Lignin 3**
C	62.8	64.0	67.2
H	4.8	5.2	5.5
O (calculated)	24.8	24.0	24.0
N	0.3	0.0	0.0
S	1.3	1.5	1.8
Na	2.5	1.9	0.3
Ash (without Na)	3.6	4.1	1.2

Table 2

In the second step, the liquid containing the renewable raw material is subjected to hydrothermal treatment and a solid is obtained in this way.

The solution prepared in the first step is heated from a starting temperature (10) over a heating time (11) to a reaction temperature (12), which is maintained over a reaction period (13). This is followed by cooling over a cooling time (14) to a final temperature (15). As a result, a solid is obtained. The pH value (16) and the conductivity (17) of the liquid containing the solid will change depending on the process conditions mentioned above.

With a suitable adjustment of the content of organic dry matter, the pH value and the concentration of inorganic ions in the first step and a suitable choice of the process conditions in the second step, conditions are set in the second step in which the particulate carbon material in a raw form separates from the solution. The process conditions of the second step are given in Table 3.

Example	10	11	12	13	14	15	16	17
-	°C	min	°C	min	min	°C	-	mS/cm
1	80	90	240	150	3600	80	9.0	19.7
2	80	90	240	150	3600	80	9.1	21.4
3	80	90	240	150	3600	80	8.6	20.2
4	80	90	240	150	3600	80	8.4	21.1
6	30	40	225	324	40	30	8.4	13.2
7	30	40	225	408	40	30	8.3	13.5
8	30	41	230	270	41	30	8.3	13.5
9	30	41	230	300	41	30	8.2	13.7
10	30	42	235	162	42	30	8.7	12.9
11	30	41	230	180	41	30	8.6	20.9

Table 3

In the third step, the raw particulate carbon material is dewatered and, if necessary, washed. The raw particulate carbon material is largely separated from the liquid containing it by a dewatering (18). The raw particulate carbon material is then washed with many times the mass of water and dewatered again (19). The process conditions for the third step are compiled in Table 4.

Example	18	19		
-	Sort	Type	Washing liquid	Amount of washing liquid kg/kg dry

				particulate carbon material
1	Centrifuge; 6000 rpm/15 min	Resuspension/centrifuge; 6000 rpm/15 min	Distilled water	3
2	Centrifuge; 6000 rpm/15 min	Resuspension/centrifuge; 6000 rpm/15 min	Distilled water	3
3	Centrifuge; 6000 rpm 15 min	Resuspension/centrifuge; 6000 rpm/15 min	Distilled water	3
4	Centrifuge; 6000 rpm/15 min	Resuspension/centrifuge; 6000 rpm/15 min	Distilled water	3
6	Centrifuge; 9000 rpm/15 min	Resuspension/centrifuge; 9000 rpm/15 min	Ludwigsfelde tap water	2
7	Centrifuge; 9000 rpm/15 min	Resuspension/centrifuge; 9000 rpm/15 min	Ludwigsfelde tap water	2
8	Centrifuge; 9000 rpm/15 min	Resuspension/centrifuge; 9000 rpm/15 min	Ludwigsfelde tap water	2
9	Centrifuge; 9000 rpm/15 min	Resuspension/centrifuge; 9000 rpm/15 min	Ludwigsfelde tap water	2
10	Centrifuge; 9000 rpm/15 min	Resuspension/centrifuge; 9000 rpm/15 min	Ludwigsfelde tap water	2
11	Centrifuge; 9000 rpm/15 min	Resuspension/centrifuge; 9000 rpm/15 min	Distilled water	2

In the fourth step, the dewatered and optionally washed raw particulate carbon material is dried and optionally milled.

The dehydrated raw carbon particulate material and remaining liquid are dried at an elevated temperature (20, see Table 5) to obtain the carbon particulate material. Subsequently, the particulate carbon material can be de-agglomerated (21, see Table 5).

Example	20	21
-	°C	-
1	105	Jet mill with classifier wheel
2	105	Jet mill with classifier wheel
3	105	Jet mill with classifier wheel
4	105	Jet mill with classifier wheel
6	105	-
7	105	-
8	105	-
9	105	-

10	105	-
11	105	-

Table 5

Quality of the particulate carbon material obtained from Examples 1–11: As a result, an expression of the particulate carbon material according to the invention is obtained (see Table 6):

Example	Carbon	Oxygen	Ash content	STSA	OAN value	pH)[1]	BB)[2]	D/G)[3]	D50)[4]	D90)[4]	D99)[4]	Average ball diameter) [5]	D50/average ball diameter	BET	Water content
	Mass% dry, ash-free	Mass% Dry, ash-free	Mass% Dry	m²/g	mL/100 g	-	%	-	µm	µm	µm	µm	-	m²/g	%
1	72.3	21.7	4.9	17.7	94.4	8.7	9.8	0.52	1.6	3.1	4.4	0.23	7.0	19.9	0.8
2	71.9	22.3	4.6	12.6	80.5	8.5	9.5	0.65	1.5	2.8	4.0	0.32	4.7	14.2	1.9
3	70.9	22.8	5.3	13.6	84.1	8.8	n.d.	n.d.	1.4	2.4	3.2	0.29	4.7	14.4	1.3
4	70.7	22.8	5.3	10.8	74.0	8.8	n.d.	n.d.	1.5	2.6	3.3	0.37	4.1	10.0	1.5
6	69.5	n.d.	n.d.	26.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15	n.d.	28.3	1.5
7	69.8	n.d.	n.d.	19.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.21	n.d.	20.2	2.4
8	70.1	n.d.	n.d.	14.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.29	n.d.	14.7	1.3
9	70.2	n.d.	n.d.	9.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.40	n.d.	10.4	1.6
10	70.4	n.d.	n.d.	2.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.56	n.d.	2.7	2
11	70.3	n.d.	n.d.	36.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	38.6	1.3
1 = in 15% suspension; 2 = resistance to bases in % of dissolved material;															
3 = from the Raman spectrum; 4 = from grain size determination using laser diffraction															
5 = calculated from STSA and granule density; n.d.: not determined															

Table 6

<u>Examples 12 A-D and reference example for the manufacture of rubber articles from SBR with the particulate carbon material from Examples 1 and 2 and with carbon black N660, respectively</u>

The carbon materials obtained according to Examples 1 and 2 are introduced into a rubber compound as a filler and vulcanised with the aid of other additives. The composition of the rubber compound is shown in Table 7.

