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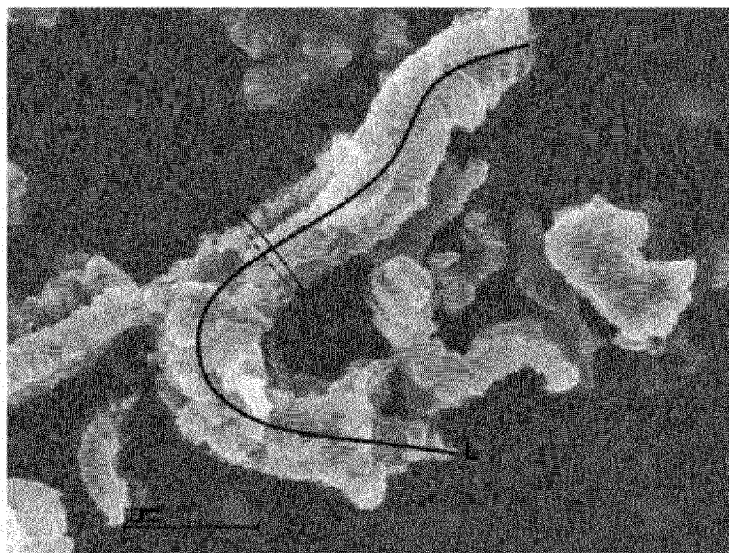


Figure 2

(57) Abstract: The present invention relates to a polypropylene composition comprising (a) a propylene polymer base resin, and (b) carbonaceous structures, wherein the carbonaceous structures (b) have a BET surface area of at least 200 m<sup>2</sup>/g and a density of less than 100 g/L, and wherein the carbonaceous structures (b) have a BET surface area of at least 200 m<sup>2</sup>/g and a density of less than 100 g/L, and wherein said polypropylene composition has a tensile modulus of at least 1715 MPa at the amount of said carbonaceous structures below 5 wt% based on the total amount of said polypropylene composition.



# **POLYPROPYLENE COMPOSITION COMPRISING CARBONACEOUS STRUCTURES AND HAVING IMPROVED MECHANICAL PROPERTIES**

## **TECHNICAL FIELD**

5 The present invention relates to a polypropylene composition comprising carbonaceous structures. It also relates to a process for producing the polypropylene composition as well as to the use of the polypropylene composition in pipes. Further, the invention is also related to an article, preferably a pipe comprising said polypropylene composition.

## **BACKGROUND OF THE INVENTION**

10 Polypropylene compositions are frequently used for the production of pipes, which themselves can be used for several purposes such as fluid transport, i.e. transport of gases or liquids. In such applications, the fluid may be pressurised, e.g. when transporting natural gas or tap water, or non-pressurised, e.g. when transporting sewage (wastewater), drainage (land and road drainage), for storm  
15 water applications or for indoor soil and waste. The transported fluid may have varying temperatures, usually within the temperature range of from about 0 °C to about 50 °C. Non-pressure pipes may also be used for cable and pipe protection. Such non-pressure pipes are herein also referred to as sewage pipes or non-pressure sewage pipes.

20 The physical requirements necessary for pipes suitable for the transport of pressurised fluids (pressure pipes) and pipes suitable for the transport of non-pressurised fluids (non-pressure pipes) differ. Pressure pipes must be able to withstand an internal positive pressure, i.e. a pressure inside the pipe, which is higher than the pressure outside the pipe. On the other hand, non-pressure pipes  
25 do not have to withstand such positive internal pressures, but are instead required to withstand positive external pressures, i.e. when the pressure outside the pipe is higher than the pressure inside the pipe. This higher external pressure may be due to earth load on the pipe when being submerged in the soil, the groundwater pressure, traffic load, or clamping forces in indoor applications.

30 Non-pressure pipes are usually made in a variety of dimensions from about 0.1 to about 3 m of inner diameter and from a variety of materials such as ceramics (mainly vitrified clay), concrete, polyvinyl chloride (PVC), polyethylene (PE), and polypropylene (PP). While ceramics and concrete are low-cost materials, they are unfortunately heavy and brittle. There has therefore been a trend during  
35 recent years to replace sewage pipes of ceramics or concrete with pipes of polymer materials such as PVC, PE or PP.

In the non-pressure pipe application area, high stiffness is a highly desirable property making it possible either to produce pipes with thinner walls at comparable ring stiffness, or to produce pipes having a very high ring stiffness in general. In addition to high stiffness, polymers used for non-pressure pipes  
5 require high impact strength. As pipes may be installed at temperatures below 0 °C, in particular good impact properties at low temperatures are required.

Because of its good processability at low production costs and high mechanical performance, PVC is one of the most dominant materials used for pipes and fittings. However, PVC materials also exhibit major disadvantages. For example,  
10 PVC has a comparably high density resulting in high weight per meter of pipe. Furthermore, the temperature range for usage of PVC is usually comparably narrow. Finally, pipes made from PVC are not weldable.

Polypropylene copolymers for pipe manufacturing are available having stiffness up to 2000 MPa. In applications where high stiffness is needed, neat  
15 polypropylene does not fulfil the requirements and therefore needs to be compounded with high stiffness fillers. When reinforced, polypropylene offers the advantage of its low density, compared to steel and concrete materials. Commonly used fillers are talc and glass fibers, which allow the reinforced material to achieve the desired mechanical properties. However, these fillers  
20 have a high density and thus contribute to increased overall density, consequently increasing the weight, of the fiber-reinforced polypropylene. Accordingly, such fillers counteract the benefit of the light weight of the polypropylene.

Another filler commonly used for reinforcement of polyolefin compositions is  
25 carbon black (CB). High carbon black loadings have detrimental effects on the processing and mechanical properties, especially since the resulting compositions have high density and thus high weight. Moreover, high amounts of carbon black make the compositions brittle and stiffness/rigidity is reduced. On the other hand, high mechanical reinforcement commonly requires large  
30 amounts of carbon black (~35-40 wt%).

Accordingly, the industries seek for a reinforced polypropylene composition fulfilling the demanding requirements of well-balanced mechanical properties such as high stiffness and high impact strength on one hand and low density on the other hand. Especially in pipe industry, components should combine the high  
35 stiffness and strength with light weight.

EP 2 368 922 is concerned with a polymer composition, comprising (a) a heterophasic polymer, which comprises (a1) a matrix comprising a propylene homopolymer and/or a propylene copolymer having an amount of comonomer

units of less than 1.0 wt%, and (a2) an elastomeric polypropylene which is dispersed within the matrix and comprises comonomer units derived from ethylene and/or a C4-8 alpha-olefin; the heterophasic polymer composition having an amorphous fraction AM in an amount of 2.0 to 7.5 wt%, and the amorphous fraction AM having an amount of ethylene- and/or C4-8 alpha-olefin-derived comonomer units of 20 to 45 wt%; and (b) talc in an amount of from 5 wt% to 40 wt%. Fillers used in the composition are calcium carbonate, talc, wollastonite, or mixtures thereof.

EP 2 550 325 describes a heterophasic polypropylene composition comprising polypropylene, an elastomeric propylene copolymer, and a mineral filler (F), wherein (i) said heterophasic polypropylene composition has a melt flow rate  $MFR_2$  of equal or below 2.0 g/10min and (ii) a polydispersity index (PI) of at least 5.0, (iii) the amount of the amorphous fraction of the xylene cold soluble fraction of the heterophasic polypropylene composition is at least 5.0 wt.-%, and (iv) the amount of mineral filler within said heterophasic polypropylene composition is in the range of 5.0 to equal or below 30.0 wt.-%. However, the filler of the composition is a heavy mineral filler such as talc, wollastonite, clay, and mica.

Furthermore, WO 2005/014713 A1 describes a moulded or extruded article of a polypropylene block, which is filled with talc, and WO 2006/114358 B1 describes a polypropylene threaded pipe filled with 10-35% talc, calcium carbonate or wollastonite, both showing the disadvantages as described above.

Carbonaceous structures have been proposed as fillers in polyolefin compositions. US 2006/231792 A1 discloses graphite nanoplatelets of expanded graphite and polymer composites produced therefrom. The graphite is expanded from an intercalated graphite by microwaves or radiofrequency waves in the presence of a gaseous atmosphere. The composition of nylon and xGnP shows improved mechanical properties such as flexural modulus, strength, and impact strength.

The graphene nanoparticles may be formed of thin, independent graphite flakes or platelets. The nanoparticles may also be shaped to have corners, or edges that meet to form points. The platelets may be fully isolated from the original graphite particle, or may be partially attached to the original particle. Also, more complex secondary structures such as cones are also included, see for example Schniepp, Journal of Physical Chemistry B, 110 (2006) pp. 8535.

Graphene nanoplatelets (GNPs) are characterized in that the material is composed of one or several layers of two-dimensional hexagonal lattice of carbon atoms. The platelets have a length parallel to the graphite plane, commonly referred to as lateral diameter, and a thickness orthogonal to the

graphite plane, commonly referred to as thickness. Another characteristic feature of GNPs is that the platelets are very thin yet have large lateral diameter, hence GNPs have a very large aspect ratio, i.e. ratio between the lateral diameter and the thickness.

- 5 Graphene nanoplatelets may also include graphene platelets that are somewhat wrinkled such as for example described in Stankovich et al, Nature 442, (2006), pp. 282. Additionally, graphene materials with wrinkles to another essentially flat geometry are included. In another aspect, the GNPs can be functionalised to improve interaction with the base resins. Non-limiting examples of surface  
10 modifications includes treatment with nitric acid; O<sub>2</sub> plasma; UV/Ozone; amine; acrylamine such as disclosed in US2004/127621 A1.

The graphene nanoparticles may be derived from treated graphite sheets, e.g. expanded graphite that can be exposed to high temperatures (e.g. in the range of from 600 to 1200 °C) so that the graphite sheets expand in dimension from  
15 100 to 1000 or more times its original volume in an accordion-like fashion in the direction perpendicular to the crystalline planes of the graphite. These agglomerates may assume an elongated shape with dimensions in the order of 1 to 100 µm.

Possible production procedures of graphene nanoplatelets and single graphene  
20 sheets have been disclosed in e.g. US 2002/054995 A1, US 2004/127621 A1, US 2006/241237 A1 and US 2006/231792 A1. Such processes are for example further discussed by Stankovich et al, Nature 442, (2006) pp.282, and by Schniepp, Journal of Physical Chemistry B, 110 (2006) pp. 853. Non-limiting examples of materials are Vor-X™ provided by Vorbeck Materials and xGNP™  
25 provided by XG Science, Lansing, MI, USA.

US2002/054995 A1 discloses how nanoplatelets can be created by high pressure mill giving an aspect ratio between the lateral diameter and the thickness of 1500:1 and a thickness 1-100 nm.

WO 03/024602 A1 discloses separated graphite nanostructures formed of thin  
30 graphite platelets having an aspect ratio of at least 1500:1. The graphite nanostructures are created from synthetic or natural graphite using a high-pressure mill. The resulting graphite nanostructures can be added to polymeric materials to create polymer composites having increased mechanical characteristics, including an increased flexural modulus, heat deflection  
35 temperature, tensile strength, electrical conductivity, and notched impact strength. The effects observed in this disclosure require filler loadings, if added to polypropylene, as high as 38 wt% - 53 wt%.

Therefore, it is an object of the present invention to provide a polypropylene composition combining advanced mechanical property profile, i.e. high stiffness/rigidity and impact strength at low density as required in pipe applications, and low filler loading required for improved processability.

