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MENETELMÄ HIILIPITOISEN PIENHIUKKASMATERIAALIN TUOTTAMISEKSI UUSIUTUVISTA RAAKAMATERIAALEISTA

METHOD FOR PRODUCING PARTICULATE CARBONACEOUS MATERIAL FROM RENEWABLE RAW MATERIALS

METHOD FOR PRODUCING PARTICULATE CARBONACEOUS MATERIAL FROM RENEWABLE RAW MATERIALS

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

Description

There are many uses for particulate carbon material. One application is the use as a filler for polymers such as elastomers, thermoplastics or duroplastics. In the production of rubber items from elastomers, fillers are used in order to influence the technical rubber properties of the cross-linked rubber items, measured as, e.g., tensile strength, hardness, rigidity or tear strength. In addition, the product properties, such as rolling resistance, abrasion and wet skid resistance, of vehicle tyres are adjusted in this way. The influencing of a filler on technical rubber properties 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, producing significant amounts of carbon dioxide depending on the quality of the carbon black. Precipitated silica is produced from water glass, whereby large quantities of carbon dioxide are also produced during water glass production.

In the course of the scarcity of fossil carbon resources (compare petroleum and coal-derived oils as carbon black raw material), the saving of chemicals (see sulfuric acid in silica precipitation), but above all in the course of the avoidance of 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. In the case of renewable raw materials, all carbon comes from atmospheric carbon dioxide. With 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, for example, as a filler is described below, which 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 (e.g., through vulcanisation) cross-linked rubber compound are influenced to varying degrees by the addition of the filler, usually together with other additives, before 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 industrial 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 carbon black or chimney carbon black.

The reinforcing effect of carbon black and/or silica correlates strongly with the primary particle size of the filler. The primary particle size is directly related to the specific surface. With this in mind, low surface carbon blacks are referred to as inactive carbon blacks, medium-surface carbon blacks as semi-active carbon blacks, and high-surface carbon blacks as active carbon blacks, whereby 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 surfaces < 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 as a guide variable is also made clear by the fact that the first digit of the ASTM carbon blacks reflects the particle size or surface. The differentiation is less pronounced with silica. Silica with a clear reinforcing effect typically have BET surfaces > 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 of the particulate material. The specific surface can be measured as an outer surface using *statistical thickness surface*, STSA for short, or as a total surface of 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 particles, the inner surface also includes the area present in the pores. A coarse-grained material that has a comparatively small outer (that is STSA) surface can nevertheless have a high overall (that is BET) surface (consisting of outer and inner surface) if it is highly porous.

Strictly speaking, only the STSA surface can be used to describe the fineness of a material via specific surface values. Conversely, the difference “BET surface minus STSA surface” is a measure of the porosity of finely divided materials, since it represents the surface 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 and the STSA surface are determined in accordance with the ASTM D 6556-14 standard. In the present invention, in contrast to this, 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 conventional carbon black. The most important method for determining the specific surface is the measurement of the 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 can be determined by evaluating the adsorption isotherm using the BET method with a nitrogen partial pressure of 0.1 to 0.3. For routine determinations, single-point measurements are sufficient.

Determining the surface by means of N_2 adsorption results in a larger surface 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): 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 the so-called t-plot evaluation method according to de Boer, later modified by Magee. Here it is assumed that the adsorption takes place locally differently in different stack heights and then has a statistical thickness. The STSA surface is also given in m^2/g and is a measure of the “outer” surface of a carbon black particle, but above all it is a measure of the rubber-active surface.

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

Carbon black and silica are made up of primary particles. These geometric units, which do not exist in isolation but are recognisable in pictorial representations, have grown together into aggregates, with the growing together taking place through strong chemical bonds. Aggregates can also be combined to form agglomerates, with the connection of several aggregates to form agglomerates taking place via weak forces. Agglomerates can be destroyed by dispersing. The degree of aggregate formation is described outdated 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. A high DBP or oil absorption value indicates a material with highly branched aggregates. In the case of carbon black in particular, the so-called 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 compound 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 as negative elsewhere. Tensile strength (ASTM D 412, DIN 53504), tear strength (DIN 53455) and the stress values at 50%, 100%, 200% and 300% elongation (DIN 53504), referred to in the following as modulus 50%, modulus 100%, modulus 200% and modulus 300% respectively, are primarily used as technical rubber parameters. The hardness (ASTM D 2240), for example, can also play a role. For these quantities, high but not too high values 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 tire, the tan delta at

0 °C is used to assess a wet grip of a tire. 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 (t*emperature sweep*). In the case described here, the dynamic mechanical analysis (DMA) is carried out with prism-shaped fittings measuring 2x10x35 mm for the temperature variation on an Eplexor 150N Dynamic Mechanical Thermal Spectrometer.

Untreated silica is a filler with polar functional groups that can interfere with cross-linking in sulfur cross-linked systems. The interference with sulfur cross-linking can be based, for example, on the adsorption of vulcanisation aids on 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 undesired re-agglomeration of the already dispersed filler particles (so-called 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 its function as a reinforcing filler, i.e., the surface chemistry of the silica is adapted to the surface chemistry of the polymer by this activation or masking. Compare to: Fritz Röthemeier, Franz Sommer, 3rd Edition, Carl Hanser Verlag Munich 2013 on page 301-302.

In order 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)tetrasulfide 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 particle size or particle 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 particles of a certain geometric size relative to the total amount of particles is stated. The specification is usually in µm. The grain size records the size of the present separated particle under the specific conditions. It depends on the dispersing medium and the quality of the dispersion. The grain size does not differentiate between particles as a result of macroscopic caking, for example due to foreign substances, particles as a result of microscopic agglomeration with insufficient dispersing effort, or particles in the form of isolated aggregates or primary particles. It indicates the expansion 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 expansions 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 extension, is also often used. 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 conventional carbon black. In contrast, one speaks of biogenic carbon black when the carbon black was produced from renewable raw materials.

Raw materials of fossil origin are above 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 constant isotope exchange.

Renewable raw materials, on the other hand, are all products that are derived from the direct use of plants or animals. If you think 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 from it. 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 recovery 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 constant isotope 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 sulfonate. 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. The lignin sulfonate is actually already a chemical derivative of lignin, as it has additional sulfonate 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 far 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 conventional 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 subject 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 by refining 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. In most cases, the parallel goal is to provide a filler made from renewable raw materials that can at least partially replace conventional carbon blacks. There are also development efforts aimed at using the renewable raw materials directly as fillers, if necessary after cleaning, fractionating or crushing them.

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 in the range of the conventional carbon blacks N220 and N375. The carbon black described here is produced in the conventional furnace process, in which 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 content of volatile components 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 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, exist that have a particle size of less than 250 nm. The carbon product is obtained from hydrothermal carbonisation of bio-material that has 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 strong incarbonation of the material given in the examples means that other elements, such as oxygen and hydrogen in particular, have to 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 lower surface groups have a negative effect on possible attachment mechanisms to the polymer.

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

For example, DE 10 2008 050 966 A1 describes a rubber compound that contains a lignin derivative, more specifically a lignin sulfonic acid derivative, up to alkali metal or alkaline earth metal salts of lignin sulfonic acid. The rubber compound produced using this lignin sulfonic acid derivative can also contain carbon black or silica. The application also claims a tire made from the aforementioned rubber compound. 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 silica/5 phr of carbon black. The term silica is used in this document for silica. An improvement in the technical rubber parameters is therefore only achieved in combination with the conventional fillers.

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

In the case of silica, it is generally known that fillers with polar functional groups, such as untreated silica, interfere with cross-linking in sulfur-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 to: Fritz Röthemeier, Franz Sommer, 3rd Edition, Carl Hanser Verlag Munich 2013 on page 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 sulfur. Silica and silicates are suitable as reinforcing light-colored fillers. By treating the silica with silanes, the mechanical properties and the processing properties are significantly improved (see Fritz Röthemeier, Franz Sommer: Kautschuktechnologie, 3rd Edition, Carl Hanser Verlag Munich 2013, page 112-113, Chapter 2.5.4.3 Füllstoffe).

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, with groups contained in the lignin reacting with functionalising agents, and these reagents can be anhydrides, esters and silanes. Furthermore, a rubber compound is disclosed, which contains functionalised lignin as a filler, possibly in a mixture with conventional 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 its use. The lignocellulose material used is treated at elevated temperature, preferably at a maximum of 120-320 °C, and partially oxidizing conditions, i.e., with the substoichiometric 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 ground state for dust firing.