	Reference	A	B	C	D	
Elastomer type	sSBR	sSBR	sSBR	sSBR	sSBR	-
Elastomer amount	100	100	100	100	100	phr

Filler type	N660	Particulate carbon material according to Example 2	Particulate carbon material according to Example 2	Particulate carbon material according to Example 1	Particulate carbon material according to Example 2	-
Filler amount	40	40	40	40	60	phr
Coupling reagent Type	-	-	Si69	Si69	Si69	-
Coupling reagent Quantity	-	-	3.2	3.2	4.8	phr
ZnO	3	3	3	3	3	phr
Stearic acid	2	2	2	2	2	phr
DPG	2	2	2	2	2	phr
CBS	1.5	1.5	1.5	1.5	1.5	phr
Sulphur	1.5	1.5	1.5	1.5	1.5	phr

phr: parts per hundred rubber, amount based to the amount of elastomer
DPG, CBS: Vulcanisation accelerator
Si69: Coupling reagent

Table 7

SBR solution (sSBR) Buna VSL 4526-0 HM from Lanxess was used as the SBR. It is a copolymer of 26% by weight styrene in addition to butadiene. Its Mooney viscosity is 65 ME (ASTM D 1646). Zinc oxide, stearic acid and sulphur were from Fischer Scientific. 2-N-cyclohexyl benzothiazole sulphenamide (CBS) was obtained from Lanxess. 1,3-Diphenylguanidine (DPG) from Sigma-Aldrich Co. LLC, USA, was used. The process oil TDAE (VIVATEC 500) was from Klaus Dahleke KG. The antioxidant 2,2,4-trimethyl-1,2-dihydroquinoline polymer TMQ was supplied by C. H. Erbslöh, Krefeld. N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) was obtained from abcr Gmbh & Co. KG, Karlsruhe. Bis(triethoxysilylpropyl)tetrasulphide, which is marketed by Evonik Industries under the name Si69®, was used as the coupling reagent.

SBR was initially introduced in an internal mixer (Haake Rheomix 600P, ThermoFisher Scientific, Karlsruhe) at 145 °C and a filling factor of 0.7, corresponding to a volume of 56 cm^3. The fillers were then added in two stages. After the optional addition of the Si69 silane, the temperature in the internal mixer was maintained in a range between 140–165 °C for 10 minutes and mixed at a speed of 60 min^{-1} for complete silanisation.

The antioxidants and vulcanisation additives were added on a two-roll mill (Polymix-110L, Servitec Maschinen Service GmbH, Wustermark) at an initial temperature of 50 °C and a constant friction of 1:1.2.

Rubber compounds reference and A (Table 7) are cross-linked using a vulcanisation process common to carbon black application. Rubber compounds B, C, and D (Table 7) are cross-linked using a vulcanisation process common to the use of silica together with Si69. The samples were vulcanised in a TP1000 laboratory press (Fontijne Grotnes BV, Vlaardingen Netherlands) at 160 °C and a pressing force of 150 kN. The optimum vulcanisation time t_{90} was determined using a rubber process analyser (Scarabaeus SIS-V50, Scarabaeus GmbH, Wetzlar).

The mechanical characterisation was carried out on DIN S2 specimens according to DIN 53504 with a Zwick/Roell-Z010 materials testing machine (Zwick GmbH & Co KG, Ulm) with an optical elongation sensor at a crosshead speed of 200 mm/min at room temperature. The stress-strain curves in the tensile test as an example of the technical rubber properties of the rubber articles obtained from Examples A-D in Table 7 are listed in the diagram in Figure 1.

In the case of examples B, C and D (in which a coupling agent is added) in particular, these show comparable properties to the filler N660. The values for the 50% modulus, 100% modulus and 200% modulus in examples B and C are at least as high as for the reference. Furthermore, it is shown that increasing the degree of filling from 40 phr (B) to 60 phr (D) of the particulate carbon material according to Example 2 with elongation in the lower range (up to 100%) leads to an increase in the stress values, i.e., the 50% modulus and the 100% modulus. In addition, it is clear that increasing the STSA surface area and the OAN value of the particulate carbon material from the values of Example 2 to the values of Example 1 at the same loading level results in an improvement in tensile strength and in higher values of the 50% modulus, 100% modulus, and 200% modulus (compare B and C). Furthermore, it is clear that the particulate carbon material from Example 2 with its STSA surface area of 12.6 m^2/g shows a comparable stress-strain curve in the tensile test as the classic carbon black N660, which has an STSA surface area of 34 $m^2/g \pm 5\ m^2/g$.

The loss factor tan delta (quotient of loss modulus E" and storage modulus E' of the elastomer material) as a function of temperature, determined in a dynamic mechanical analysis (*temperature sweep*), is shown in Figure 2 and Table 8.

The mixtures with N660 (reference) and those with the particulate carbon material from Example 2 without a coupling agent (Example 12 A) show similar glass transition temperatures ($T_{g,SBR}$ = -2.91 °C; see peak in the curve of tan delta versus temperature in Figure 2). These two blends also exhibit similar stiffness in the rubber plateau region above the glass transition temperature. The tan delta curves are close together, wherein although the curve for the reference mixture is slightly lower than that of example 12 A from about 76 °C and thus indicates a slightly lower energy loss.

The use of the particulate carbon material from Example 2 in combination with a coupling agent (Example 12 B) leads to significant changes. Compared to reference and 12 A, the glass transition temperature of the mixture from example 12 B is shifted upwards to $T_{g,SBR} = -0.48$ °C. Under the conditions of low dynamic elongation (0.5%), the energy loss properties of the composite 12 B are significantly improved compared to the reference with N660, which can be seen from the deeper curve in the temperature range above the glass transition temperature.