## 5 SUMMARY OF THE INVENTION

It was found that this object can be achieved by an improved polypropylene composition comprising

- (a) a propylene polymer base resin, and
- (b) carbonaceous structures

10 wherein the carbonaceous structures (b) have a BET surface area of at least 200 m<sup>2</sup>/g and a density of less than 100 g/L, , and wherein said polypropylene composition has a tensile modulus of at least 1715 MPa at the amount of said carbonaceous structures below 5 wt% based on the total amount of said polypropylene composition

15 The term “carbonaceous structure” refers to partially dispersed clusters of a plurality of carbonaceous components, wherein each carbonaceous component is constituted by allotropes of carbon, in particular graphite and graphene. According to the present invention, the carbonaceous structures (b) of the present invention may be reduced graphite oxide worm-like (rGOW) structures,  
20 or particles. The rGOW structure may comprise any number of reduced oxidized graphene platelets, wherein at least some of the platelets are in a plane that is not parallel with that of an adjacent platelet, as shown in Fig. 1b. Although the rGOW platelets are referred to as planar, they are typically not as planar as, for example, graphene sheets, but rather include wrinkles and deformities that result  
25 from the oxidation/reduction processes by which the particles have been treated. As a result, the rGOW platelets are thicker than graphene sheets although they still retain a generally planar shape having a diameter that is several times greater than the thickness of the platelet. As can be seen in the photomicrograph of Fig. 2, these platelets include multiple sub-sections that are at distinct angles  
30 to each other. This unevenness contributes to the high surface area and low bulk density of the particles.

An adjacent platelet is defined as a platelet that is joined directly to the given platelet on either major side of the given platelet. A platelet is not adjacent if it is joined to the given platelet via only a third platelet. A platelet may be at an  
35 angle to a first adjacent platelet on one side and retain a parallel structure with a second adjacent platelet on the opposed side. Many of the platelets in an rGOW structure can remain in a graphite configuration (see Fig. 1a) in which

they are parallel to each other and remain bound together by van der Waals forces. This is for example illustrated by stacks s1 and s2 in Fig. 1b. Particles of rGOW structures do not typically have extensive graphitic structures and different embodiments of rGOW structures may be limited to parallel platelet composite structures containing fewer than 15, preferably fewer than 12, more preferably fewer than 11 adjacent parallel platelets. rGOW structures exhibit a structure where any dimension of the structure, such as length L or diameter d, is greater than the sum of thicknesses w of all the graphene platelets in the particle. For example, if the thickness w of a single graphene platelet is about 1 nm, then an rGOW structure comprising 1,000 platelets would be greater than 1  $\mu$ m in both length L and diameter d. These three-dimensional particles also have an extension of at least 50 nm along each of the x, y and z axes as measured through at least one origin in the particle. An rGOW structure is not a planar structure and has a morphology that distinguishes it from both graphite (stacks of graphene platelets) and individual graphene sheets. It is notable however, that rGOW structures can be exfoliated into single platelets, or stacks of platelets, that can have at least one extension along any of x, y and z axes that is less than 100 nm, preferably less than 50 nm, more preferably less than 10 nm, or even more preferably less than 5 nm. After an rGOW structure has been exfoliated, the resulting single platelets or stacks of parallel platelets are no longer rGOW structures.

The rGOW structures described herein can comprise a plurality of graphene platelets and in various embodiments may include greater than 10, preferably greater than 100, more preferably greater than 1000 graphene platelets. In various embodiments, the particles may be linear or serpentine, can take roughly spherical shapes, and in some cases may be cylindrical. The structure of an rGOW structure can be described as accordion-like because of the way the particle expands longitudinally due to the alternating edges at which the platelets remain joined. For example, as shown in Fig. 1b, at least some of the adjacent graphene planes are not parallel and are at angles to each other. As may be seen in Fig. 1b, at least some of the adjacent graphene planes may be positioned at an angle  $\alpha$  relatively each other, wherein the angle  $\alpha$  may for example be about 25°. Various embodiments may include one or more pairs of adjacent graphene platelets that are joined at angles of, for example, 10°, 25°, 35°, 45°, 60° or 90°. Different adjoining pairs of graphene platelets may remain joined at different edges or points, so the graphene platelets are not necessarily canted in the same direction. If the adjacent graphene platelets remain attached randomly to each other at platelet edges after expansion, the structure will extend in a substantially longitudinal direction.

As may be seen in Figs. 1b and 2, the rGOW structure has a transverse extension, or diameter  $d$ , and a longitudinal extension being substantially perpendicular to the transverse extension, or length  $L$ . Further, each of the platelets in the rGOW structure has an extension in the longitudinal direction, or thickness  $w$ . rGOW structures thus have elongated, expanded, worm-like structures that can have an aspect ratio, i.e. length  $L$ /diameter  $d$ , that can be preferably 1:1 or more, more preferably 2:1 or more, more preferably 3:1 or more, more preferably 5:1 or more or most preferably 10:1 or more. Usually, the aspect ratio is not more than 100:1 or preferably 50:1. The length  $L$  of an rGOW structure is the longest line that passes through a central longitudinal core of the particle from one end to the other (Fig. 2). This line may be curved or linear, or have portions that are curved or linear, depending on the specific particle. The line runs substantially perpendicular to the average plane of the platelets in any particular portion along the line.

The length  $L$  of the carbonaceous structures (b) is preferably at least 1.0  $\mu\text{m}$ , more preferably at least 2.0  $\mu\text{m}$ , more preferably at least 5.0  $\mu\text{m}$ , more preferably at least 10  $\mu\text{m}$  or more preferably at least 100  $\mu\text{m}$ . Usually, the length  $L$  of the carbonaceous structures (b) is not more than 1000  $\mu\text{m}$ .

The diameter  $d$  of the carbonaceous structures (b) is deemed to be the diameter of the smallest circle that can fit around the structure at its midpoint (Fig. 2). The diameter  $d$  of the carbonaceous structures (b) (diameter of the circle shown in Fig. 2) can be, for example, is preferably less than 200  $\mu\text{m}$ , more preferably less than 100  $\mu\text{m}$ , more preferably less than 50  $\mu\text{m}$ , more preferably less than 20  $\mu\text{m}$ , more preferably less than 10  $\mu\text{m}$ , more preferably less than 5  $\mu\text{m}$ , more preferably less than 2  $\mu\text{m}$  or more preferably less than 1  $\mu\text{m}$ . Further, the diameter  $d$  is preferably greater than 50 nm, and most preferably greater than 100 nm, more preferably greater than 400 nm, and most preferably greater than 800 nm. Preferred diameter ranges include 50 nm to 200  $\mu\text{m}$ , 100 nm to 100  $\mu\text{m}$ , 500 nm to 100  $\mu\text{m}$ , 500 nm to 50  $\mu\text{m}$ , 2.0  $\mu\text{m}$  to 30  $\mu\text{m}$ , 2.0  $\mu\text{m}$  to 20  $\mu\text{m}$ , 2.0  $\mu\text{m}$  to 15  $\mu\text{m}$ , 2.0  $\mu\text{m}$  to 10  $\mu\text{m}$ , 1.0  $\mu\text{m}$  to 5  $\mu\text{m}$ , 100 nm to 5  $\mu\text{m}$ , 100 nm to 2  $\mu\text{m}$ , 100 nm to 1  $\mu\text{m}$ . The diameter  $d$  of the carbonaceous structures (b) along its length  $L$  need not be constant and can vary by a factor of greater than 2, greater than 3 or greater than 4 along the length  $L$  of the carbonaceous structures (b).

The carbonaceous structures (b) may contain carbon, oxygen and hydrogen and may be essentially void of other elements. A particle is essentially void of an element if the element is absent or is present only as an impurity. In specific embodiments, the carbonaceous structures (b) can comprise greater than 80%, greater than 90%, greater than 95% or greater than 99% carbon by weight. Some



carbonaceous structures (b) may include oxygen, and particularly covalently bound oxygen, at concentrations by weight of greater than 0.1%, greater than 0.5%, greater than 1.0%, greater than 5.0%, greater than 10.0%, greater than 14.0%, less than 25%, less than 15%, less than 10%, less than 5.0%, less than 3%, less than 2% or less than 1.0%. Hydrogen content may be greater than 0.1% or greater than 1% by weight. Further, hydrogen content may be less than 1%, less than 0.1% or less than 0.01% by weight. Heteroatoms such as nitrogen or sulfur may be present at amounts greater than 0.01% or greater than 0.1% by weight.

The carbonaceous structures (b) being reduced graphite oxide worm-like (rGOW) structures can exhibit a low density. Preferably, the carbonaceous structures (b) have a density of less than 100 g/L, more preferably of less than 50 g/L, more preferably of less than 30 g/L, more preferably of less than 20 g/L, more preferably of less than 10 g/L, and preferably greater than 5 g/L, more preferably greater than 10g/L or greater than 15 g/L when measured using ASTM D7481-09. If the rGOW structures are in the form of clusters, the density may be between 15 g/L and 100 g/L. In these preferred embodiments, the carbonaceous structures (b) have a density of between 15 and 100 g/L.

On the other hand, if the densities are between 5 g/L and 15 g/L, the rGOW structures are in the form of worms or densified worms. In these other preferred embodiments, the carbonaceous structures (b) have a density of between 5 and 15 g/L.

Preferably, the carbonaceous structures (b) have a BET surface area of at least 200 m<sup>2</sup>/g, more preferably of at least 300 m<sup>2</sup>/g, more preferably of at least 500 m<sup>2</sup>/g, more preferably of at least 600 m<sup>2</sup>/g, and most preferably of at least 650 m<sup>2</sup>/g, measured according to ASTM D6556-04. Usually, the carbonaceous structures (b) have a BET surface area of not more than 10000 m<sup>2</sup>/g, measured according to ASTM D6556-04.

The carbonaceous structures (b) may also exhibit high structure, and when measured using oil absorption number (OAN) can exhibit structures of preferably greater than 500 mL/100 g, more preferably greater than 1000 mL/100 g, more preferably greater than 1500 mL/100 g or most preferably greater than 2000 mL/100 g (measured according to ASTM D2414-16). Usually, the carbonaceous structures (b) exhibit structures, measured using oil absorption number (OAN), of preferably smaller than 50000 mL/100 g, measured according to ASTM D2414-16.

Preferably, the carbonaceous structures (b) have volatile content of less than 30 %, more preferably of less than 25 %, more preferably of less than 20 %, more

preferably of less than 15 %, more preferably of less than 10 %, and most preferably of less than 7 %.

One indicator of the oxygen content in the carbonaceous structures (b) is the volatile material content of the structure. The carbonaceous structures (b) have a volatile content, as measured by thermogravimetric analysis (TGA) from 125°C to 1000°C under inert gas, preferably of greater than 1%, more preferably greater than 1.5%, more preferably greater than 2.0%, more preferably greater than 2.5%, and most preferably greater than 5%,. Further, the volatile content by the same technique is preferably less than 30%, more preferably less than 25%, more preferably less than 20%, more preferably less than 15%, and most preferably less than 10%. The high oxygen content lowers the conductivity of the material and makes it insulating. Therefore, graphene oxide used as filler is reduced in order to lower the oxygen content. The oxygen content of the rGOW structures, when compared to the parent graphite oxide, can be reduced by at least 25%, at least 50% or at least 75%. Similarly, the energetic content of the structures (as measured by Differential Scanning Calorimetry, DSC) can be reduced by, for example, at least 25%, at least 50% or at least 75%. The decomposition energy of the rGOW structures can be, for example, less than 150 J/g, less than 100 J/g, less than 50 J/g or less than 20 J/g.

Preferably, the added amount of said carbonaceous structures (b) is in the range of from 0.1 to 2 wt.%, more preferably 0.2 to 1 wt.% and most preferably 0.3 to 0.8 wt.%, based on the total weight of the insulating polyolefin composition.