Furthermore, a process for obtaining carbonised lignin with a defined particle 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 is separated from the liquid containing the carbonised lignin, subjecting the lignin-containing liquid to hydrothermal carbonisation at temperatures in the range of about 150 °C to about 280 °C, and adjusting the particle size distribution of the carbonized lignin by adjusting the H^+ ion concentration in the lignin-containing liquid before and/or during the hydrothermal carbonisation. It is thus known that adjusting the H^+ ion concentration of a liquid containing lignin can influence the distribution of the particle size of the product obtained, i.e., the size of the agglomerates. 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 compounds after cross-linking, shows comparable performance in terms of technical rubber parameters to a conventional carbon black with a similar BET/STSA surface. In addition, the object of the invention is to provide an efficient method with regard to the use of energy and auxiliary materials, by means of which the material according to the invention can be produced.

The object is achieved by a method for producing a particulate carbon material having the features of claim 1.

As mentioned above, the renewable raw material used is preferably lignin-containing biomass and here in particular lignin-containing biomass with 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 dissolved and then separated from the insoluble components of the woody biomass (e.g., KRAFT process) or the woody biomass is depolymerised in such a way that the lignin remains predominantly as a solid (e.g., hydrolysis process). Depending on the type 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 dehydrated. If the lignin is dissolved in a liquid containing the lignin, the lignin can usually be precipitated from this, for example using acids or gases with an acidic effect, 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 conventional 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, in particular preferably greater than 0.23 Bq/g carbon, but preferably 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 grew up to 0.42 Bq/g carbon during the time of the nuclear weapons tests and is now returning to about the original level. In 2009, 0.238 Bq/g carbon was measured. In order to differentiate the present carbon material from materials with an artificially enriched ^{14}C content, the ^{14}C content in the present carbon material is at most 0.45 Bq/g carbon.

The carbon content in relation to the ash-free dry substance of more than 60% by mass and less than 80% by mass, preferably more than 65% by mass and less than 75% by mass, further preferably more than 68% by mass and less than 74% by mass, furthermore 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 particulate carbon material, which can be used as a filler, from renewable raw materials such as wood flour, etc., which are used directly as a filler and 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-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 conventional carbon black that was produced using the usual carbon black production processes or the variants of *bio-based* carbon blacks, which 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 more than 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 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 over the hydrothermal carbonisation, which usually has BET surfaces of less than 2 m^2/g, whereby the STSA surfaces - 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 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 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, in particular preferably between 20 m^2/g and 70 m^2/g.

Advantageously, the BET surface of the present particulate carbon material differs from the STSA surface 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, most preferably < 0.005 cm^3/g. This distinguishes the present particulate carbon material from finely divided porous materials such as ground biogenic powdered activated carbon, which in addition to a BET surface of usually more than 500 m^2/g can also have an STSA surface of at most 10 m^2/g.

The advantage of the STSA surface, 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 particles 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.

Primary particles have advantageously grown together to form 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%, in particular 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/100g and 150 ml/100g 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/100g and 150 ml/100g, more preferably between 70 ml/100g and 130 ml/100g, more preferably between 75 ml/100g and 130 ml/100g, in particular preferably between 80 ml/100 g and 120 ml/100 g. The OAN absorption is determined according to the ASTM D2414-00 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 present particulate carbon material and, for example, polymers.

The present particulate carbon material 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 most preferably less than 2 mS/cm. The electrical conductivity (determined as the conductance 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 value of > 6, preferably > 7, more preferably > 8 in a 15% suspension in distilled water. The pH value 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 value of the present product is, for example, its good compatibility with the other components of the polymer mixture.

It is also advantageous if the present particulate carbon material 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 area ratio D/G, 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 conventional carbon black and in addition - due to its proportion of amorphous carbon and the elements bound to it - further 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%, in particular less than 15%, in particular less than 10% of the present particulate carbon material 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;
- Suspension in distilled water so that the dry matter content is 5%,
- Increasing the pH value of the distilled water to a value of around 9 by adding caustic soda,
- increasing the temperature of the pH-adjusted suspension of carbon material present and distilled water to about 80 °C,
- Stirring 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,
- Centrifugation of the suspension for 15 minutes at 9000 rpm,
- Separation of the liquid phase and drying of the remaining solid residue, and
- Weighing of the dried residue.

The base resistance in percent is determined by dividing the dry mass of the weighed residue by the dry mass 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 present particulate carbon material differs from lignin in that its resistance to bases is significantly increased. This has the advantage that the present particulate carbon material, 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 present 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, by 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 not through the thermal treatment were largely separated, but continue to be available for connection 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, even 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 particles present separately under the specific conditions) is less than 30 µm, preferably less than 20 µm, more preferably less than 15 µm, even 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, even 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 the present particulate carbon material when used in polymers, for example, does not cause any defects due to the maximum size of the separated particles present, which, for example, lead to premature tearing or breaking of the polymer or to lead to surface defects during extrusion.

The average sphere 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 particle measured over the Q3 distribution of grain size. The average sphere diameter is calculated using the following formulas:

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

substituting 2. and 3. into 1. yields the following relationship:

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

The particle 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 characterizes the fineness of the primary particles.

In a preferred embodiment, the present particulate carbon material has

- a ^{14}C content that corresponds to that of renewable raw materials, preferably greater than 0.20 Bq/g carbon, in particular preferably greater than 0.23 Bq/g carbon, but preferably 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;
- a STSA surface of at least 5 m^2/g and at most 200 m^2/g;
- an Oil Absorption Number (OAN) between 50ml/100g and 150ml/100g; 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 conventional carbon black. A form of the present particulate carbon material that is comparable to conventional carbon black is given, for example, by the fact that the particulate carbon material

- consists of less porous primary particles,
- of which several are grown together to form aggregates, and
- these are, in turn, 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 conventional carbon blacks. The shape can be determined, for example, by REM images.

The particulate carbon material that can be used as a 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 that corresponds to that of renewable raw materials, preferably greater than 0.20 Bq/g carbon, in particular preferably greater than 0.23 Bq/g carbon, but preferably 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;

- a STSA of at least 5 m^2/g and at most 200 m^2/g;
- an OAN of 50ml/100g – 150ml/100g;
- a surface chemistry comparable to silica; and
- a form that largely corresponds to the form of conventional carbon black.

By advantageously combining the properties of a conventional 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 conventional carbon black and enables this interaction potential is additionally supplemented via a mechanism similar to that of silica, for example by coupling reagents.

The particulate carbon material can be used, for example, as a filler or reinforcing filler. The present particulate carbon material can be used, for example, in rubber and rubber compounds 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 present particulate carbon material. 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 present particulate carbon material 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, polybutylene terephthalates, polyepoxides; cellulose products such as cellulose acetate or cellulose nitrate, vulcanised fibre, polylactic acid, polyhydroxyalkanoates, chitin, casein, gelatine; formaldehyde resins, such as melamine-formaldehyde resin, urea-formaldehyde resin, melamine-phenol resins, phenol-formaldehyde resins; silicone polymer, natural rubber, styrene-butadiene copolymers, polybutadiene, polyisoprene, isobutylene-isoprene copolymers, ethylene-propylene-diene copolymers, acrylonitrile-butadiene copolymers, chloroprene, fluororubber or acrylic rubber and mixtures thereof.

Another object of the disclosure are rubber compounds, which are characterised in that they contain at least one rubber and at least one present particulate carbon material.

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, in particular preferably 50% by mass to 80% by mass, based on the mass of the rubber.

The rubber compound preferably contains at least the particulate carbon material present and, in addition, naturally occurring mineral, silicate, calcareous or calcareous fillers.

The rubber compound preferably contains the present particulate carbon material and a coupling agent, preferably an organosilane. The organosilanes can be, for example, bis(trialkoxysilylalkyl) oligosulfide or polysulfide, for example bis(triethoxysilylpropyl) disulfide or bis(triethoxysilylpropyl) tetrasulfide, mercaptosilanes, aminosilanes, silanes with unsaturated hydrocarbon groups, for example vinyl silanes. Finally, silanes with large saturated hydrocarbon groups, for example dodecyltriethoxysilane, can also act as coupling agents, although 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, in particular preferably 6% by mass to 12% by mass, based on the mass of the particulate carbon material.