It can be seen that the elastomer material, which contains the particulate carbon material from Example 2 and a coupling agent, has lower values for tan delta above the glass transition temperature than the reference with N660, which means that a comparatively reduced rolling friction can be expected for a tyre made of this material.

	tan delta 60 °C	tan delta 0 °C
Reference N660	0.1020	1.4342
Example 12 A	0.1035	1.4023
Example 12 B	0.0840	1.6208

Table 8

It can also be seen in Figure 2 that the tan delta for Example 12 B at 0 °C is higher than the reference, suggesting an improved wet grip in a tyre made from the composite from Example 12 B.

<u>Comparative Example 13 for the production of rubber articles from SBR with untreated lignin</u>

According to the state of the art, untreated lignin has already been used in rubber compounds. The following comparative example shows the differential effect of untreated lignin and the carbon material of the present invention in a rubber compound.

For comparison purposes, lignin 3 from Table 2 is introduced into a rubber compound as a filler and vulcanised with the aid of other additives. The composition of the rubber compound corresponds to the composition in Example 12 B, wherein however instead of the particulate carbon material from Example 2, untreated lignin 3 is now used. The rubber compound for Example 13 is cross-linked using a conventional vulcanisation process for the use of silica together with Si69.

The stress-strain curve in a tensile test as an example of the technical rubber properties of the rubber article obtained is shown in the diagram in Figure 3 together with the results of example 12 A and 12 B.

It can be seen that the effect in the rubber compound caused by untreated lignin (Example 13) is significantly weaker than the effect caused by the carbon material according to the invention itself (Example 12 A) even when using the coupling agent silane Si69 and remains particularly clearly behind the effect of the carbon material according to the invention in combination with silane Si69 (Example 12 B).

Example 14 for determining the ^{14}C content of the product from Example 2

The material from Example 2 was sent to the Poznań Radiocarbon Laboratory, Foundation of the A. Mickiewicz University, ul. Rubiez 46, 61-612 Poznań for determination of the ^{14}C content. The method used is described by the head of the laboratory, Tomasz Goslar, on the Institute's website. The essential contents for lignin are summarised below.

Procedure for ^{14}C dating using the AMS technique with the steps:

a) chemical pre-treatment
b) production of CO_2 and graphitisation
c) AMS ^{14}C measurement
d) calculation and calibration of the ^{14}C age

a) The methods of chemical pre-treatment are basically described in Brock, et al., 2010, Radiocarbon, 52, 102–112.

Plant residue samples are treated with 1 M HCl (80 °C, 20+ min), 0.025–0.2 M NaOH (80 °C) and then with 0.25 M HCl (80 °C, 1 h). After treatment with each reagent, the sample is washed with deionised water (Millipore) to pH = 7. For the first HCl treatment, a longer time (20+) is applied when evolution of gas bubbles is still visible from the sample. The NaOH treatment step is repeated a number of times, generally until no further colouration of the NaOH solution occurs (the solution colouration is caused by humic acids dissolved in NaOH), but the NaOH treatment is stopped when there is a risk of the complete dissolution of the sample.

b) In the case of organic samples, the CO_2 is produced by burning the sample.

Combustion of the sample is carried out in a sealed (under vacuum) quartz tube together with CuO and Ag wool at 900 °C for 10 hours. The resulting gas (CO_2 + water vapour) is then dried in a vacuum apparatus and reduced with hydrogen (H_2) using 2 mg of Fe powder as a catalyst. The resulting mixture of carbon and iron is then pressed into a special aluminium holder as described by Czernik J., Goslar T., 2001, Radiocarbon, 43, 283–291. The standard samples are prepared in the same way, e.g., as for samples not containing ^{14}C (coal or IAEA C1 Carrara Marmor) and samples of the "International Modern ^{14}C Standard" (oxalic acid II).

c) The measurements described here were carried out in the AMS ^{14}C laboratory of the A. Mickiewicz University in Poznań.

The ^{14}C content in the carbon sample is measured using the "Compact Carbon AMS" spectrometer (manufacturer: National Electrostatics Corporation, USA) which is described in the article Goslar T., Czernik J., Goslar E., 2004, Nuclear Instruments and Methods B, 223–224, 5–11. The measurement is based on the comparison of the intensities of ^{14}C, ^{13}C, and ^{12}C ion beams obtained for each sample and each standard (modern standard: "Oxalic acid II" and Standard for ^{14}C-free carbon "Background") was measured. In each AMS run, 30–33 samples of unknown age were measured alternately with 3–4 modern standard measurements and 1–2 background measurements. When dating organic samples, the background is represented by charcoal.

d) Conventional ^{14}C age is calculated using the correction for isotope fractionation (according to Stuiver, Polach 1977, Radiocarbon 19, 355) based on the $^{13}C/^{12}C$ ratio determined in the AMS spectrometer simultaneously with the $^{14}C/^{12}C$ ratio (note: the measured values of $\delta^{13}C$ depend on the isotope fractionation during CO_2 reduction and the isotope fractionation inside the AMS spectrometer, and as such they cannot be compared with the $\delta^{13}C$ values obtained with conventional mass spectrometers that are determined on gas samples). The uncertainty of the calculated ^{14}C age is determined using the uncertainty resulting from the counting statistics, as well as the scatter (standard deviation) of the individual $^{14}C/^{12}C$ results. The uncertainties of the $^{14}C/^{12}C$ ratios measured on the standard samples are also taken into account. The reported 1-sigma uncertainty of the conventional ^{14}C age is the best approximation of the absolute uncertainty of the measurement.

The calibration of the ^{14}C age is performed using the OxCal ver. 4.2 (2014) program, the basics of which are described in Bronk Ramsey C., 2001, Radiocarbon, 43, 355–363, while the current version is in Bronk Ramsey C., 2009, Radiocarbon, 51, 337–360 and Bronk Ramsey C. and Lee S., 2013, Radiocarbon, 55, 720–730. The calibration is done against the latest version of the ^{14}C calibration curve, i.e., INTCAL13 (Reimer PJ, et al. 2013, Radiocarbon, 55(4), 1869–1887).

The analysis gives the age of the carbon sample for archaeological purposes. However, the measurement result can also be given as a specific activity. In the present case of the material from Example 2, the analysis for the specific activity gave a value of 243.30 ± 0.52 Bq/kgC or Bq/kg carbon.