The graphitic structure of an rGOW structure can be investigated by Raman spectroscopy. Pure graphite has a Raman spectrum with a strong G band (1580  $\text{cm}^{-1}$ ) and non-existent D band (1350  $\text{cm}^{-1}$ ). Graphite oxide exhibits a strong D band as well as G band. Reduced graphite oxide and rGOW structures have a strong D band that in many cases is stronger than the G band (FWHM). The ratio of the D band to G band may be greater than 1.0, greater than 1.1 or greater than 1.2.

Structures of rGOW can often be differentiated from graphite and similar materials due to differences in crystallinity. Crystallinity of rGOW structures can be determined by Raman spectroscopy and in various embodiments the rGOW structures can exhibit crystallinity values of less than 40%, less than 30% or less than 20%. X-ray diffraction can also be helpful in differentiating between graphite and materials such as graphite oxide and rGOW structures that exhibit different interlayer spacing than graphite. Graphite has a strong XRD peak between 25° and 30°, while rGOW structures typically have no discernible peak in this range.

It is worth noting that the definition of carbonaceous structures (b) according to the present invention does not include carbon nanotubes.

The processes described herein below can be used to produce reduced graphene oxide worm (rGOW) structures, or particles. First, graphite oxide  
5 from graphite, such as graphite particles, is produced. Graphite particles are combined with a mixture of mineral acids such as nitric acid and sulfuric acid. This mixture is then reacted with a strong oxidizer such as chlorate ion, which can be provided via an aqueous chlorate salt solution. The chlorate may be added to a reaction vessel at a constant rate. After a pre-  
10 determined amount of chlorate has been added, the system is allowed to purge for an extended period to complete the oxidation reaction and allow the resulting chlorine dioxide to vent from the reaction mixture. The resulting graphite oxide slurry can then be neutralized and/or concentrated, for example by using the methods described herein.

15 The starting material graphite particles may be in any form such as powder, granules or flakes. Suitable graphite can be obtained from any available source, and in some cases natural graphite from Superior Graphite has been found to provide acceptable results. Other providers of graphite include Alfa Aesar and Asbury Carbons. In some embodiments, graphite particles may  
20 have a  $D_{90}$  of less than 100  $\mu\text{m}$ .

The acid solution that is to be combined with the graphite can be a mixture of mineral acids such as nitric and sulfuric acid. The graphite, nitric acid and sulfuric acid may be combined in any order, but in many embodiments the graphite is added after the nitric acid has been mixed with the sulfuric acid.

25 Although other concentrations can be used, unless otherwise stated, the embodiments described herein use 68-70 % nitric acid and 96-98% sulfuric acid. Preferably, the weight ratio of nitric acid (on an anhydrous basis, not including the weight attributable to the water content) to sulfuric acid can be, for example, between 0.2 and 0.4, more preferably between 0.25 and 0.35  
30 or most preferably between 0.26 and 0.32.

It has been found that water can inhibit the graphite oxidation process and that reducing the water content relative to the acid content can improve reaction kinetics. This allows for a greater amount of graphite to be oxidized with a fixed amount of acid, or allows for the same amount of graphite to be  
35 oxidized with less acid. Preferably, the ratio of the weight of total acid to graphite can be less than 15:1, more preferably less than 20:1, more preferably less than 30:1, or most preferably less than 40:1. Specific ranges include preferably between 10:1 and 20:1, more preferably between 10:1

and 30:1, and most preferably between 15:1 and 25:1. Preferably, the weight ratio of total water to graphite can be less than 10.0:1, more preferably less than 9.0:1, more preferably less than 8.0:1, more preferably less than 7.0:1 or most preferably less than 6.0:1. One way of obtaining a lower acid to graphite ratio is to lower the total water to acid ratio. As used herein, "total water" is the sum of all sources of water that enter the reaction vessel, including water from the aqueous chlorate solution and water from the nitric acid. The water to acid ratio is the total water compared to the total amount of acid added, on an anhydrous basis. It is calculated at the time that all of the aqueous chlorate solution has been added and the process is transitioning from the oxidation phase to the purge phase. Preferably, the total water to acid ratio is less than 0.43:1, more preferably less than 0.40:1, more preferably less than 0.35:1, more preferably less than 0.30:1 or most preferably less than or equal to 0.26:1.

After the nitric acid, sulfuric acid and graphite have been placed in the reaction vessel, chlorate addition is started. Chlorate ion ( $\text{ClO}_3^-$ ) can be delivered as an aqueous solution of a chlorate salt or as a dry powder. Chlorate salts may be selected from those including an ammonium or alkali metal cation, such as potassium or sodium chlorate. Preferably, the chlorate salt concentration (including the cation) in aqueous solution can be, by weight, greater than or equal to 40%, more preferably greater than or equal to 50%, more preferably greater than 55% or most preferably greater than 60%. The weight ratio of chlorate to water of the chlorate solution can be in the range of preferably 0.8:1 to 2:1, more preferably 1:1 to 2:1 or most preferably 1:1 to 1.5:1. The total amount of chlorate used is proportional to the amount of graphite being oxidized and the weight ratio of chlorate to graphite can be, for example, between 2:1 and 10:1, more preferably between 2:1 and 8:1 or most preferably between 3:1 and 6:1. Preferably, the weight ratio of chlorate to water in the aqueous chlorate feed is greater than 1:1 and the ratio of chlorate to graphite is greater than 3:1. Chlorate may be provided to the reaction mixture at a constant or varied rate during the course of the reaction. In some embodiments, it is provided at a constant rate of between 1 and 3 or between 1.5 and 2.5 grams of chlorate per hour per gram of graphite.

Preferably, a flow of gas, such as from a sparger, can be used to agitate the reaction mixture and/or aid in the removal of chlorine dioxide ( $\text{ClO}_2$ ) from the system. Appropriate gases and gas mixtures include nitrogen and air. Chlorine dioxide is both toxic and reactive. To help retain the concentration of chlorine dioxide at safe levels in the reaction mixture and in the headspace above, a constant flow of gas, such as nitrogen or air, can serve

as a diluent to keep the chlorine dioxide below unsafe levels. The sparger gas flow can serve to carry the chlorine dioxide gas to a trap for safe destruction or disposal of the chlorine dioxide. Preferably, a flow of gas through the reaction medium can also accelerate the removal of chlorine dioxide from the medium, removing a product of reaction and thus accelerating the oxidation process. In some cases, a gas flow such as in a bubble column reactor can be used in the absence of any other agitation, such as stirring or shaking.

Preferably, a flow of gas, such as from a sparger, can be used to agitate the reaction mixture and/or aid in the removal of chlorine dioxide from the system. Appropriate gases and gas mixtures include nitrogen and air. Chlorine dioxide is both toxic and reactive. If the level of chlorine dioxide in the reaction medium reaches saturation, pure chlorine dioxide bubbles can develop with the potential to explosively decompose. To help retain the concentration of chlorine dioxide at safe levels in the reaction mixture and in the headspace above, a constant flow of gas, such as nitrogen or air, can serve as a diluent to keep the chlorine dioxide below unsafe levels. After exiting the headspace area, the chlorine dioxide can be trapped and disposed of safely. In some cases, the gas flow can also be accompanied by stirring.

In instances where the reaction medium is agitated, by stirring for example, chlorine dioxide can be removed by sweeping the headspace of the reaction vessel. The lower explosive limit (LEL) of chlorine dioxide is 10% by volume, so the target limit for chlorine dioxide levels in the headspace is typically below this level. Levels can be maintained below 10% by supplying sweeping gas at about 10 times the rate of chlorine dioxide production. If the reaction rate is faster, then the volume of gas should be increased proportionally. The transfer of chlorine dioxide from the liquid medium to the headspace is dependent on the size of the gas/liquid interface. As the volume of a reaction vessel is increased, the ratio of the area of the gas/liquid interface to the volume of reaction medium decreases according to  $L^2/L^3$  where  $L$  is the characteristic length scale of the reaction vessel. As a result, as the size of the reaction vessel increases, the reaction time and purge time need to be increased to provide for the transfer of chlorine dioxide to the headspace. This leads to extended production times that are not tenable in a production scale operation.

It has been found that gas flow through the reaction medium can be effective at removing chlorine dioxide during the chlorate addition reaction phase,

after completion of chlorate addition during the purge phase, or during both phases. Gas flow, such as sparging, is particularly effective for larger, production scale systems because it is not dependent on the size of the surface area and headspace interface. One example of an oxidation system 210 is shown schematically in Fig. 3a. System 210 uses mechanical impeller 212 for agitating the reaction medium 220. Chlorine dioxide gas entering the headspace from reaction medium 220 is represented by arrow 214. Sweeping gas, such as nitrogen, is provided through gas inlet 216. Sweeping gas including chlorine dioxide is removed via gas exit 218 which leads to a trap or vent for disposal or reclamation.

Fig. 3b schematically represents an embodiment of a hybrid reaction system 230. System 230 includes mechanical impeller 212 as in the embodiment of Fig. 3a. However, system 230 also includes sparger 232 that is positioned at the bottom of the reaction vessel and is fed by sparging gas source 234. In the embodiment illustrated, the sparger is a ring with 12 to 16 holes drilled in the top to channel gas bubbles under the impeller 212. The spinning impeller breaks down and disperses the gas bubbles to create a large gas/liquid interface. This large surface area of gas/liquid interface provides for efficient transfer of chlorine dioxide from the liquid to the gaseous phase. The sparging gas then carries chlorine dioxide from the reaction medium 220 into the headspace. The sparging gas can also dilute chlorine dioxide that is present in the headspace. Gas exit 218 provides a pathway for the mixture of sparging gas, water and chlorine dioxide to leave the reaction vessel. One type of system that uses gas flow through the reaction medium for agitation and mass transfer, without relying on mechanical agitation, is a bubble column reactor. A bubble column reactor can include a sparger but does not use a mechanical agitator.

Fig. 3c schematically depicts a bubble column system 250 that relies exclusively on sparging gas for agitation and chlorine dioxide removal. Note that the bubble column of system 250 has a large height to diameter ratio and a low surface interface area to volume ratio. Preferably, bubble column reactors can have height to diameter ratios of greater than 5:1, more preferably greater than 10:1 or most preferably greater than 20:1. They can be made of any material that is resistant to low pH, including glass or PTFE lined steel. As can be seen from Fig. 3c, the residence time of a gas bubble is extended due to the height of the column of reaction medium. One specific embodiment includes a cylindrically shaped reaction vessels having a diameter of 6 inches and a height of 40 inches. In this embodiment, this

reaction vessel can be charged up to the 25 inch level with graphite and acid, leaving about 15 inches for headspace and the addition of sodium chlorate solution. The headspace of the bubble column reactor provides extra volume for expansion of the liquid phase that occurs as a result of the bubble volume contribution to the liquid reaction medium. The absence of a stirring apparatus can free up space in the vessel and allows for attachment of accessories such as pressure inlets, gas exit vents, probes and pressure relief systems that might be difficult to include with reactor designs that include stirrers or other agitation devices.

Spargers used to provide sparging gas to bubble columns or alternative reaction vessels can be of any design that can provide an adequate supply of small bubbles capable of providing the desired amount of liquid/gas interface. The sparger is in fluid communication with a gas supply, such as nitrogen or air. Spargers can be made of materials that are resistant to the low pH conditions of the graphite oxidation reaction medium. For example, the spargers can be made from nickel alloys, polymers such as PTFE, or glass. Sparger shapes can be selected to maximize the distribution of bubbles across the cross-sectional area of the vessel. In various embodiments, the spargers can take the shape of a ring, a disk, a plate, a sphere, a cylinder or a spoked design where a plurality of perforated arms extend from a central axis. Spargers can include a plurality of holes on either the upper surface, the lower surface, or both. In other embodiments, the sparger can be made from a porous material, such as sintered glass, that does not include readily defined holes or perforations. In some cases, multiple spargers can be used, and each sparger can be controlled independently to allow for tuning of the bubble pattern.