When using an organosilane together with an expression of the present particulate carbon material 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 that are comparable to those that are obtained when using a semi-active carbon black or a silica can be achieved together with an organosilane.

When using an organosilane together with the present particulate carbon material, selected rubber technical 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 compound contains the particulate carbon material present 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 polyethylene 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 sulfur bridges. However, they react with the surface of the present carbon material to consume the functional groups so that these affect the sulfur cross-linking less. Thus, the triethoxyalkylsilanes do not act like a coupling agent. In addition to avoiding disturbed sulfur 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, in the cross-linked state a performance comparable to that of the carbon black can be achieved with regard to selected technical rubber characteristics.

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

Preferred rubber characteristics are the modulus 50% and modulus 200% determined in a tensile test. High values for the modulus 50% and modulus 200% 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 tire 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, especially in particular 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 tire industry, with high values being preferred for tan delta 0 °C The tan delta increase is more preferably at least 10% compared to the carbon black reference.

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

This rubber compound 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, silicate, calcareous or calcareous fillers.

This rubber compound 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, silicate, calcareous 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 composite can be improved.

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

In addition to natural rubber (NR), synthetic rubbers are also suitable for the production of the present rubber compounds. Preferred synthetic rubbers are described, for example, by W. Hofmann, Kautschuktechnologie, 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 thereof.

The present rubber compounds may contain further rubber auxiliaries, such as reaction accelerators, ageing inhibitors, heat stabilisers, light stabilisers, ozone inhibitors, processing aids, plasticisers, tackifiers, blowing agents, dyes, pigments, waxes, extenders, organic acids, retarders, metal oxides as well as activators, such as diphenylguanidine, triethanolamine, polyethylene glycol, alkoxy-terminated polyethylene glycol or hexanetriol, which are known to the rubber industry.

Sulfur, organic sulfur donors or free-radical generators can serve as cross-linking agents. The present rubber compounds can also contain vulcanisation accelerators.

The blending of the rubbers with the particulate carbon material, optionally carbon blacks, optionally silicas, optionally rubber auxiliaries and optionally organosilanes, can be carried out in customary mixing units, such as roll mills, internal mixers and mixing extruders. Such rubber compounds are usually prepared in an internal mixer, with the rubbers, the particulate carbon material, any carbon blacks, any silica, any rubber auxiliaries and any organosilanes first being 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 compound 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 the so-called raw mixture for the subsequent process steps, such as shaping and vulcanisation.

The present rubber compounds 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 present rubber compounds are suitable for the production of rubber articles, i.e., articles made from the fully cross-linked or vulcanised elastomers, so-called moulded bodies, for example for the production of pneumatic tires, tire treads, tire sidewalls, cable jackets, hoses, drive belts, conveyor belts, roller coverings, tires, 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 present particulate carbon. 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.

The plastic mixture preferably contains the present particulate carbon material 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 residues, 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, in particular preferably 6% by mass to 12% by mass, based on the mass of the plastic.

Plastics can be, for example, polyethylene (PE), polypropylene (PP), polyvinyl acetate (PVA) or thermoplastic elastomers (TPE). The present plastics mixtures are preferably used for the production of cables, pipes, fibres, foils, in particular agricultural foils, technical plastics and injection moulded articles.

The present particulate carbon material is produced in a method according to the invention as claimed in claim 1, which in particular enables the STSA surface and the OAN value to be adjusted to the range specified above.

According to the invention, a multi-stage, in particular four-stage process for the hydrothermal treatment, in particular carbonisation, of renewable raw materials, in particular of renewable raw materials with a proportion of more than 80% Klason lignin, according to claim 1 is provided.

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 matching 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 present particulate carbon material. In particular, pH value 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 and the OAN value of the particulate carbon material obtained in the fourth step is 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 such a way that, if the STSA surface is increased as required

- 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 is also preferably adjusted 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.

Preferably, with a desired increase in the STSA surface, 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%, more preferably less than 20%, more preferably less than 30%, in particular preferably less than 40%, each based on the dry matter of the renewable raw material.

Preferably, the STSA surface and the OAN value of the particulate carbon material obtained in the fourth step is 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 adjusted in that at a desired lowering 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 value 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 is also preferably adjusted by lowering the temperature of the hydrothermal treatment and/or shortening the residence time in the hydrothermal treatment when the STSA surface is reduced as desired.

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 only during the hydrothermal treatment in the second step are brought about conditions which lead to the formation of the particulate carbon material with the corresponding STSA surface and OAN value. Only by carrying out the process in this way is it possible to bring about particle formation and a reaction at the same time, which in the end leads to a particulate carbon material that also differs from the renewable raw material used, for example, in terms of its carbon content or its resistance to bases.

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

the polymerisation of the renewable raw material is largely suppressed in the second step or is limited to such an extent that a particulate carbon with a corresponding STSA surface and OAN value is obtained, and beyond the particle size distribution, i.e., the size distribution of the agglomerates or of the particles present separated under certain conditions, direct influence can be exerted on the size of the primary particles, which is recorded 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 and the BET surface of the particulate carbon material.

Preference is given to recruitment and 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

one or more of the following metrics:

- 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 value of the liquid containing the renewable raw material before and after the second step;

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

Advantageously, the STSA surface and the OAN value of the particulate carbon material obtained in the fourth step are increased by adjusting

- the concentration of the organic dry matter of the renewable raw material in the liquid containing the renewable raw material preferably to a value between 5% by mass and 40% by mass, more preferably between 10% by mass and 20% by mass,
- the pH value of the liquid containing the renewable raw material at 20 °C to 25 °C preferably to a value ≥ 7, further preferably ≥ 8, in particular preferably ≥ 8.5, further 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, furthermore preferably between 10 and 50 mS/cm, furthermore preferably between 10 and 40 mS/cm, in particular 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 is preferably controlled 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 is preferably controlled to a duration between 1 minute and 6 hours, preferably between 30 minutes and 4 hours, more preferably between 1 hour and 3 hours,

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

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

- 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 adjusted 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 occurs.

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

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

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

- a slightly higher concentration of inorganic ions is required than initially results after adjusting the organic dry matter content of the renewable raw material in the liquid containing it and adjusting the pH value, and
- subsequently, the concentration of inorganic ions can be increased further by adding salts until 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 at 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 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 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 brought about during the hydrothermal treatment in the second step not only by the selected process conditions but additionally by an increase in the concentration of 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 is complete, no further solids, for example during the cooling phase at the end of the second step, or by increasing the concentration of the organic dry matter in the liquid containing the particulate carbon material, for example by evapouration in the third step is formed.

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 value 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 is 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, as a result of which
- the STSA surface 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/100g and 100 ml/100g.

The method of the present invention may 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, in particular preferably less than 10 µm.

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

The process works in the liquid phase, always working below the critical point of water.

The present invention will now be explained with reference to examples. 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 N 660
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 rubber-technical characteristic values of cross-linked rubber particles made of SBR, which are provided with the particulate carbon material according to the invention but without any further additive, with the particulate carbon material according to the invention and a reagent for masking the functional groups, and with the particulate carbon material according to the invention and a coupling reagent.
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 embodiment examples, the method according to the invention 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 with an adjusted content of organic dry matter (3) is prepared.

The lignin is then completely dissolved in the lignin-containing liquid. For this purpose, the pH value 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 given in Table 1,

Example	1		2		3	4	5	6		7	8		9
-	ml	Type	Type	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	Tap water in Ludwigsfelde	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	-	0.0	15.9
7	3854	Tap water in Ludwigsfelde	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	-	0.0	15.9
8	3854	Tap water in Ludwigsfelde	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	-	0.0	15.9
9	3854	Tap water in Ludwigsfelde	Lignin 3	1092	14.8	80	2	NaOH	54.00	9.6	-	0.0	15.9
10	3854	Tap water in Ludwigsfelde	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 change depending on the process conditions mentioned above. With a suitable setting 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 from the solution separates. 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 method conditions of the third step are summarised in Table 4.