Example 15 for the production of rubber articles from SBR with the particulate carbon material from Example 2 in the presence of a functional group masking reagent:

The carbon material obtained according to embodiment 2 is introduced as a filler into a rubber compound and vulcanised with the aid of other additives. The composition of the rubber compound and its processing corresponds to that in Example 12 B (Table 7), wherein however the silane Si69 is replaced by an equimolar amount of triethoxymethylsilane, which corresponds to a use of 1.06 phr. Further processing is analogous to Example 12.

The triethoxymethylsilane is not capable of being incorporated into the cross-linking via sulphur bridges. However, it reacts with the surface of the carbon material according to the invention, consuming the functional groups. The functional groups that react with the silane are replaced by methyl groups on the outside, which, compared to the unmodified starting material, leads to compatibilisation of the filler surface with the non-polar rubber matrix.

For example, the carbon material of the present invention treated with triethoxymethylsilane provides higher tensile strength in rubber than the carbon material used without the silane but, as expected, lags behind the carbon material in combination with the coupling silane Si69.

The stress-strain curve in a tensile test as an example of the technical rubber properties of the rubber articles obtained in Figure 4 shows that it can be useful in selected rubber systems and for selected applications to mask the functional groups.

Examples 16 A and B and reference for the production of rubber articles from NR/BR with the particulate carbon material from Example 2 and with carbon black N660:

The carbon material obtained according to Example 2 is introduced as a filler into a mixture of NR and BR and vulcanised with the aid of other additives.

In the case of A and the Reference, a mixture (pre-mix) of NR and BR is first produced in an internal mixer (Haake Rheomix 600P, ThermoFisher Scientific, Karlsruhe) at a starting temperature of 120 °C, which is then treated with the respective filler and other components. In contrast thereto, with B, also in the internal mixer (starting temperature 35 °C, speed 60 min^{-1}), a masterbatch is first produced from BR, the filler, and silane, which is then further processed with NR and the remaining components (also in the internal mixer, starting temperature 120 °C, speed 60 min^{-1}). The quantitative composition of both processing variants is identical.

The stress-strain curve in a tensile test as an example of the technical rubber properties of the rubber articles obtained from Examples A and B are shown in the diagram in Figure 5. These show that the carbon material according to the invention can be used for reinforcement in NR/BR mixtures. Furthermore, it can be seen that the order of processing has an influence on the performance of the filler in the articles made of the respective NR/BR rubber composite in the cured state. In this way, the modulus and tensile strength can be influenced.

Example 17 A and B and Reference for the manufacture of rubber articles from NBR using the particulate carbon material from Example 4 and N990, respectively

The carbon material obtained according to exemplary embodiment 4 is introduced into NBR as a filler and vulcanised with the aid of further additives but without a coupling agent. The composition of the rubber compound is shown in Table 9.

	Reference	A	B
Perbunan 3945	100.0	100.0	100.0
ZnO	5.0	5.0	5.0
Stearic acid	1.0	1.0	1.0
Mesamoll II	15.0	15.0	15.0
Talc	80.0	80.0	80.0
N 550	30.0	30.0	30.0
N 990	80.0	40.0	
Material from Example 4		**40.0**	**80.0**
Vulkanox 4010	3.0	3.0	3.0
Sulphur	0.5	0.5	0.5
MBTS	1.0	1.0	1.0
TMTD	3.0	3.0	3.0

Table 9

The mixtures are produced on a Haake Rheomix 600 (tangential rotor geometry, 78 cm^3) with an initial temperature of 40 °C and a rotor speed of 100 min^{-1}. First the NBR polymer is mixed for 2 minutes, then stearic acid, ZnO, optionally material from Example 4 and talc for 2 minutes, N990 and Mesamoll II optionally additionally for a further 4 minutes, antioxidants for a further 3 minutes and the vulcanisation chemicals for a further 2 minutes. The optimal vulcanisation time was determined using a *Rubber Process*

Analyser and the mixture was vulcanised at 160 °C for a minute value of (t_{90} +1/mm layer thickness).

The Shore A hardness was determined according to DIN 53505: 2000-08, the tensile test according to DIN 53504:2009-10 and storage for 72 hours at 70 °C in Lubrizol OS 206304 oil according to DIN ISO 1817:2008-08].

The values shown in Table 10 were determined.

Example	Reference	A	B
Hardness, Shore A	83	84	85
Tensile strength (MPa)	9.9	11.1	11.4
Elongation at break (%)	235	253	248
modulus (MPa) 50%	4.7	5.3	5.6
100%	6.6	7.5	8.0
200%	9.7	10.8	11

Table 10

It is clear that comparable or even slightly improved values in the tensile test are achieved both with partial and with complete replacement of the N990 by the carbon material according to the invention from Example 4 without the addition of a coupling agent, see Figure 6. The same applies to the changes in values shown in Table 11 after storage in oil. When replacing inactive carbon blacks such as N990, the use of the carbon material according to the invention in its quality according to Example 4 without a coupling agent is sufficient to achieve comparable values.

Changes after storage in engine oil for 72 h/70 °C	Reference	A	B
By weight%	-2.6	-2.6	-2.7
By volume%	-3.4	-3.3	-3.3
By hardness	+3	+3	+3
In the tensile strength %	+6	+12	+11
In the elongation at break %	-9	-6	-10

Table 11

PIENHIUKKASHIILIMATERIAALIA UUSIUTUVISTA RAAKAMATERIAALEISTA

PATENTTIVAATIMUKSET

1. Pienhiukkashiilimateriaali uusiutuvista raakamateriaaleista, jonka pienhiukkashiilimateriaalin

– ^{14}C-pitoisuus on uusiutuvia raakamateriaaleja vastaava, ollen suurempi kuin 0,20 Bq/g hiiltä ja pienempi kuin 0,45 Bq/g hiiltä,

– STSA-pinta-ala on ainakin 5 m^2/g ja enintään 200 m^2/g, ja

– öljyabsorptioarvo (OAN) on välillä 50 ml/100 g ja 150 ml/100 g,

ja joka on **tunnettu** siitä, että

– hiilipitoisuus on tuhkattoman kuiva-aineen perusteella välillä 60 painoprosenttia ja 80 painoprosenttia.

2. Patenttivaatimuksen 1 mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että sen BET-pinta-ala eroaa sen STSA-pinta-alasta enintään 20 %.