Preferably, the graphite oxidation process is started by combining the nitric acid and sulfuric acid in the reaction vessel. The graphite is then added to the mixture and agitation is started by sparging the mixture with nitrogen.

Sodium chlorate solution is fed to the reaction mixture at a constant rate of about 2 g/h chlorate per gram of graphite. After the target amount of chlorate has been added, e.g., 5 g per gram of graphite, the addition process is ceased and the purging phase is started. Sparging is continued and the chlorine dioxide concentration in the reaction mixture is monitored. When the chlorine dioxide level drops below a threshold, for instance 1000, 100, 10, 1 or 0.1 ppm by weight, the reaction is deemed complete and the graphite oxide product can be transferred to the concentration and purification stage described below.

In other embodiments, different techniques for transferring chlorine dioxide from the reaction medium to the head space can be used. For example, a vacuum source such as a vacuum pump can be used to reduce the vapor pressure in the head space. The low pressure in the reaction vessel causes  
5 bubbles of chlorine dioxide to form in the reaction medium. The chlorine dioxide bubbles rise upward through the liquid into the headspace. A trap or other chlorine dioxide removal device can be positioned between the reaction vessel and the vacuum source. In some cases, gas bubble formation in the reaction medium can also agitate the medium and keep  
10 graphite oxide particles suspended in the fluid.

Graphite oxide produced as provided above can be purified and concentrated using techniques including filtration and centrifugation. It has been found that dead end filtration, such as with a Buchner funnel, is ineffective at purification and concentration of graphite oxide because the  
15 resulting filter cake becomes too impermeable for obtaining reasonable wash rates. As an alternative to dead end filtration, various tangential flow filtration techniques were attempted. Tangential flow filtration involves passing a slurry or suspension through a tubular membrane and collecting permeate through pores that pass through the walls of the tubular  
20 membrane. Tangential flow membranes can include ceramic tubular membranes as well as hollow fiber polymer membranes such as those made from polysulfone or polyvinylidene difluoride (PVDF). Ceramic membranes typically have flow channels between 3 and 6 mm in diameter while hollow fiber polymer membranes have flow channels of about 0.7 to 1.4 mm in  
25 diameter. Tangential flow rates for ceramic membranes are usually about 5 to 10 m/s but are typically lower for polymer membranes and can be, for example, about 1 or 2 m/s. As the graphite oxide slurry has a corrosive pH, ceramic membranes may be preferred over polymer membranes, although polymer membranes may be appropriate for some embodiments. In various  
30 embodiments using ceramic membranes, linear flow rates can be less than 7 m/s, less than 5 m/s, less than 4 m/s, less than 3 m/s or less than or equal to 2 m/s. In these and other embodiments, the linear flow rates can be greater than 1 m/s, greater than 2 m/s, greater than 4 m/s or greater than 6 m/s. In some cases, undesirable shear was realized due to the use of a  
35 backpressure valve in the recirculation loop that drives the pressure gradient across the membrane. This left a large pressure drop resulting in shear formation at the backpressure valve. This shear inducing problem was solved by eliminating the backpressure valve and enclosing and pressurizing the entire retentate recirculation system, including the



headspace above the retentate reservoir. In this manner, a pressure gradient across the filtration membrane can be maintained without the use of the backpressure valve in the recirculation loop. The enclosed system can be limited to pressure differentials of, for example, no more than 15 psi, 10 psi or 5 psi. In some embodiments, shear conditions can be further reduced by limiting the fluid flow path to curves and elbows of less than 90°, for example, 45° or less.

One embodiment of a tangential flow system 300 is illustrated schematically in Fig. 4. Tangential flow membrane 310 can be a tangential flow membrane capable of filtering acidic aqueous suspensions. In one set of embodiments, ceramic membranes from Pall Corporation can be used. For instance, useful membranes may have a pore exclusion size of 0.1, 0.2, 0.65, 0.8 and 1.4  $\mu\text{m}$  and can have a membrane area of greater than 0.1  $\text{m}^2$ , greater than 0.2  $\text{m}^2$  or greater than 0.5  $\text{m}^2$ . Prior to contacting the filter membrane, 7.5 liters of graphite oxide slurry, produced as described herein, are quenched with from 15 to 60 liters of DI water. The quenched slurry is then pumped from the quench tank to the retentate reservoir 320 using transfer pump 340. Retentate reservoir 320 can be pressurized to, for example, greater than 2, greater than 5, or greater than 8 psi. This allows for the elimination of a backpressure valve that would conventionally be placed between the exit of the membrane 310 and retentate reservoir 320. The quenched slurry is flowed into recirculation loop 330 that includes tangential flow membrane 310. The graphite oxide slurry is diafiltered at a transmembrane pressure of 9 psi until the volume is reduced to about 5 liters. This volume is then washed with 20 to 30 liters of DI water by continuing diafiltration and adding water via DI water conduit 350 to retentate reservoir 320 at the same rate at which the permeate is lost through permeate drain 360. Pressure is maintained in retentate tank 320 by pressurizing the headspace in the tank with pressurized gas source 370. The diafiltration process continues until impurities such as sulfate, nitrate and chlorate are reduced to acceptable levels, for example, <1000 ppm sulfate or <300 ppm nitrate. These levels can be confirmed using, for example, ion chromatography, or can be monitored in line using conductivity detectors. If impurities are not reduced to acceptable levels, additional water can be added to retentate reservoir 320, and diafiltration can continue until the desired levels are reached. Once these levels are obtained, the filtration process is continued without water replenishment until the graphite oxide particles are concentrated to between 7.5 and 15% by weight in water. This concentrated slurry is then drained and is ready for high temperature spray drying and reduction as described below.

The resulting rGOW particles exhibited good morphology with a BET surface area of greater than 600 m<sup>2</sup>/g. The particles were analyzed for metal content by ICP and were found to contain on average, by weight, < 30 ppm Fe, < 20 ppm K, <1000 ppm Na, less than 20 ppm Si, less than 20 ppm Ti and less than 5 ppm (below the detection limit) of each of Ag, Al, As, B, Ba, Ca, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Pt, Sb, Te, Ti, V, W, Zn and Zr.

The graphite oxide can be reduced by removing some or all of the bound oxygen groups from the graphite oxide. This process can also result in high inter-graphene platelet pressure that expands the graphite oxide to produce rGOW particles. This is different from some known reduction processes whereby individual graphene oxide sheets are exfoliated from a graphite oxide particle and subsequently reduced in a separate step. For example, in one known process, graphite oxide can be exfoliated in dilute solution and then chemically reduced or thermally reduced using, for example, a spray reduction process.

As described herein, a high temperature spray drying and reduction process can be preferably used that allows for simultaneously drying and thermally reducing the graphite oxide particles to rGOW particles. In contrast to individual reduced graphene oxide sheets, rGOW particles include a plurality of reduced graphene oxide sheets that are joined together, but in which at least some of the reduced graphene oxide sheets are positioned in non-parallel planes. By spraying a high concentration graphite oxide slurry into a high temperature environment, e.g., greater than 300°C, the particles can be dried and reduced in a period of time less than, for example, one second. In certain embodiments, the residence time in the high temperature zone can be from 0.5 to 5 seconds. The particles are exposed instantly to a temperature that exceeds the accelerated decomposition temperature threshold. Any additional energy released into the system by the decomposition reaction can be retained in the system and provides additional energy for maintaining temperature and for vaporizing the water fraction from the graphite oxide particles. A controlled, continuous feed of slurry into the high temperature environment allows the exotherm to be controlled and exploited, in contrast to the batch heating of dried graphite oxide with its associated safety hazards. An apparatus for high temperature drying, decomposition and reduction is described below, along with a method embodiment of using the apparatus to prepare rGOW particles.

One embodiment of a high temperature spray drying and thermal reduction system 400 is shown in cross-section in Fig. 5. High temperature chamber 410 is in fluid communication with spray nozzle 420 and electrical gas heater

440. High temperature chamber 410 can be electrically heated, such as by resistance coils that are held in place around the chamber by clips 450. Dry, reduced graphite oxide particles can be collected at outlet 460. Reduced particles can be cooled using cooling gas received via cooling gas inlet 470.

- 5 High temperature chamber 410 can be cylindrically shaped and is sized based on the desired rate of production. Spray nozzle 420 is constructed and arranged to provide graphite to the interior of the high temperature chamber 410. Nozzle 420 can be liquid cooled and can provide an atomized spray of a graphite oxide slurry to chamber 410. The slurry can comprise a  
10 suspension of graphite oxide particles in water and the graphite oxide particles can have an average size, for example, of between 5 and 50  $\mu\text{m}$ , and may fall into a size range having a D90 of less than 100, less than 50, less than 35 or less than 10  $\mu\text{m}$ . Spray nozzle 420 can provide an atomized flow of from about 300 to 1000 mL per hour of a slurry containing between  
15 7.5% and 15% graphite oxide by weight. Additional nozzle configurations can provide increased flow rates for larger systems and multiple nozzles may be used with a single high temperature chamber.

Conditions for operating one set of embodiments with the apparatus of Fig. 5 are provided below in Table 1.

|                                    |                        |
|------------------------------------|------------------------|
| Slurry pumping rate to spray dryer | 300-900 ml/hr          |
| Spray Dry Vessel temp              | 700-730 °C             |
| Drying gas temp and flow rate      | 900 °C at 100-200 slpm |
| Atomizing gas flow rate            | 12-30 slpm             |

20 Table 1

As detailed above, rGOW particles can exhibit useful properties such as high surface area and low density. The multiple steps involved with producing rGOW particles such as oxidation, purification, concentration, drying and reduction can all affect the properties of the final rGOW particles.

- 25 A flow chart illustrating one embodiment of the production of rGOW particles from graphite is provided in Fig. 6. Graphite particles are placed in mixture of nitric acid and sulfuric acid and sparging is started. A supply of chlorate is provided to the graphite reaction mixture to oxidize the graphite to graphite oxide (GO). The reaction is allowed to run to completion during a  
30 purging phase in which sparging is continued to remove chlorine dioxide gas. The resulting slurry of GO is at a very low pH (less than .5) and is subsequently quenched with DI water. The quenched slurry is pumped to a tangential filtration system where it is purified and concentrated. The

concentrated slurry is further neutralized by the addition of a base. The neutralized slurry is then fed to a high temperature spray dryer where it is simultaneously dried and chemically reduced to produce rGOW particles.

In this context, reference is made to WO2019/070514, and in particular the example section therein, which provides further details as to the production of rGOW structures or rGOW particles as described and used herein.

It has been found that the polypropylene composition according to the present invention achieves an unexpectedly increased stiffness/rigidity at lower filler loadings compared to conventional filler-loaded polymer compositions. At the same time, the Young's modulus and the thermal conductivity are increased. Furthermore, the processability in the production process was excellent due to the greatly increased homogeneity of the carbonaceous structures distributed in the polypropylene resin matrix.

The inventors have found that carbonaceous structures that are compounded in a propylene polymer base resin may change their morphology during compounding in the compounder, assumingly due to the dedensification. Thus, the final polypropylene composition of the present invention possesses new advanced and surprising properties, which enable new applications in the pipe area.