Example	18	19		
-	Type	Type	Washing liquid	Amount of washing liquid kg/kg dry particulate carbon material
1	Centrifuge; 6000 rpm / 15 min	Resuspension / centrifuge; 6000 rpm / 15mm	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	Tap water in Ludwigsfelde	2
7	Centrifuge; 9000 rpm / 15 min	Resuspension / centrifuge; 9000 rpm / 15 min	Tap water in Ludwigsfelde	2
8	Centrifuge; 9000 rpm / 15 min	Resuspension / centrifuge; 9000 rpm / 15 min	Tap water in Ludwigsfelde	2

9	Centrifuge 9000 rpm / 15 min	Resuspension / centrifuge; 9000 rpm / 15 min	Tap water in Ludwigsfelde	2
10	Centrifuge; 9000 rpm / 15 min	Resuspension / centrifuge; 9000 rpm / 15 min	Tap water in Ludwigsfelde	2
11	Centrifuge; 9000 rpm / 15 min	Resuspension / centrifuge; 9000 rpm / 15 min	Distilled water	2

Table 4

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

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 sphere diameter)[6]	D50 / average sphere diameter	BET	Water content
	% by mass, dry,	% by mass, dry,	% by mass, dry	m²/g	ml/100g	-	%	-	µm	µm	µm	µm	-	m²/g	%

	ash-free	ash-free													
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 the grain size determination using laser diffraction

5 = calculated from STSA and particle density, n.d. not determined

Table 6

<u>Examples 12 A-D and reference example for the production of rubber articles from SBR with the particulate carbon material from Examples 1 and 2 and with carbon black N 660</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	-	-	3.2	3.2	4.8	phr

Quantity						
ZnO	3	3	3	3	3	phr
Stearic acids	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
Sulfur	1.5	1.5	1.5	1.5	1.5	phr

Phr: parts per hundred rubber Amount related to the amount of elastomer

DPG, CBS vulcanisation accelerator

Si69: coupling reagent

Table 7

Solution SBR (sSBR) Buna VSL4526-0 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 sulfur were from Fischer Scientific. 2-N-cyclohexyl benzothiazole sulfenamide (CBS) was from Lanxess. 1,3-Diphenylguanidine (DPG) was used by Sigma-Aldrich Co. LLC, USA. 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 Aber Gmbh & Co. KG, Karlsruhe. Bis(triethoxysilylpropyl)tetrasulfide, 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 addition of the silane Si69, if necessary, the temperature in the internal mixer was kept in a range between 140-165°C for 10 min 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 composites Reference and A (Table 7) are cross-linked using a vulcanisation process common to carbon black application. Rubber composites 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 B.V., Vlaardingen Netherlands) at 160 °C and a press force of 150 kN. The optimum vulcanisation time t_{90} was determined using a rubber process analyzer (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 strain 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 rubber properties of the rubber articles obtained from examples A - D of Table 7 are shown in the diagram in Figure 1.

In particular in the case of examples B, C and D (in which a coupling agent is added), these show comparable properties to the filler N660. The values for the modulus 50%, modulus 100% and modulus 200% of examples B and C are at least as high as for the reference. Furthermore, it is shown that increasing the filling ratio from 40 phr (B) to 60 phr (D) of the particulate carbon material according to example 2 leads to an increase in the stress values, i.e., the modulus 50% and the modulus 100%, when stretched in the lower range (up to 100%). In addition, it is clear that increasing the STSA surface and 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 higher values of the modulus 50%, modulus 100% and modulus 200% (compare B and C). Furthermore, it is clear that the particulate carbon material from Example 2 with its STSA surface of 12.6 m^2/g shows a comparable stress-strain curve in the tensile test as the conventional carbon black N660, which has an STSA surface 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 coupling agent (Example 12 A) show similar glass transition temperatures ($T_{g,SBR}$ = -2.91 °C; see peak of the curve 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, although the curve of 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 12B) 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 strain (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 N 660, which means that a comparatively reduced rolling friction can be expected for a tire 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 of Example 12 B at 0 °C is higher than the reference, suggesting improved wet grip of a tire made from the composite of Example 12B.

Comparative example 13 for the production of rubber articles from SBR with untreated lignin

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 composite.

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, but instead of the particulate carbon material from Example 2, untreated lignin 3 is now used. The rubber composite 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 is particularly clearly behind the effect of the carbon material according to the invention in combination with silane Si69 (Example 12 B) remains.

Example 14 for Determining the ^{14}C Content of the Product from Example 2

The material from Example 2 for the determination of the ^{14}C content was sent to the

Poznań Radiocarbon Laboratory, Foundation of the A. Mickiewicz University, ul. Rubież 46, 61-612 Poznań. 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 deionized water (Millipore) until 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 few times, generally until no further colouration of the NaOH solution occurs (the colouration of the solution is caused by humic acids dissolved in NaOH), but the NaOH treatment is stopped if there is a risk of 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., samples that do not contain ^{14}C (coal or IAEA C1 Carrara marble) and samples of the “International Modern ^{14}C standard” (oxalic acid II).

c) The measurements described here are 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 ion beams of ^{14}C, ^{13}C und ^{12}C measured for each sample and standard (modern standard: “Oxalic acid II” and Standard for ^{14}C-free carbon “Background”). In each AMS run, 30-33 samples of unknown age are 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 δ^{13} values depend on isotope fractionation during CO_2 reduction and isotope fractionation within the AMS spectrometer, and as such cannot be compared to $\delta\ ^{13}C$ values determined with conventional mass spectrometers 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 described in Bronk Ramsey C., 2009, Radiocarbon, 51, 337-360 and Bronk Ramsey C. and Lee S., 2013, Radiocarbon, 55, 720-730. The calibration is performed with respect the latest version of the ^{14}C calibration curve, i.e., INTCAL13 (Reimer P. J., 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), but the silane Si69 is replaced by triethoxymethylsilane in an equimolar amount, which corresponds to the 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 sulfur 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 externally by methyl groups, 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 Si69 coupling silane.

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 or 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 mixed with the respective filler and other components is transferred. In contrast to this, in B, also in the internal mixer (starting temperature 35 °C, speed 60 min^{-1}), a master batch 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 compound in the cross-linked 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 or N 990

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 acids	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
Sulfur	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, optionally N990 and Mesamoll II additionally for a further 4 minutes, antioxidants for a further 3 minutes and the vulcanisation chemicals for a further 2 minutes. The optimum vulcanisation time was determined using a rubber process analyzer 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 oil Lubrizol OS 206304 according to DIN ISO 1817:2008-08].

The values shown in Table 10 were determined.

Example	Reference	A	B
Shore A hardness	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 N 990 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 N 990, 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 72h/70 °C	Reference	A	B
At weight%	-2.6	-2.6	-2.7
At volume%	-3.4	-3.3	-3.3
At hardness	+3	+3	+3
In the tensile strength %	+6	+12	+11
In the elongation at break %	-9	-6	-10

Table 11

MENETELMÄ HIILIPITOISEN PIENHIUKKASMATERIAALIN TUOTTAMISEKSI UUSIUTUVISTA RAAKAMATERIAALEISTA

PATENTTIVAATIMUKSET

1. Monivaiheinen menetelmä uusiutuvien raakamateriaalien hydrotermaaliseksi käsittelemiseksi, jossa

– ensimmäisessä vaiheessa tarjotaan käyttöön uusiutuvaa raakamateriaalia sisältävää nestettä,

– joka toisessa vaiheessa altistetaan hydrotermaaliselle käsittelylle lämpötilassa, joka on välillä 150 °C ja 250 °C,

– kolmannessa vaiheessa kiintoaines, jota on jäljellä toisen vaiheen mukaisen hydrotermaalisen käsittelyn jälkeen, erotetaan nesteestä, ja

– kiintoaineksen jäännöskosteus poistetaan suurimmaksi osaksi kuivaamalla neljännessä vaiheessa saaden pienhiukkashiilimateriaalia,

tunnettu siitä, että neljännessä vaiheessa saadun pienhiukkashiilimateriaalin STSA-pinta-alaa ja OAN-arvoa ohjataan sovittamalla keskenään

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– uusiutuvaa raakamateriaalia sisältävän nesteen pH-arvo,

– epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– hydrotermaalisen käsittelyn lämpötila, ja

– viipymäaika hydrotermaalisessa käsittelyssä,

siten, että STSA-pinta-alaksi säädetään ainakin 5 m^2/g ja enintään 200 m^2/g, ja OAN-arvoksi säädetään ainakin 50 ml/100 g ja enintään 150 ml/100 g,

ja jossa pienhiukkashiilimateriaalin vesipitoisuus on alle 5 painoprosenttia.