3. Patenttivaatimuksen 1 tai 2 mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että sen uusiutuvia raakamateriaaleja vastaava ^{14}C-pitoisuus on suurempi kuin 0,23 Bq/g hiiltä ja pienempi kuin 0,45 Bq/g hiiltä.

4. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että sen hiilipitoisuus on tuhkattoman kuiva-aineen perusteella välillä 60 painoprosenttia ja 75 painoprosenttia, edullisesti välillä 65 ja 75 painoprosenttia.

5. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että sen STSA-pinta-ala on välillä 8 m^2/g ja 100 m^2/g.

6. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että sen BET-pinta-ala eroaa sen STSA-pinta-alasta enintään 15 %, edullisesti enintään 10 %.

7. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että pienhiukkashiilimateriaalin tislatussa vedessä olevan 15 % suspension sähkönjohtavuus on alle 5 mS/cm, edullisesti alle 3 mS/cm ja erityisen edullisesti alle 2 mS/cm.

8. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että pienhiukkashiilimateriaalin tislatussa vedessä olevan 15 % suspension pH-arvo on > 6, edullisesti > 7.

9. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että Raman-spektrin D/G-signaalisuhde on välillä 0,20 ja 0,90, edullisesti välillä 0,40 ja 0,75.

10. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että raekoon Q3-jakauman D90 on alle 30 µm, edullisesti alle 20 µm.

11. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että tuhkattoman pienhiukkashiilimateriaalin happipitoisuus on välillä 20 painoprosenttia ja 30 painoprosenttia, edullisesti välillä 20 painoprosenttia ja 25 painoprosenttia.

12. Jonkin edellä olevan patenttivaatimuksen mukainen pienhiukkashiilimateriaali, **tunnettu** siitä, että uusiutuvat raakamateriaalit ovat ligniiniä sisältävää biomassaa.

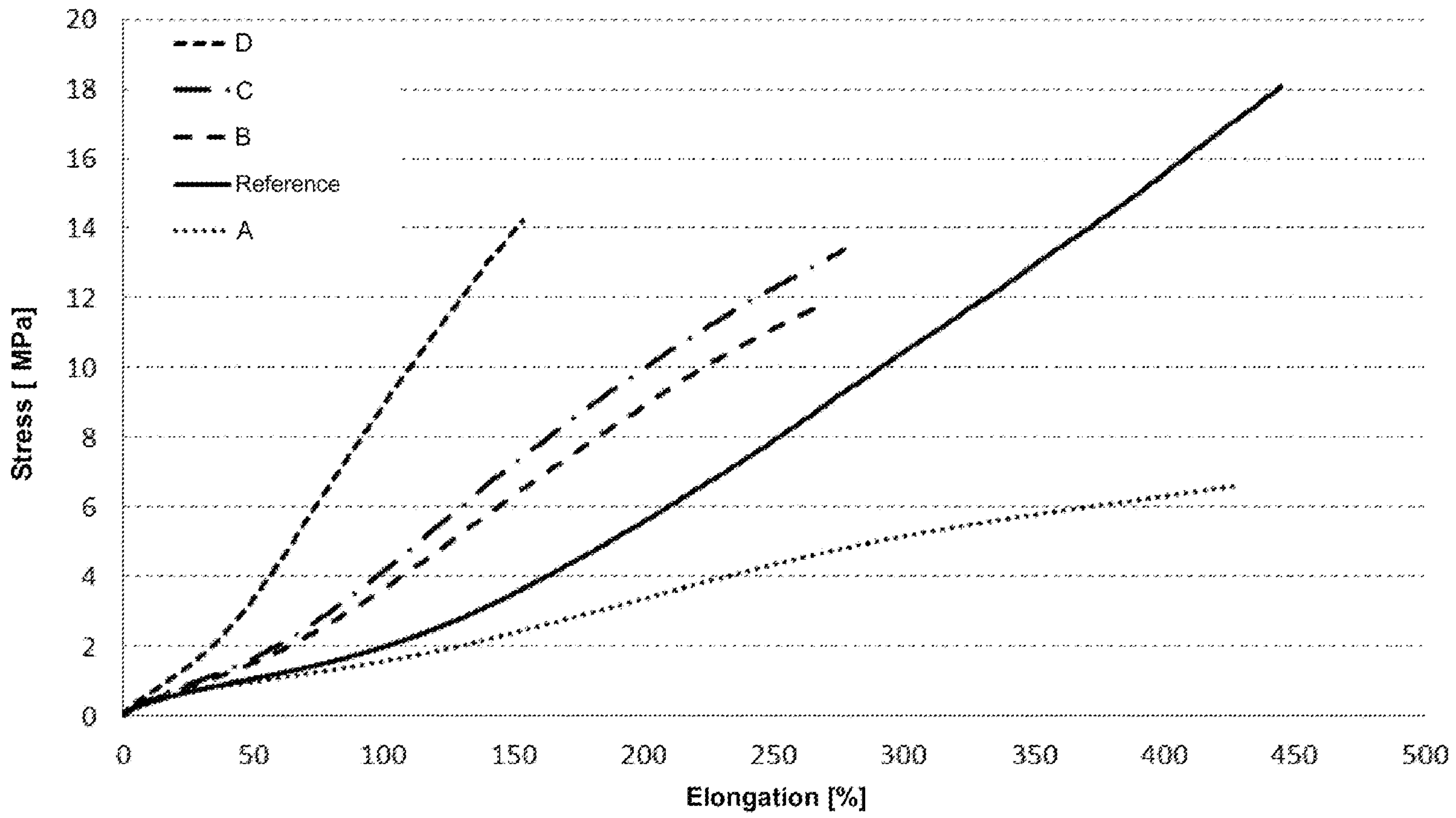
D
C
B
Reference
A
Stress [MPa]
20
18
16
14
12
10
8
6
4
2
0
0
50
100
150
200
250
300
350
400
450
500
Elongation [%]