Young's modulus, also known as the elastic modulus or tensile modulus, is a commonly known technical term that represents a measure of the stiffness of a solid material. It is a mechanical property of linear elastic solid materials, and defines the relationship between stress (force per unit area) and strain (proportional deformation) in a material.

The term "copolymer" refers to a polymer made from at least two monomers. It includes, for example, copolymers, terpolymers and tetrapolymers.

It is a specific feature of the process according to the present invention that the carbonaceous structures incorporated into the base resin are intimately mixed in the compounding step and change their morphology thereby. Without wishing to be bound by theory, it is assumed that clusters and/or stacks of graphene platelets are at least partly exfoliated in the compounding step to drastically increase BET surface area and decrease the lateral diameter of the nanoparticles. As a result, the increase in tensile modulus and thermal conductivity of the polypropylene compositions of the present invention is surprisingly achieved by an increase in BET surface area and a decrease in lateral diameter of the carbonaceous structures after compounding. Further, the increased tensile modulus and thermal conductivity of the polypropylene

compositions of the present invention may also be explained by good dispersion as a consequence of the specific physical features of carbonaceous structures, allowing an improved exfoliation in the polymer matrix and thus less agglomerates. Thus, a superior homogeneity in the distribution of the carbonaceous structures in the propylene polymer matrix is achieved which is thought to be responsible for the improved property profile of the inventive compositions.

The polypropylene composition of the present invention may comprise a propylene polymer base resin, optionally being a polymeric blend comprising one or more propylene polymers, and carbonaceous structures, wherein the weight percentage of carbonaceous structures is from 1 wt% to 20 wt%, preferably from 2 to 15 wt%. Further preferred weight ranges may be from 1 to 10 wt%, more preferably from 2 to 10 wt%, and most preferably from 3 to 10 wt%. Further preferred ranges are from 1 to 6 wt%, from 2 to 5 wt% or from 3.5 to 8 wt%. Any of the above limits may be combined with each other. The lower limit is due to mechanical requirements and the upper limit is due to limitation in the viscosity and surface roughness of the composition.

The polypropylene composition of the present invention surprisingly provides a combination of advantages. Not only does it improve processability due to comparatively low viscosity (higher MFR<sub>2</sub> values) than conventional polyolefin compositions containing carbon black filler. Unexpectedly, the carbonaceous structures according to the present invention provide higher stiffness/rigidity expressed by tensile modulus as well as higher impact strength at lower loadings. Moreover, the thermal conductivity of the polymer composition is improved.

The polypropylene composition of the present invention preferably exhibits a tensile modulus of at least 1900 MPa, more preferably at least 2100 MPa, determined according to ISO 527-2, at a filler loading of 5 wt%, preferably from 0.1 to 5 wt%, more preferably from 2 to 5 wt%, and most preferably from 3.5 to 5 wt%, based on the weight of the total polypropylene composition. Also preferably, the polypropylene composition of the present invention exhibit a tensile modulus of at least 1700 MPa, more preferably at least 1715 MPa, even more preferably at least 1740 MPa, determined according to ISO 527-2, at a filler loading of 1 wt%, preferably from 0.1 to 1 wt%, and most preferably from 0.5 to 1 wt%, based on the weight of the total polypropylene composition.

The polypropylene composition according to the present invention preferably has a stress at break of at least 25 MPa, more preferably of at least 28 MPa, and most preferably of at least 30 MPa at a loading of said carbonaceous structures

of below 5 wt%, preferably from 0.1 to 5 wt%, more preferably from 2 to 5 wt%, and most preferably from 3.5 to 5 wt%, based on the weight of the total polypropylene composition. Also, preferably, the polypropylene composition according to the present invention preferably has a stress at break of at least 21.5 MPa, more preferably of at least 22 MPa, and most preferably of at least 23 MPa at a loading of said carbonaceous structures of below 1 wt%, preferably from 0.1 to 1 wt%, and most preferably from 0.5 to 1 wt%, based on the weight of the total polypropylene composition.

The polypropylene composition of the present invention preferably exhibits a tensile strength of at least 29 MPa, more preferably at least 30.5 MPa, determined according to ISO 527-2, at a filler loading of 5 wt%, preferably from 0.1 to 5 wt%, more preferably from 2 to 5 wt%, and most preferably from 3.5 to 5 wt%, based on the weight of the total polypropylene composition.

The polypropylene composition according to the present invention preferably has a shear storage modulus  $G'$  of at least 830 MPa at 23°C, more preferably of at least 900 MPa at 23 °C, and most preferably of at least 990 MPa at 23 °C at a loading of said carbonaceous structures of below 5 wt%, preferably from 0.1 to 5 wt%, more preferably from 2 to 5 wt%, and most preferably from 3.5 to 5 wt%, based on the weight of the total polypropylene composition. Moreover, the polypropylene composition according to the present invention preferably has  $G'$  of at least 820 MPa at 23°C, more preferably of at least 850 MPa at 23 °C, and most preferably of at least 900 MPa at 23 °C at a loading of said carbonaceous structures of below 3 wt%, preferably from 0.1 to 3 wt%, more more preferably from 0.5 to 3 wt%, and most preferably from 1.5 to 3 wt%, based on the weight of the total polypropylene composition. Furthermore, the polypropylene composition according to the present invention preferably has a shear storage modulus  $G'$  of at least 820 MPa at 23°C, more preferably of at least 830 MPa at 23 °C, and most preferably of at least 835 MPa at 23 °C at a loading of said carbonaceous structures of below 1 wt%, preferably from 0.1 to 1 wt%, and most preferably from 0.5 to 1 wt%, based on the weight of the total polypropylene composition.

Hence, in comparison to a polypropylene composition not comprising any carbonaceous structures, the polypropylene composition according to the present invention show an increase in the shear storage modulus  $G'$  of preferably at least 1%, more preferably at least 2% and most preferably of at least 3% at a loading of said carbonaceous structures of below 1 wt%, preferably from 0.1 to 1 wt%, and most preferably from 0.5 to 1 wt%, based on the weight of the total polypropylene composition. Moreover, in comparison to a polypropylene

composition not comprising any carbonaceous structures, the polypropylene composition according to the present invention show an increase in  $G'$  of preferably at least 5%, more preferably at least 7% and most preferably of at least 10% at a loading of said carbonaceous structures of below 3 wt%,  
5 preferably from 0.1 to 3 wt%, more preferably from 0.5 to 3 wt%, and most preferably from 1.5 to 3 wt%, based on the weight of the total polypropylene composition. Furthermore, in comparison to a polypropylene composition not comprising any carbonaceous structures, the polypropylene composition according to the present invention show an increase in the shear storage  
10 modulus  $G'$  of preferably at least 10%, more preferably at least 15% and most preferably of at least 20% at a loading of said carbonaceous structures of below 5 wt%, preferably from 0.1 to 5 wt%, more preferably from 2 to 5 wt%, and most preferably from 3.5 to 5 wt%, based on the weight of the total polypropylene composition.

15 The polypropylene according to the present invention has a density in the range 0.860-0.970 g/cm<sup>3</sup> and is selected from the group consisting of isotactic polypropylene with tacticity of at least 50%; random and heterophasic propylene copolymers; and blends of these polymers including other olefinic or non-olefinic polymers, where these other polymers do not exceed 40 wt% of the total  
20 propylene polymer composition. The polypropylene can be e.g. a commercially available polymer or can be prepared according to or analogously to known polymerization process described in the chemical literature.

The polypropylene can be unimodal or multimodal with respect to one or more of molecular weight distribution, comonomer distribution or density distribution.  
25 A multimodal polyolefin may have at least two polymer components which have different weight average molecular weight, preferably a lower weight average molecular weight (LMW) and a higher weight average molecular weight (HMW). A unimodal polyolefin is typically prepared using a single stage polymerization, e.g. solution, slurry or gas phase polymerization, in a manner well-known in the  
30 art. A multimodal (e.g. bimodal) polypropylene can be produced by mechanically blending two or more, separately prepared polymer components or by in-situ blending in a multistage polymerization process during the preparation process of the polymer components. Both mechanical and in-situ blending are well-known in the field. A multistage polymerization process may preferably be carried out in  
35 a series of reactors, such as a loop reactor which may be a slurry reactor and/or one or more gas phase reactor(s). Preferably a loop reactor and at least one gas phase reactor is used. The polymerization may also be preceded by a pre-polymerization step.

Other examples of propylene polymers are: homopolypropylene, e.g. isotactic polypropylene; or propylene copolymers such as EPDM (ethylene copolymerized with propylene and a diene such as hexadiene, dicyclopentadiene, or ethylidene norbornene). The comonomers can be incorporated randomly or in block and/or graft structures.

According to the present invention, the olefin polymer may comprise or may be a heterophasic olefin copolymer, e.g. a heterophasic propylene copolymer. The heterophasic propylene copolymer may preferably be a heterophasic copolymer comprising a propylene random copolymer as matrix phase (RAHECO) or a heterophasic copolymer having a propylene homopolymer as matrix phase (HECO). A random copolymer is a copolymer where the comonomer part is randomly distributed in the polymer chains and it also consists of alternating sequences of two monomeric units of random length (including single molecules). It is preferred that the random propylene copolymer comprises at least one comonomer selected from the group consisting of ethylene and C<sub>4</sub>-C<sub>8</sub> alpha-olefins. Preferred C<sub>4</sub>-C<sub>8</sub> alpha-olefins are 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-heptene or 1-octene, more preferred 1-butene. A particularly preferred random propylene copolymer may comprise or consist of propylene and ethylene. Furthermore, the comonomer content of the polypropylene matrix is preferably 0.5 to 10 wt%, more preferably 1 to 8 wt% and even more preferably 2 to 7 wt %. For combining optimum processability with the required mechanical properties, the incorporation of the comonomer can be controlled in such a way that one component of the polypropylene contains more comonomer than the other. Suitable polypropylenes are described e.g. in WO 03/002652.

In another embodiment of the present invention the polypropylene composition can also contain further additive(s), such as antioxidant(s), stabiliser(s), processing aid(s), filler(s), metal deactivator(s), flame retardant additive(s), acid or ion scavenger(s), additional inorganic filler(s), or any mixtures thereof. Additives are typical use in total amount of from 0.01 wt% to 10 wt%.

Non-limiting examples of antioxidants are e.g. sterically hindered or semi-hindered phenols, aromatic amines, aliphatic sterically hindered amines, organic phosphites or phosphonites, thio compounds, and mixtures thereof.

Preferably, the antioxidant is selected from the group of diphenyl amines and diphenyl sulfides. The phenyl substituents of these compounds may be substituted with further groups such as alkyl, alkylaryl, arylalkyl or hydroxy groups.



Preferably, the phenyl groups of diphenyl amines and diphenyl sulfides are substituted with *tert*-butyl groups, preferably in meta or para position, which may bear further substituents such as phenyl groups.

5 More preferred, the antioxidant is selected from the group of 4,4'-bis(1,1'-dimethylbenzyl)diphenylamine, para-oriented styrenated diphenylamines, 6,6'-di-*tert*-butyl-2,2'-thiodi-p-cresol, tris(2-*tert*-butyl-4-thio-(2'-methyl-4'-hydroxy-5'-*tert*-butyl)phenyl-5-methyl)phenylphosphite, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline, or derivatives thereof. Of course, not only one of the above-described antioxidants may be used but also any mixture  
10 thereof.

The amount of an antioxidant is preferably from 0.005 to 2.5 wt%, based on the weight of the polypropylene composition. The antioxidant(s) are preferably added in an amount of 0.005 to 2 wt%, more preferably 0.01 to 1.5 wt%, even more preferably 0.04 to 1.2 wt%, based on the weight of the polypropylene  
15 composition. In a further preferable embodiment, the polypropylene composition may comprise free radical generating agent(s), one or more antioxidant(s) and one or more scorch retarder(s).