2. Patenttivaatimuksen 1 mukainen menetelmä, **tunnettu** siitä, että epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä määritetään mittaamalla uusiutuvaa raakamateriaalia sisältävän nesteen sähkönjohtavuus.

3. Patenttivaatimuksen 1 tai 2 mukainen menetelmä, **tunnettu** siitä, että neljännessä vaiheessa saadun pienhiukkashiilimateriaalin STSA-pinta-alaa ja OAN-arvoa ohjataan sovittamalla keskenään

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– uusiutuvaa raakamateriaalia sisältävän nesteen pH-arvo,

– epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– hydrotermaalisen käsittelyn lämpötila, ja

– viipymäaika hydrotermaalisessa käsittelyssä,

ja haluttu STSA-pinta-ala säädetään siten, että jos STSA-pinta-alaa on tarkoitus suurentaa,

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatiota alennetaan uusiutuvaa raakamateriaalia sisältävässä nesteessä, ja/tai

– uusiutuvaa raakamateriaalia sisältävän nesteen pH-arvoa kohotetaan, ja/tai

– epäorgaanisten ionien konsentraatiota alennetaan uusiutuvaa raakamateriaalia sisältävässä nesteessä.

4. Patenttivaatimuksen 1 tai 2 mukainen menetelmä, **tunnettu** siitä, että neljännessä vaiheessa saadun pienhiukkashiilimateriaalin STSA-pinta-alaa ja OAN-arvoa ohjataan sovittamalla keskenään

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– uusiutuvaa raakamateriaalia sisältävän nesteen pH-arvo,

– epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– hydrotermaalisen käsittelyn lämpötila, ja

– viipymäaika hydrotermaalisessa käsittelyssä,

ja haluttu STSA-pinta-ala säädetään siten, että jos STSA-pinta-alaa on tarkoitus pienentää,

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatiota kohotetaan uusiutuvaa raakamateriaalia sisältävässä nesteessä, ja/tai

– uusiutuvaa raakamateriaalia sisältävän nesteen pH-arvoa alennetaan, ja/tai

– epäorgaanisten ionien konsentraatiota kohotetaan uusiutuvaa raakamateriaalia sisältävässä nesteessä.

5. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että lämpötila ja viipymäaika säädetään toisessa vaiheessa niin, että STSA-pinta-alan, joka on välillä 5 m^2/g ja 200 m^2/g, ja OAN-arvon, joka on välillä 50 ml/100 g ja 150 ml/100 g, saamiseksi

– tarvitaan korkeampi epäorgaanisten ionien konsentraatio kuin mitä alun perin saadaan uusiutuvan raakamateriaalin orgaanista kuiva-ainepitoisuutta säätämällä sitä sisältävässä nesteessä ja pH-arvoa säätämällä, ja

– sen jälkeen suoritetaan epäorgaanisten ionien konsentraation lisäkorotus lisäämällä suoloja, kunnes saavutetaan sähkönjohtavuuden avulla mitattu epäorgaanisten ionien konsentraatio, joka on sopiva toisen vaiheen menetelmäolosuhteille.

6. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraation säätäminen uusiutuvaa raakamateriaalia sisältävässä nesteessä, uusiutuvaa raakamateriaalia sisältävän nesteen pH:n säätäminen ja/tai epäorgaanisten ionien konsentraation säätäminen uusiutuvaa raakamateriaalia sisältävässä nesteessä suoritetaan ensimmäisessä vaiheessa.

7. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraation säätäminen uusiutuvaa raakamateriaalia sisältävässä nesteessä, uusiutuvaa raakamateriaalia sisältävän nesteen pH:n säätäminen ja/tai epäorgaanisten ionien konsentraation säätäminen uusiutuvaa raakamateriaalia sisältävässä nesteessä suoritetaan ensimmäisessä vaiheessa ja toisessa vaiheessa.

8. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraation säätäminen uusiutuvaa raakamateriaalia sisältävässä nesteessä, uusiutuvaa raakamateriaalia sisältävän nesteen pH:n säätäminen ja/tai epäorgaanisten ionien konsentraation säätäminen uusiutuvaa raakamateriaalia sisältävässä nesteessä suoritetaan toisessa vaiheessa.

9. Patenttivaatimuksen 7 tai 8 mukainen menetelmä, **tunnettu** siitä, että uusiutuva raakamateriaali liuotetaan ensimmäisessä vaiheessa täydellisesti uusiutuvaa raakamateriaalia sisältävään

nesteeseen, ja haluttujen pienhiukkasten muodostumista hydrotermaalisen käsittelyn aikana toisessa vaiheessa ei saada aikaan vain valituilla menetelmäolosuhteilla vaan myös kohottamalla uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatiota uusiutuvaa raakamateriaalia sisältävässä nesteessä, alentamalla uusiutuvaa raakamateriaalia sisältävän nesteen pH:ta tai kohottamalla epäorgaanisten ionien konsentraatiota uusiutuvaa raakamateriaalia sisältävässä nesteessä.

10. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että haluttujen pienhiukkasten muodostumisen päätyttyä toisessa vaiheessa, saadaan aikaan orgaanisen kuiva-aineen konsentraation aleneminen pienhiukkashiilimateriaalia sisältävässä nesteessä, pienhiukkashiilimateriaalia sisältävän nesteen pH:n kohoaminen tai epäorgaanisten ionien konsentraation aleneminen pienhiukkashiilimateriaalia sisältävässä nesteessä.

11. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että neljännessä vaiheessa saadun pienhiukkashiilimateriaalin STSA-pinta-alaa ja OAN-arvoa säädetään ohjaamalla

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä edullisesti arvoon, joka on välillä 5 painoprosenttia ja 40 painoprosenttia,

– uusiutuvaa raakamateriaalia sisältävän nesteen pH 20 °C:ssa - 25 °C:ssa edullisesti arvoon, joka on ≥ 7, edullisemmin ≥ 8,

– epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä arvoon, joka on välillä 10 mS/cm ja 200 mS/cm,

– hydrotermaalisen käsittelyn lämpötila edullisesti maksimiarvoon, joka on välillä 150 °C ja 250 °C, ja/tai

– viipymäajan kesto hydrotermaalisessa käsittelyssä välille, joka on 1 minuutti ja 6 tuntia.

12. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että

– orgaanisen kuiva-aineen konsentraatio ligniiniä sisältävässä nesteessä ensimmäisessä vaiheessa on välillä 10 painoprosenttia ja 20 painoprosenttia,

– ligniiniä sisältävän nesteen pH ensimmäisessä vaiheessa on yli 8,5 ja alle 10,5,

– epäorgaanisten ionien konsentraatio ligniiniä sisältävässä nesteessä ensimmäisessä vaiheessa on sellainen, että sähkönjohtavuus on välillä 10 mS/cm ja 25 mS/cm,

– hydrotermaalisen käsittelyn maksimilämpötila toisessa vaiheessa on välillä 210 °C ja 240 °C, ja

– ligniiniä sisältävän nesteen viipymäaika hydrotermaalisessa käsittelyssä toisessa vaiheessa on välillä 120 ja 240 minuuttia, jolloin

– näin tuotetun pienhiukkashiilimateriaalin STSA-pinta-alan, joka mitataan kolmannen vaiheen dehydraation ja neljännen vaiheen kuivaamisen jälkeen, arvo on välillä 5 m^2/g ja 50 m^2/g, ja OAN-arvo on välillä 50 ml/100 g ja 100 ml/100 g.

13. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että uusiutuva raakamateriaali liuotetaan täydellisesti ensimmäisessä vaiheessa uusiutuvaa raakamateriaalia sisältävään nesteeseen.

14. Jonkin patenttivaatimuksen 1 - 12 mukainen menetelmä, **tunnettu** siitä, että uusiutuvaa raakamateriaalia ei liuoteta täydellisesti ensimmäisessä vaiheessa uusiutuvaa raakamateriaalia sisältävään nesteeseen, mutta jossa

– uusiutuvan raakamateriaalin orgaanisen kuiva-aineen konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä,

– uusiutuvaa raakamateriaalia sisältävän nesteen pH-arvo, ja

– epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä

säädetään siten, että toisen vaiheen hydrotermaalisen käsittelyn aikana tapahtuvan lämpötilan nousun johdosta uusiutuva raakamateriaali liukenee aluksi täydellisesti ennen kuin kolmannessa vaiheessa erotettava kiintoaines muodostuu toisessa vaiheessa.

15. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että menetelmä suoritetaan jatkuvatoimisesti, jossa toisen vaiheen hydrotermaalisen käsittelyn menetelmäolosuhteet pidetään vakioina ja uusiutuvaa materiaalia sisältävän nesteen pH:ta ja sähkönjohtavuutta säädellään jatkuvatoimisesti ensimmäisessä vaiheessa.

16. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että neljännessä vaiheessa saadun pienhiukkashiilimateriaalin STSA-pinta-alaa ja OAN-arvoa ohjataan säätämällä epäorgaanisten ionien konsentraatio uusiutuvaa raakamateriaalia sisältävässä nesteessä arvoon, joka on välillä 10 mS/cm ja 50 mS/cm (määritettynä PCE-PHD1:n mittausanturilla 20 °C:ssa - 25 °C:ssa) niin, että STSA-pinta-ala säädetään välille 5 m^2/g ja 200 m^2/g, ja OAN-arvo välille 50 ml/100 g ja 150 ml/100 g.

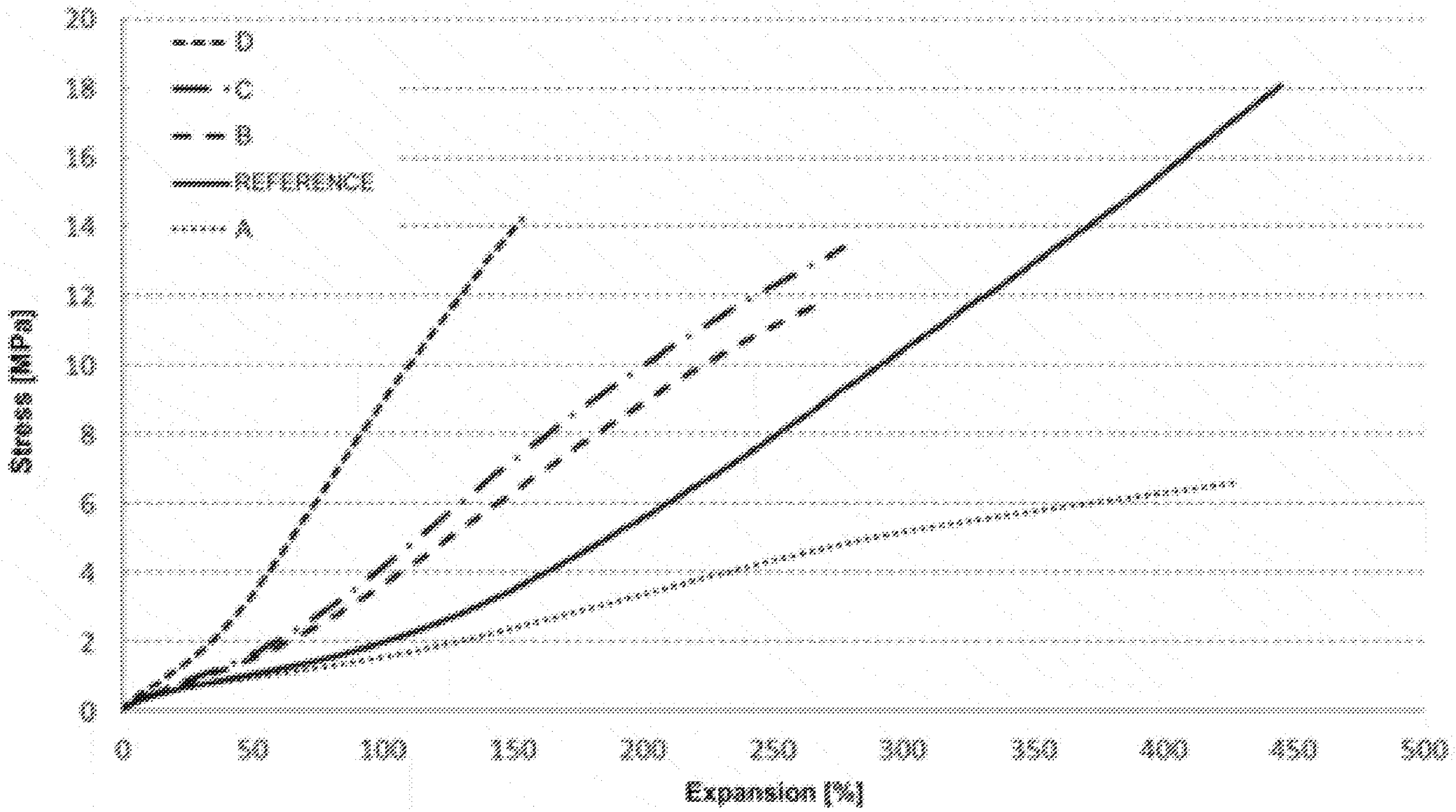

D
C
B
REFERENCE
A
Stress [MPa]
0
2
4
6
8
10
12
14
16
18
20
0
50
100
150
200
250
300
350
400
450
500
Expansion [%]