Figure 1

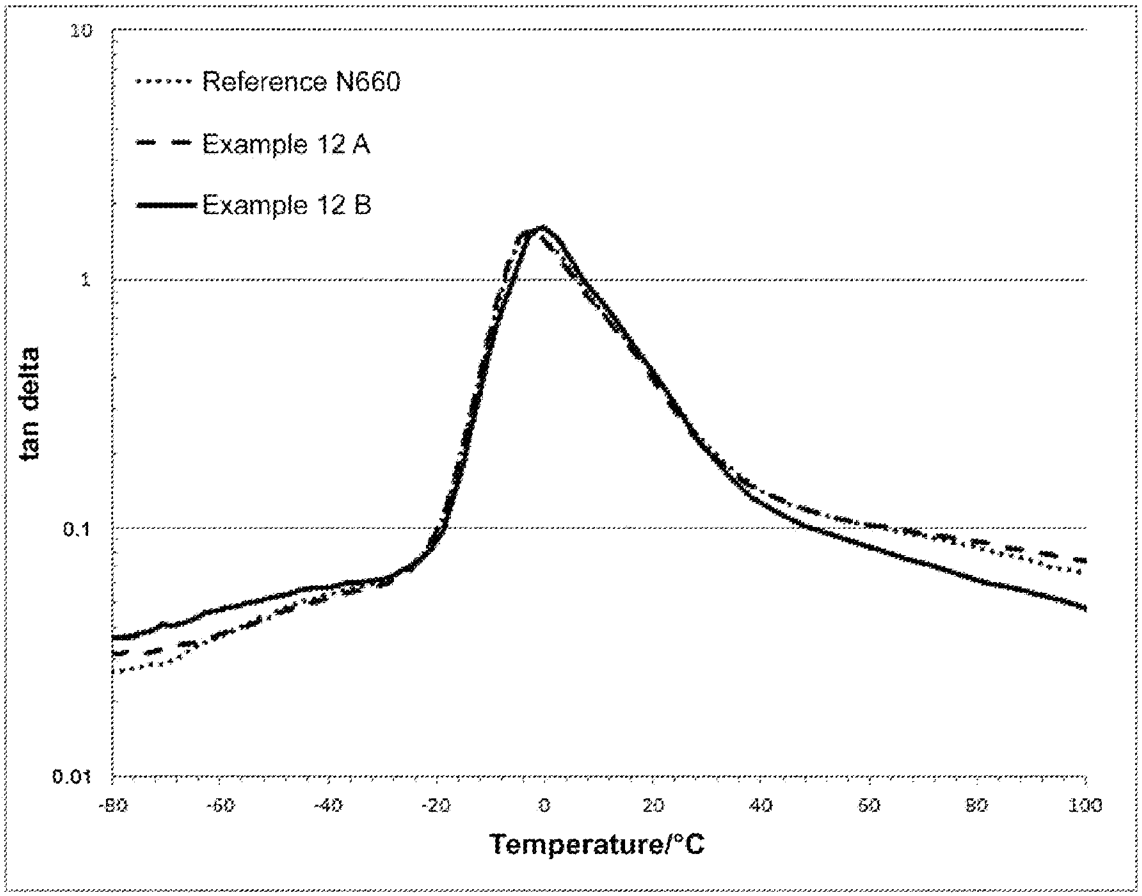10
1
0.1
0.01
tan delta
Reference N660
Example 12 A
Example 12 B
-80
-60
-40
-20
0
20
40
60
80
100
Temperature/°C

Figure 2

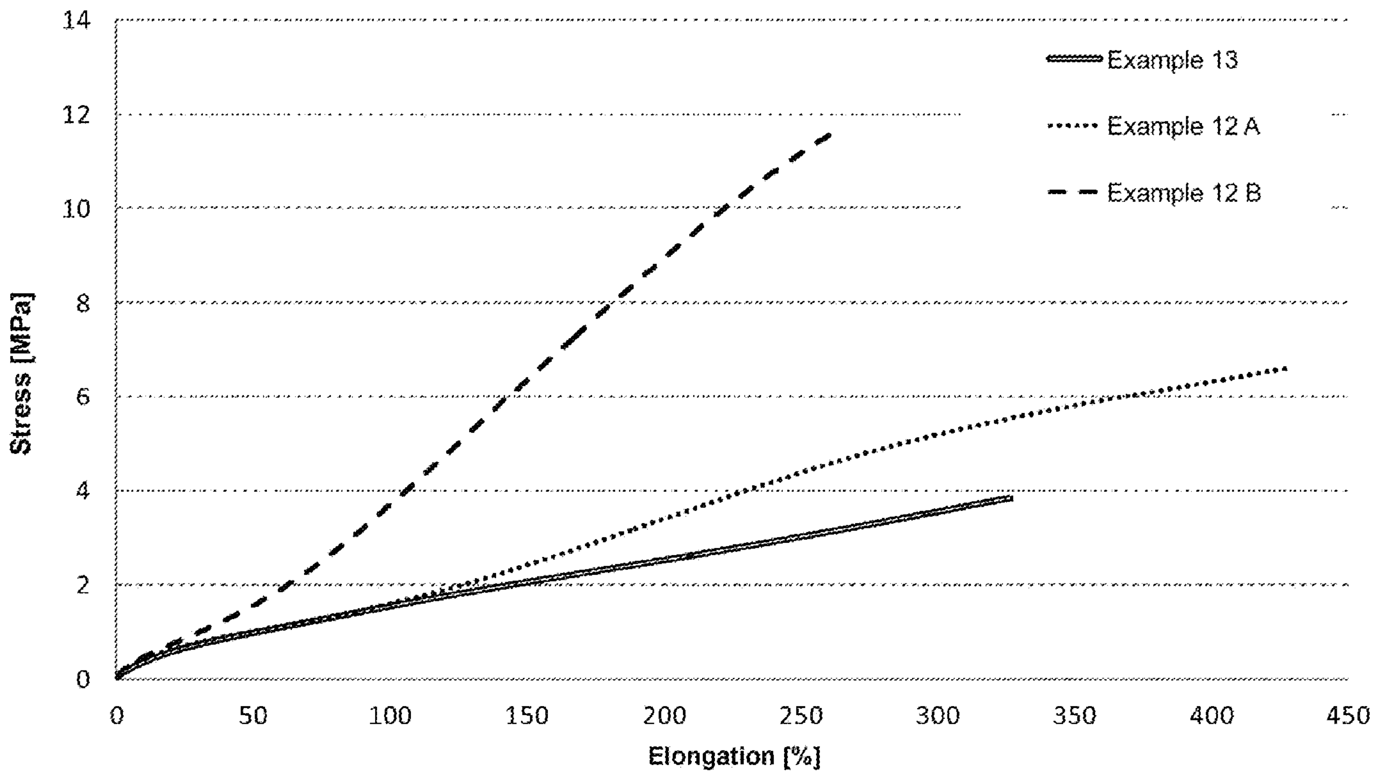
14
12
10
8
6
4
2
0
Stress [MPa]
0
50
100
150
200
250
300
350
400
450
Elongation [%]
Example 13
Example 12 A
Example 12 B