Examples of processing aids include but are not limited to metal salts of carboxylic acids such as zinc stearate or calcium stearate; fatty acids; fatty  
20 amides; polyethylene wax; copolymers of ethylene oxide and propylene oxide; petroleum waxes; non-ionic surfactants and polysiloxanes.

Non-limiting examples of additional fillers are clays precipitated silica and silicates; fumed silica calcium carbonate.

It is intended throughout the present description that the expression  
25 "compounding" embraces mixing of the material according to standard methods to those skilled in the art. Non-limiting examples of compounding equipments are continuous single or twin screw mixers such as Farell™, Werner and Pfleiderer™, Kobelco Bolling™ and Buss™, or internal batch mixers, such as Brabender™ or Banbury™.

30 Any suitable process known in the art may be used for the preparation of the reinforced polypropylene compositions of the present invention such as dry-mixing, solution mixing, solution shear mixing, melt mixing, extrusion, etc. It is however preferred to prepare the semiconductive polyolefin composition by melt-mixing said olefin polymer base resin (a) with carbonaceous structures (b) in an  
35 extruder, such as a Brabender compounder.

The present invention is also directed to a process for producing the preferred inventive polypropylene composition, comprising pre-mixing the carbonaceous

structures and optionally another solid conductive filler such as carbon black. Pre-mixing as used herein shall indicate that the mixing occurs before the resulting mixture is contacted and mixed with the olefin polymer base resin. The premixing may be conducted in a dispersant such as isopropanol. Preferably, the  
5 olefin polymer base resin is subsequently added to the dispersed carbonaceous structures and/or filler mixture, before the complete mixture is introduced into a compounder, preferably an extruder, such as a Brabender compounder.

The present invention also provides a polypropylene composition obtained by melt-mixing the propylene polymer base resin (a) with carbonaceous structures  
10 (b). Preferably, melt-mixing is performed in an extruder. Preferably, melt-mixing is carried out at a temperature in the range of 125 °C to 230 °C, more preferably 135 °C to 220 °C.

All embodiments of the polypropylene composition described above are also preferred embodiments of the polypropylene composition obtained by melt-mixing the propylene polymer base resin (a) with carbonaceous structures (b).  
15

The object can also be achieved by the use of such a polypropylene composition in an article, preferably a pipe.

Therefore, the object of the present invention is also achieved by an article made of the polypropylene composition according to the present invention. Preferably,  
20 the article comprising the polypropylene composition of the present invention is a pipe, more preferably pipes for the transport of fluids, and even more preferably pipes for the transport of fluids, wherein said fluid has a temperature of at least 50 °C, preferably at least 70 °C.

Further, the present invention is concerned with a polypropylene composition obtainable by such a process.  
25

Below, the invention is described by virtue of non-limiting examples.

The present invention further provides the use of carbonaceous structures being reduced graphite oxide worm-like (rGOW) structures (b) for improving the stiffness/rigidity at lower filler loadings of a polypropylene composition comprising a propylene polymer base resin (a) compared to conventional filler-loaded polymer compositions. Of course, said polypropylene composition also comprises said carbonaceous structures, preferably in the amounts as described herein. Preferably, the use of carbonaceous structures being reduced graphite oxide worm-like (rGOW) structures (b) improve the thermal stiffness/rigidity at  
30 lower filler loadings and at the same time the Young's modulus and the thermal conductivity of a polypropylene composition comprising a propylene polymer base resin (a). It has been surprisingly found that the addition of carbonaceous  
35

structures (b) to said polyolefin composition not only improves, i.e. enhances, the stiffness/rigidity at lower filler loadings of the polypropylene composition. At the same time also the Young's modulus and/or the thermal conductivity of said polypropylene composition are improved. All preferred embodiments of the carbonaceous structures being reduced graphite oxide worm-like (rGOW) structures (b) and of the polypropylene composition described above are also preferred embodiments of the use of the carbonaceous structures being reduced graphite oxide worm-like (rGOW) structures (b).

## BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described by way of examples with reference to the accompanying drawings, of which:

- Fig. 1a        Schematic graphite configuration
- Fig. 1b        Schematic structure of a rGOW structure
- Fig. 2        SEM of an rGOW structure
- Fig. 3a-c      Three different embodiments of a graphite oxidation system
- Fig. 4        Engineering diagram of one embodiment of a purification and concentration system
- Fig. 5        Cross-sectional view of one embodiment of a high temperature spray dryer
- Fig. 6        Flow chart showing the process of one embodiment of a method to produce rGOW particles

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

### Examples

#### **1. Materials**

##### **(a) Polymer Base Resins**

PP1 is the commercially available product BorECO BA212E (Borealis Polyolefine GmbH, Austria) being a composition from a random-heterophasic copolymer and 0.9 wt% talc with a MFR<sub>2.16</sub> of 0.3 g/10 min, an XCS content of 2.7 wt% and a density of 900 kg/m<sup>3</sup>.

##### **(b) Carbonaceous structures**

CS-1 is a carbonaceous structure which forms worm-like structures and is obtained from Cabot Corporation, Boston, MA, USA. The properties of the carbonaceous structure are summarized in Table 2.

| Sample | BET (m <sup>2</sup> /g) | Form  | Density (g/L) |
|--------|-------------------------|-------|---------------|
| CS-1   | 674                     | Worms | 8             |

Table 2

**(c) Fillers**

The talc used in the comparative examples is the commercial product Mistrion 75-6 A of Luzenac having a particle size d<sub>95</sub> of 25.6 µm and a particle size d<sub>50</sub> of 8.2 µm, both measured by laser diffraction (Malvern Mastersizer) according to ISO 13320-1:1999, and a specific surface according to BET measurement of 8.0 m<sup>2</sup>/g.

**2. Measurement methods****(a) Melt Flow Rate**

- 10 The MFR<sub>2</sub> was measured with 2.16 kg load at 230°C for polypropylene according to ISO 1133. The MFR<sub>5</sub> was measured with 5 kg load at 230°C for polypropylene according to ISO 1133. The MFR<sub>21</sub> was measured with 21.6 kg load at 230°C for polypropylene according to ISO 1133.

**(b) Melt temperature (T<sub>m</sub>)**

- 15 Differential Scanning Calorimetry (DSC) experiments were run on a TA Instruments Q2000 device calibrated with Indium, Zinc, Tin according to ISO 11357-1. The measurements were run under nitrogen atmosphere (50 mL min<sup>-1</sup>) on 5±0.5 mg samples in a heat/cool/heat cycle with a scan rate of 10 °C/min between -30 °C and 225 °C according to ISO 11357-3. Melting (T<sub>m</sub>) and  
20 crystallisation (T<sub>c</sub>) temperatures were taken as the peaks of the endotherms and exotherms in the cooling cycle and the second heating cycle respectively.

**(c) Tensile Tests**

- The tensile modulus for comparative examples 1 to 3, CE1 to CE3, was determined according to ISO 527-2 at +23 °C and a cross head speed of  
25 1 mm/min on injection moulded specimen (specimen type 1B, 4 mm thickness) prepared by injection moulding in line with ISO 1873-2.

- The tensile modulus for the inventive examples 1 to 3, IE1 to IE 3, as well as comparative example 4, CE4, was determined according to ISO 527-2 at +23 °C and a cross head speed of 1 mm/min on compression moulded specimen  
30 (specimen type 5A, 2 mm thickness) prepared by compression moulding in line with ISO 1873-2.

Tensile strength, strain at strength, strain and strength at yield as well as stress and strain at break were measured using the same methods apart from a cross head speed of 20 mm/min.

**(d) Thermal conductivity**

- 5 The thermal conductivity of the composites has been tested by means of the Laser flash method (ISO 18755; LFA 447, Netzsch GmbH) at 3M (ESK).

**(e) Polymer density**

The polymer density is measured according to the density immersion method described in ISO 1183.

10 **(f) Density of carbonaceous structures**

Densities are determined using a method similar to ASTM D7481 – 09, i.e. weighing a specified volume of material after at least three taps.

**(g) BET**

BET is determined using ASTM D6556-04.

15 **(h) Volatility**

Volatilities are determined using thermogravimetric analysis under nitrogen.

**(i) Scanning Electron Microscopy (SEM) for Figure 2**

- The powder sample was sprinkled onto an aluminum stub affixed with conductive carbon sticker for SEM imaging. The SEM micrograph was taken using a Zeiss  
20 Ultraplus field emission SEM using the InLens secondary electron detector. An acceleration voltage of 10kV, aperture of 7  $\mu\text{m}$  and a working distance of 2.6 mm were used to acquire this image.

**(j) Glass transition temperature ( $T_g$ ) and storage modulus ( $G'_{23^\circ\text{C}}$ )**

- 25 Glass transition temperature,  $T_g$ , and storage modulus  $G'_{23^\circ\text{C}}$  were determined by dynamic mechanical analysis (DMTA) according to ISO 6721-7. The measurements were done in torsion mode on compression moulded samples (40x10x1 mm<sup>3</sup>) between -100 °C and +150 °C with a heating rate of 2 °C/min and a frequency of 1 Hz. The  $T_g$  was determined from the curve of the loss angle ( $\tan(\delta)$ ), the storage modulus ( $G'$ ) was used at 23°C.

30 **(k) Compounding**

Filled polypropylene compositions having incorporated talc were prepared as follows:

For the comparative example, the polymer PP1 was extruded together with talc in the amounts according to table 2 was compounded via a twin screw extruder

TSE prism 24 under consistent processing conditions (450 rpm, temperature profile: 190->200->6x215->2x210 °C).

Filled polypropylene compositions having incorporated carbonaceous structures were prepared as follows:

- 5 The inventive samples were produced using a Brabender mixer (Plasticoder PLE-331). The mixer was preheated to 210°C prior to the addition of the resin PP1. The rotation speed was set to 10 rpm. The resin was added first followed by the filler. As soon as all the components were added, the rotation speed was increased to 50 rpm and kept for 10 minutes. After the mixing was done, the composition was pelleted and samples were prepared for the relevant tests.

### 3. Results

In the following Tables properties of the obtained compositions are shown.

|                  | CE1  | CE2  | CE3  |
|------------------|------|------|------|
| Content PP1      | 100  | 84   | 73.8 |
| Content talc     | 0    | 15.0 | 25.0 |
| MFR <sub>2</sub> |      | 1.09 | 1.30 |
| Tensile modulus  | 1666 | 2179 | 2909 |

Table 3

|                              | CE4   | IE1   | IE2   | IE3   |
|------------------------------|-------|-------|-------|-------|
| Content PP1 [wt%]            | 100   | 99    | 97    | 95    |
| Content CS-1 [wt%]           | 0     | 1     | 3     | 5     |
|                              |       |       |       |       |
| DSC                          |       |       |       |       |
| T <sub>m</sub> [°C]          | 167.2 | 167.2 | 167.6 | 167.0 |
| T <sub>k</sub> [°C]          | 129.4 | 128.2 | 128.1 | 128.3 |
|                              |       |       |       |       |
| DMTA                         |       |       |       |       |
| G' (23°C) [MPa]              | 813   | 838   | 902   | 995   |
| Peak1 (T <sub>g</sub> ) [°C] | -58   | -56   | -50   | -52   |
| G' increase %                | 0.0   | 3.1   | 10.9  | 22.4  |
|                              |       |       |       |       |
| Tensile Test                 |       |       |       |       |
| Tensile modulus [MPa]        | 1691  | 1744  |       | 2105  |
| Tensile strength [MPa]       | 28.5  | 27.7  |       | 30.7  |

|                    |       |      |      |  |      |
|--------------------|-------|------|------|--|------|
| Strain at strength | [%]   | 4.3  | 4.9  |  | 5.5  |
| Strength at yield  | [MPa] | 28.5 | 27.7 |  | --   |
| Strain at yield    | [%]   | 4.3  | 4.9  |  | --   |
| Stress at break    | [MPa] | 21.0 | 23.0 |  | 30.7 |
| Strain at break    | [%]   | 30.0 | 13.6 |  | 5.2  |
|                    |       |      |      |  |      |
| E-Mod/G' (23°C)    |       | 2.1  | 2.1  |  | 2.1  |

Table 4

In Table 3 the tensile-modulus data of the different compositions of the comparative examples can be seen. For all the compositions comprising talc as a filler an increase in tensile modulus is observed. For the samples comprising talc (CE2 and CE3), a gradual increase in tensile modulus is observed that reaches values of ~2,100-3,000 MPa at a loading range of 15-25 wt%. The CS-5-based inventive examples (IE1-IE3) exhibit a superior and steep increase of the reinforcement level that reaches values of greater than 2100 MPa at a filler content of only 5 wt%

Thus, the inventive embodiments substantially increase tensile strength of the filled polypropylene resin compared to the previously known fillers.