FIGURE 1

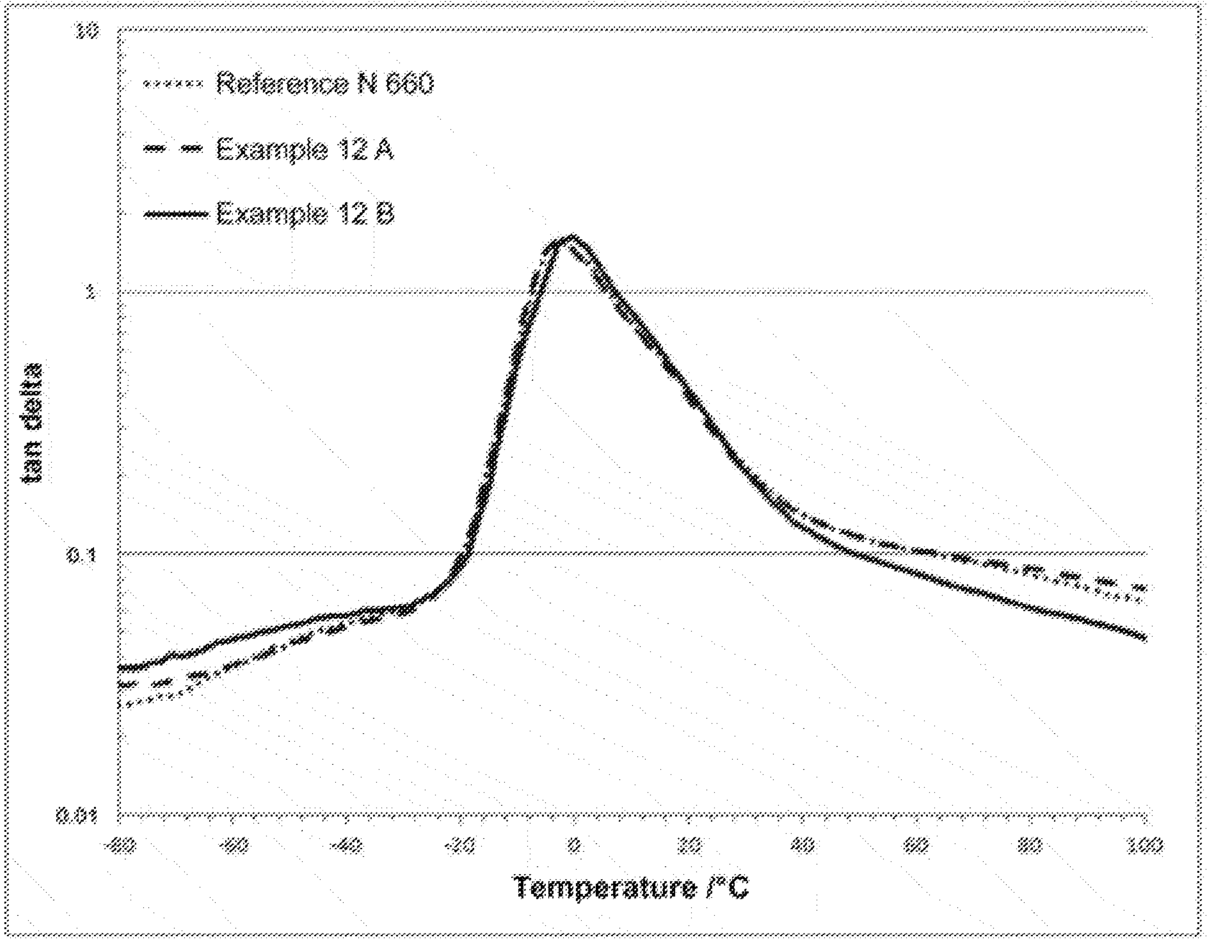
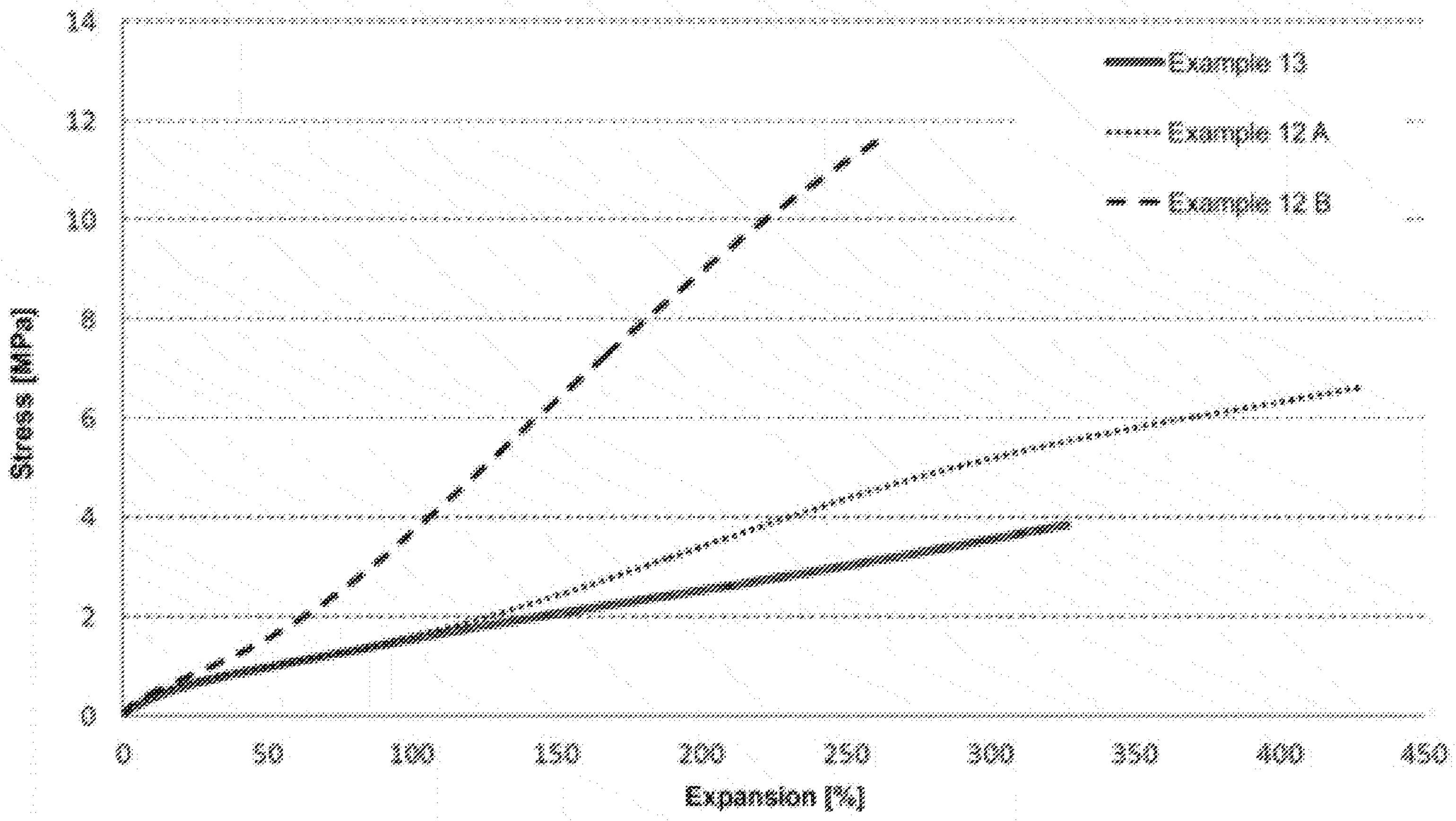

10
1
0.1
0.01
tan delta
Reference N 660
Example 12 A
Example 12 B
-80
-60
-40
-20
0
20
40
60
80
100
Temperature /°C

FIGURE 2



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

FIGURE 3

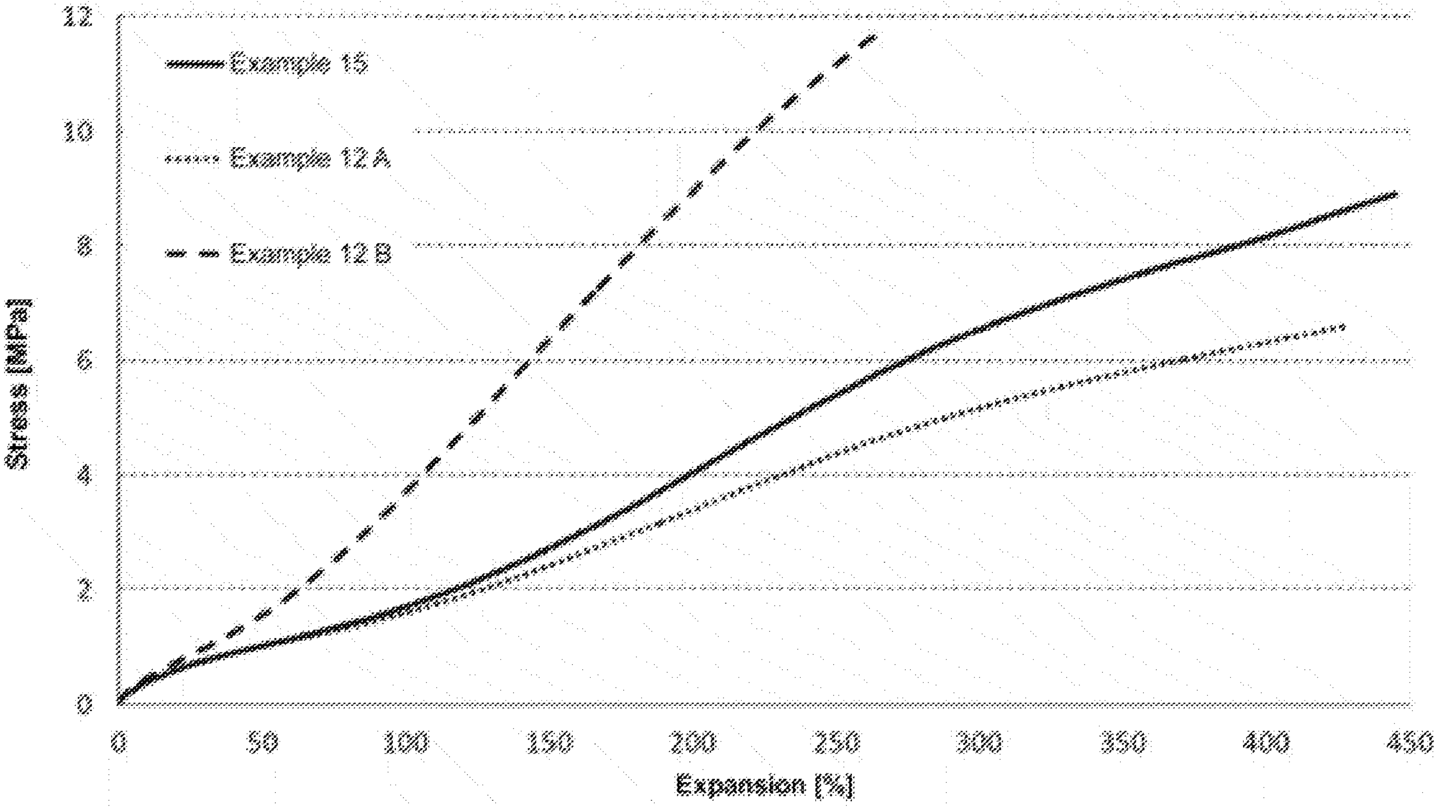

Example 15
Example 12 A
Example 12 B
Stress [MPa]
0
2
4
6
8
10
12
Expansion [%]
0
50
100
150
200
250
300
350
400
450