Figure 3

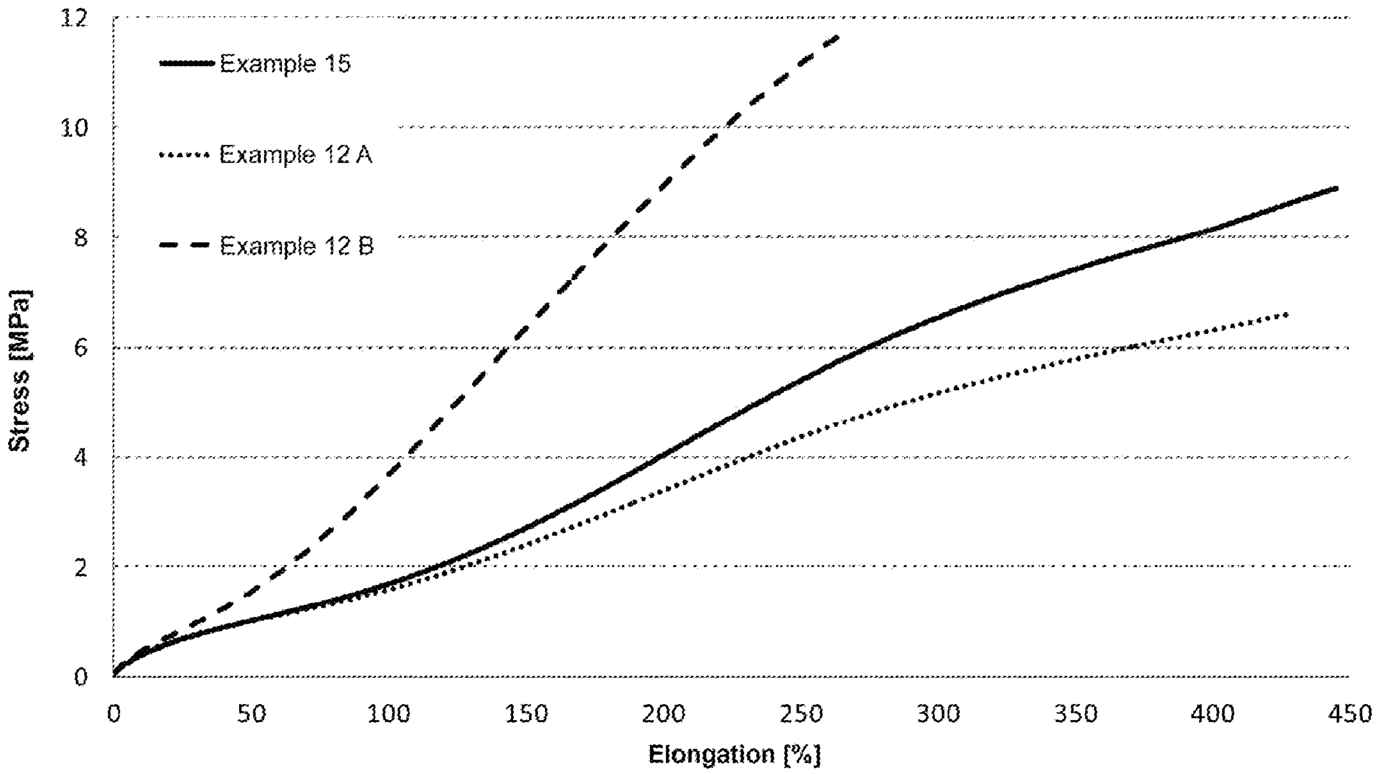
Example 15
Example 12 A
Example 12 B
Stress [MPa]
0
2
4
6
8
10
12
Elongation [%]
0
50
100
150
200
250
300
350
400
450