Although the present invention has been described with reference to various embodiments, those skilled in the art will recognize that changes may be made without departing from the scope of the invention. It is intended that the detailed description be regarded as illustrative, and that the appended claims including all the equivalents are intended to define the scope of the invention.

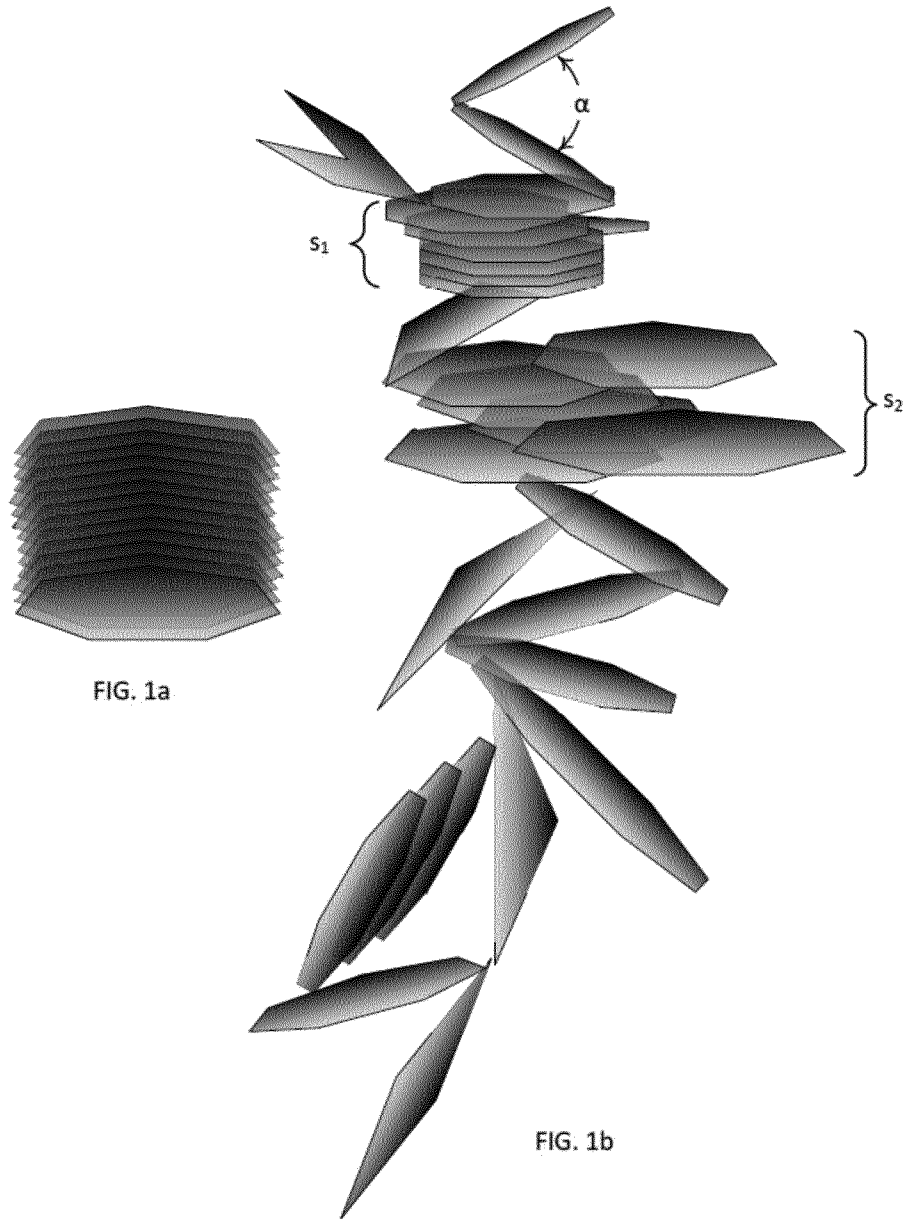
## CLAIMS

1. A polypropylene composition comprising
  - (a) a propylene polymer base resin, and
  - (b) carbonaceous structures
- 5 wherein the carbonaceous structures (b) have a BET surface area of at least 200 m<sup>2</sup>/g and a density of less than 100 g/L, and wherein said polypropylene composition has a tensile modulus of at least 1715 MPa at the amount of said carbonaceous structures below 5 wt% based on the total amount of said polypropylene composition.
- 10 2. The polypropylene composition according to claim 1, wherein the carbonaceous structures (b) have a density of between 5 and 100 g/L.
3. The polypropylene composition according to any of the preceding claims, wherein the carbonaceous structures (b) have a density of between 5 and 15 g/L.
- 15 4. The polypropylene composition according to any one of the preceding claims, wherein the length L of the carbonaceous structures (b) is at least 1 μm.
5. The polypropylene composition according to any one of the preceding claims, wherein the diameter d of the carbonaceous structures (b) is from  
20 50 nm to 200 μm.
6. The polypropylene composition according to any one of the preceding claims, wherein the carbonaceous structures (b) have an aspect ratio of length L to diameter d that is 1:1 or more.
7. The polypropylene composition according to any one of the preceding  
25 claims, wherein said composition has a shear storage modulus of at least 830 MPa, determined according to ISO 527-2, at a loading of said carbonaceous structures of below 5 wt%, based on the weight of the total polypropylene composition.
8. The polypropylene composition according to any one of the preceding  
30 claims, wherein the added amount of said carbonaceous structures is in the range of from 0.1-10 wt% based on the total weight of the polyolefin composition.
9. The polypropylene composition according to any one of the preceding claims, wherein said polypropylene composition has stress at break of at



least 25 MPa at a loading of said carbonaceous structures of below 5 wt%, based on the weight of the total polypropylene composition.

10. The polypropylene composition according to any one of the preceding claims, further comprising a solid conductive filler (c) different from carbonaceous structures.
11. The polypropylene composition according to claim 10, wherein the solid conductive filler (c) is carbon black.
12. A pipe for transport of fluids, comprising the polypropylene composition as defined in any one of the claims 1-11.
13. The pipe according to claim 12, wherein said pipe is subjected to internal or external positive pressure.
14. Use of a polypropylene composition as defined in any one of the preceding claims 1 to 11 as a pipe for transport of fluids.
15. Use of carbonaceous structures being reduced graphite oxide worm-like (rGOW) structures (b) for improving the stiffness at lower filler loadings of a polypropylene composition comprising a propylene polymer base resin (a) according to claims 1 to 11.