FIGURE 4

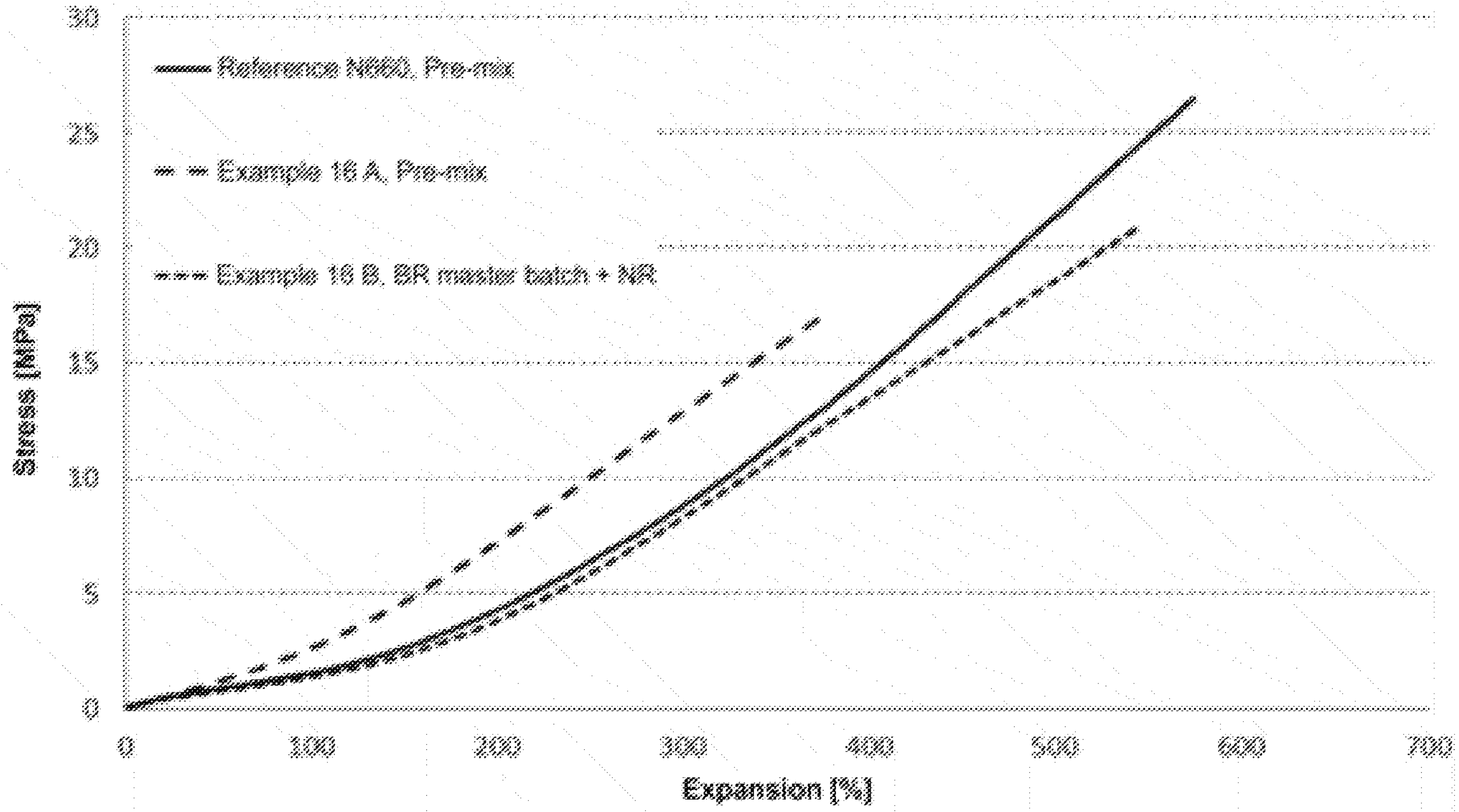

Stress [MPa]
30
25
20
15
10
5
0
Reference N660, Pre-mix
Example 16 A, Pre-mix
Example 16 B, BR master batch + NR
0
100
200
300
400
500
600
700
Expansion [%]

FIGURE 5

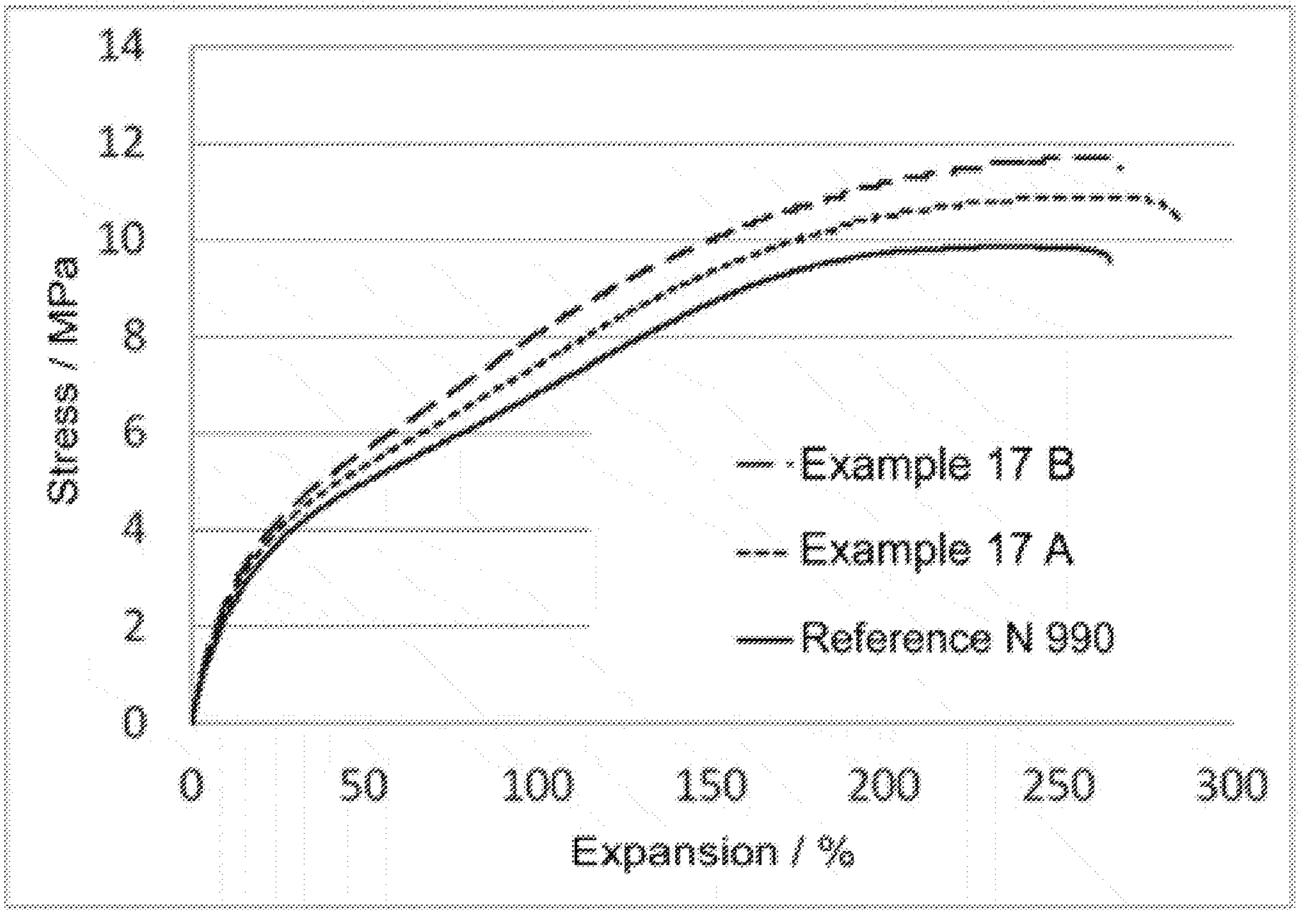

14
12
10
8
6
4
2
0
Stress / MPa
0
50
100
150
200
250
300
Expansion / %
Example 17 B
Example 17 A
Reference N 990

FIGURE 6