Figure 4

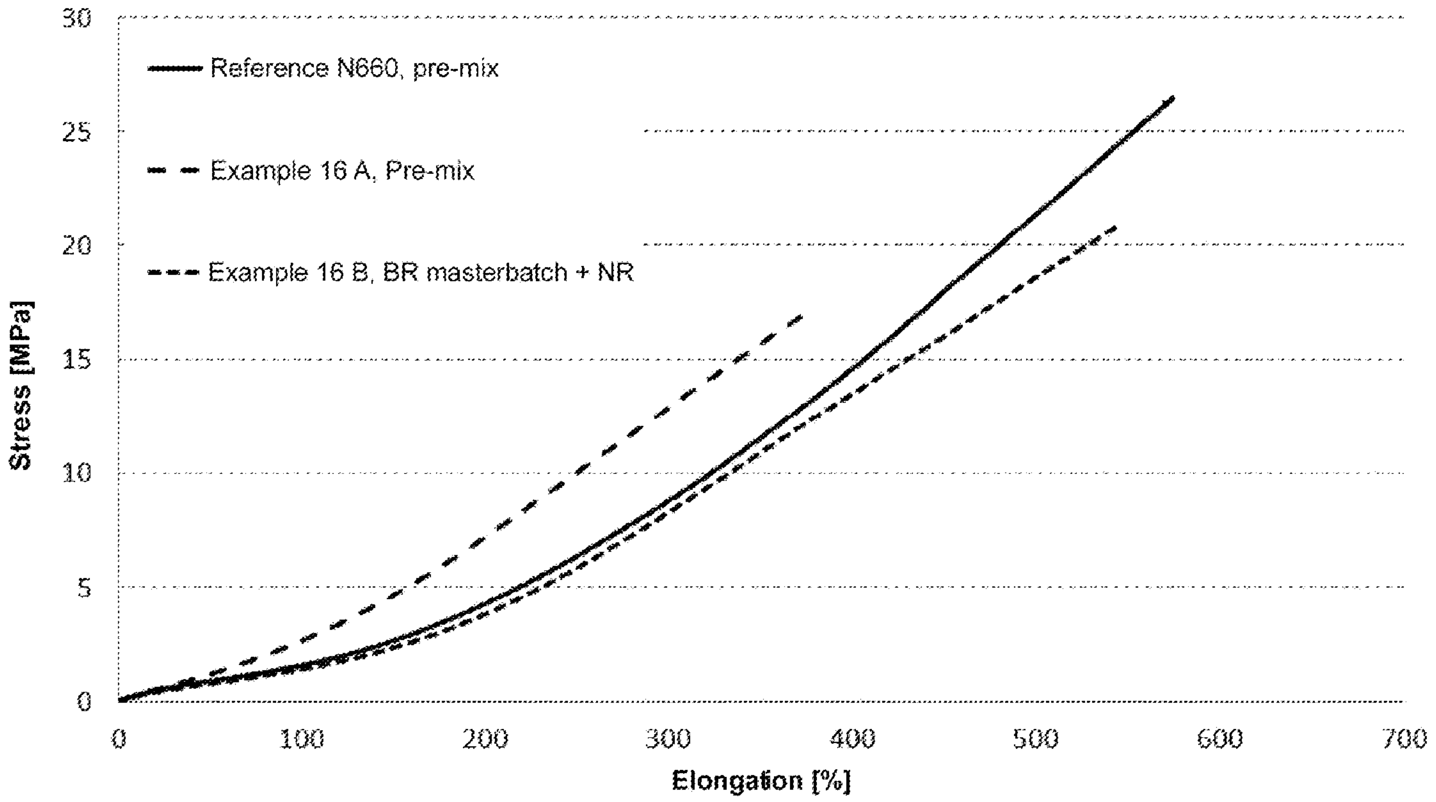
30
25
20
15
10
5
0
Stress [MPa]
0
100
200
300
400
500
600
700
Elongation [%]
Reference N660, pre-mix
Example 16 A, Pre-mix
Example 16 B, BR masterbatch + NR

Figure 5

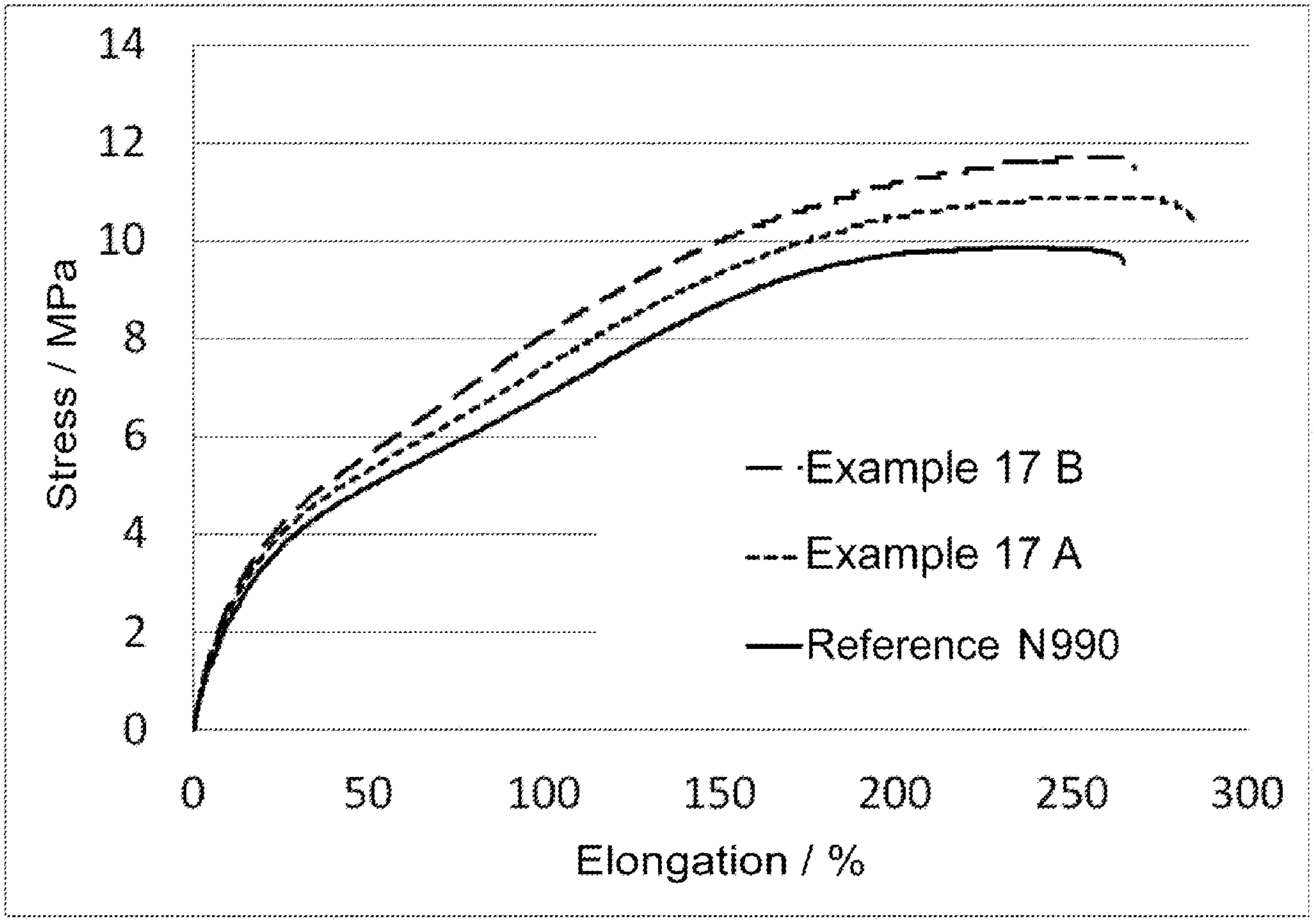
14
12
10
8
6
4
2
0
Stress / MPa
0
50
100
150
200
250
300
Elongation / %
Example 17 B
Example 17 A
Reference N990

Figure 6