Figures 1a and 1b

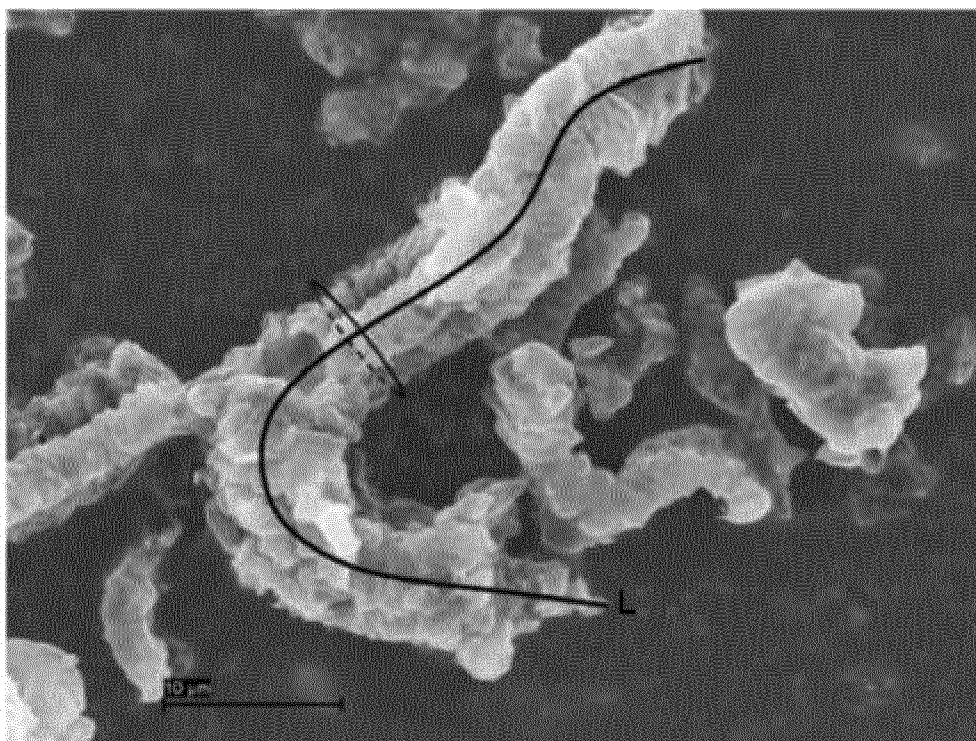


Figure 2

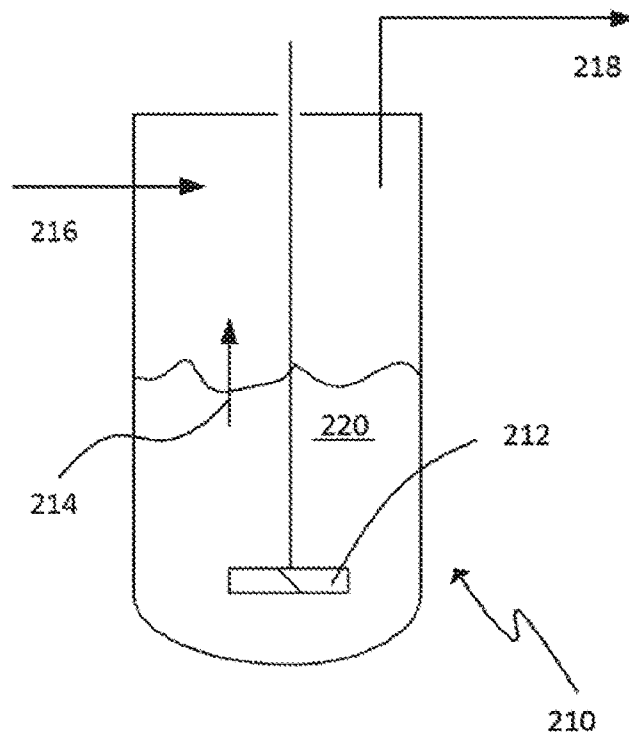


Figure 3a

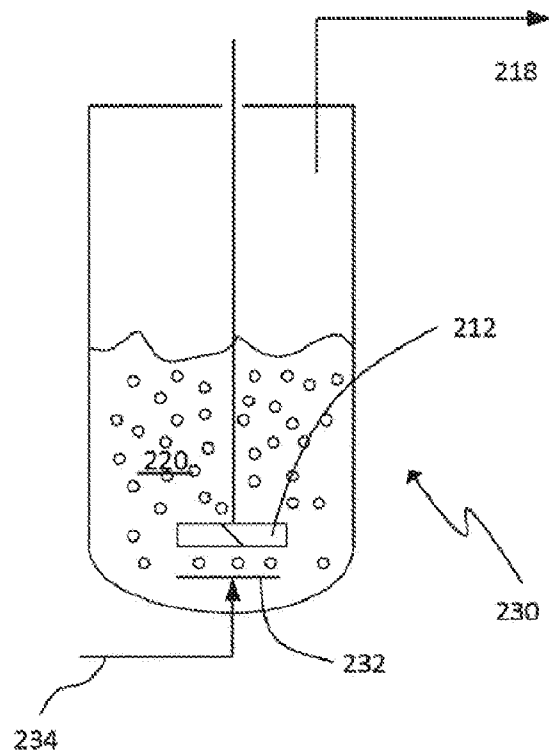


Figure 3b

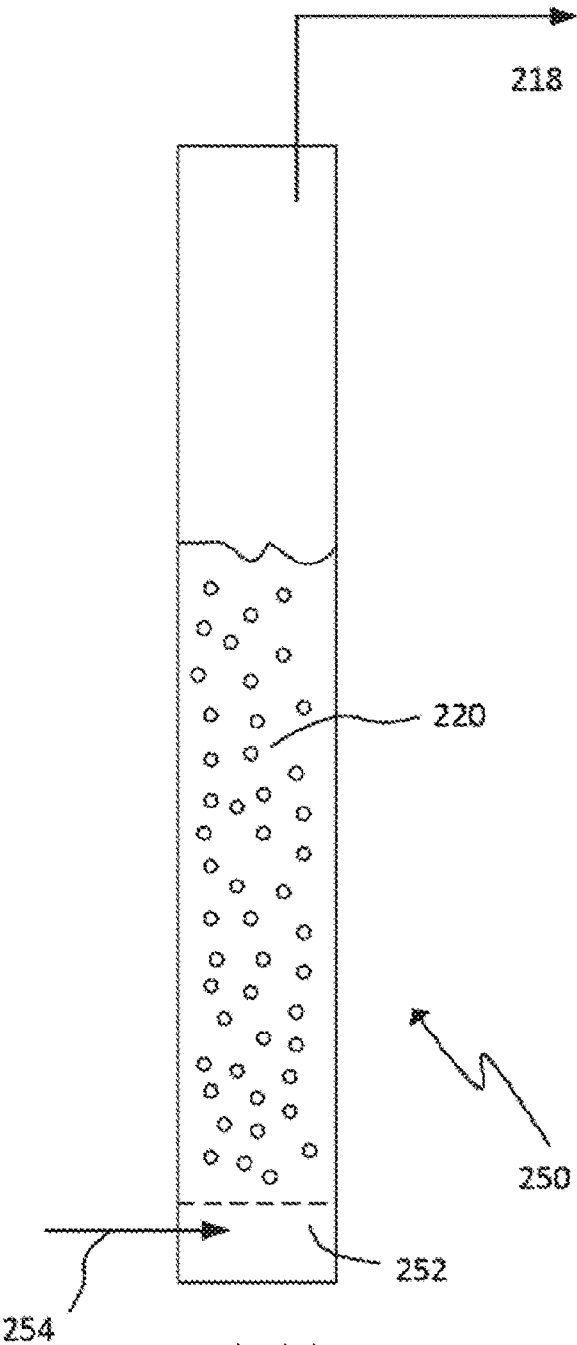


Figure 3c

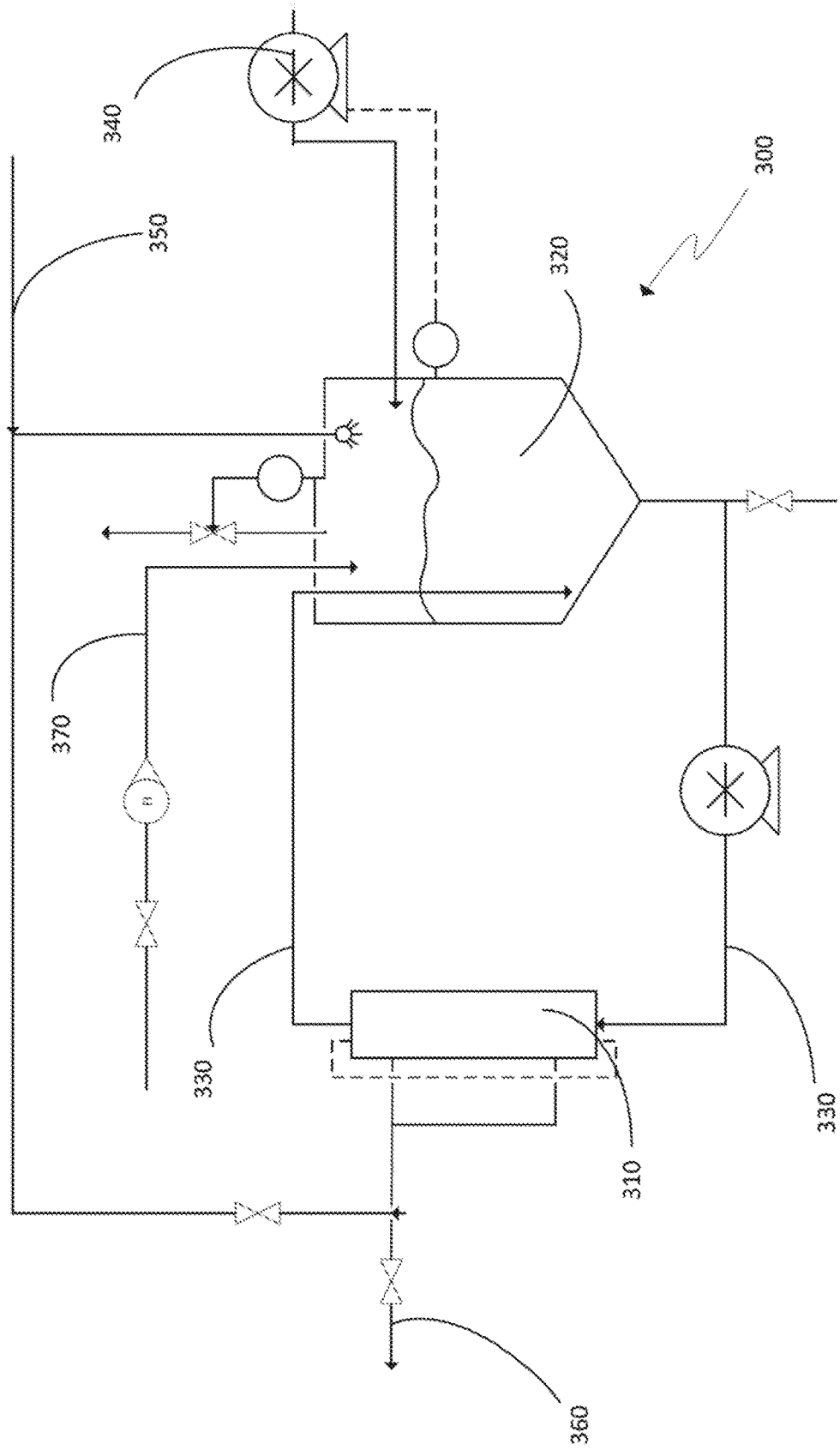


Figure 4

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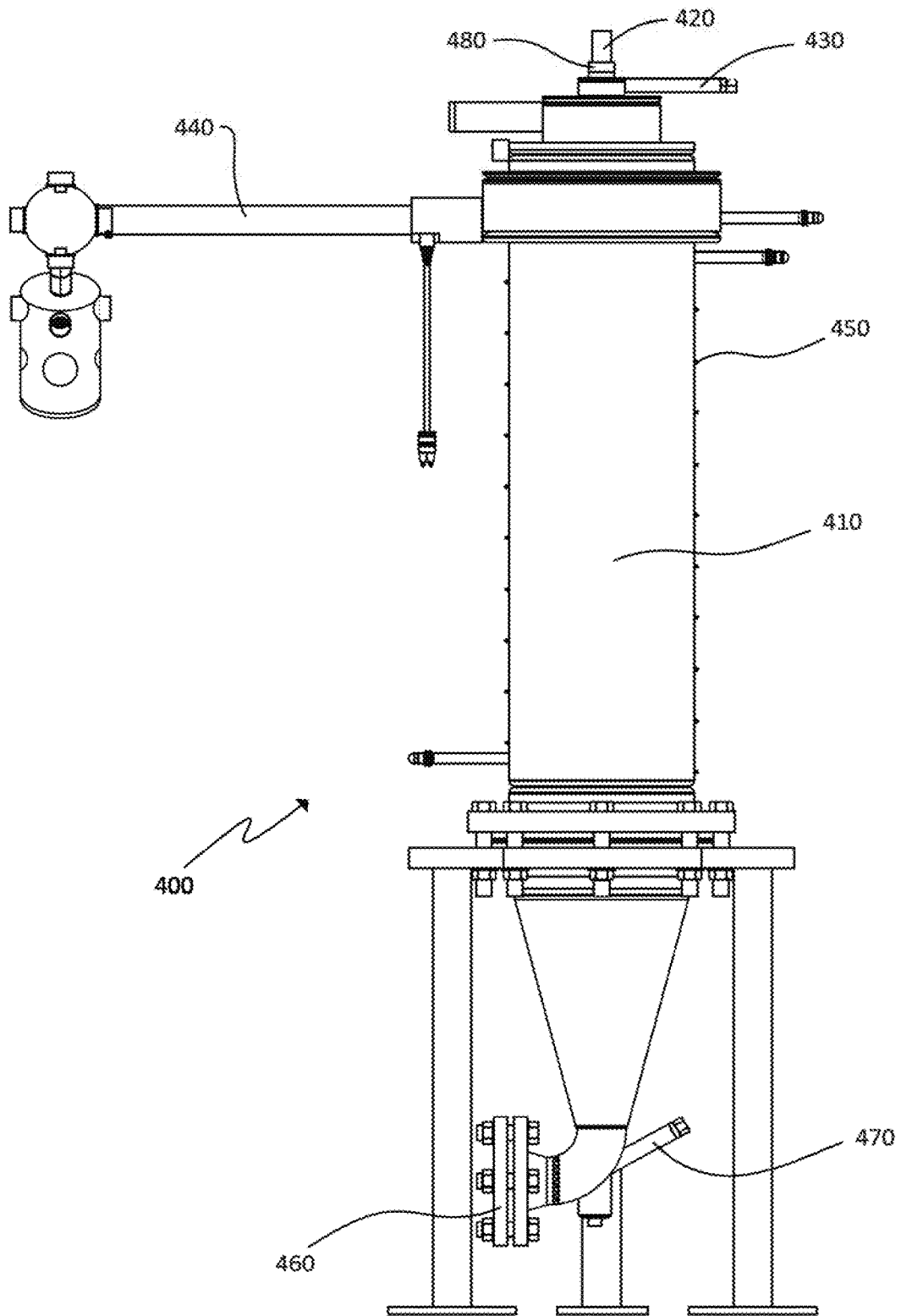


Figure 5

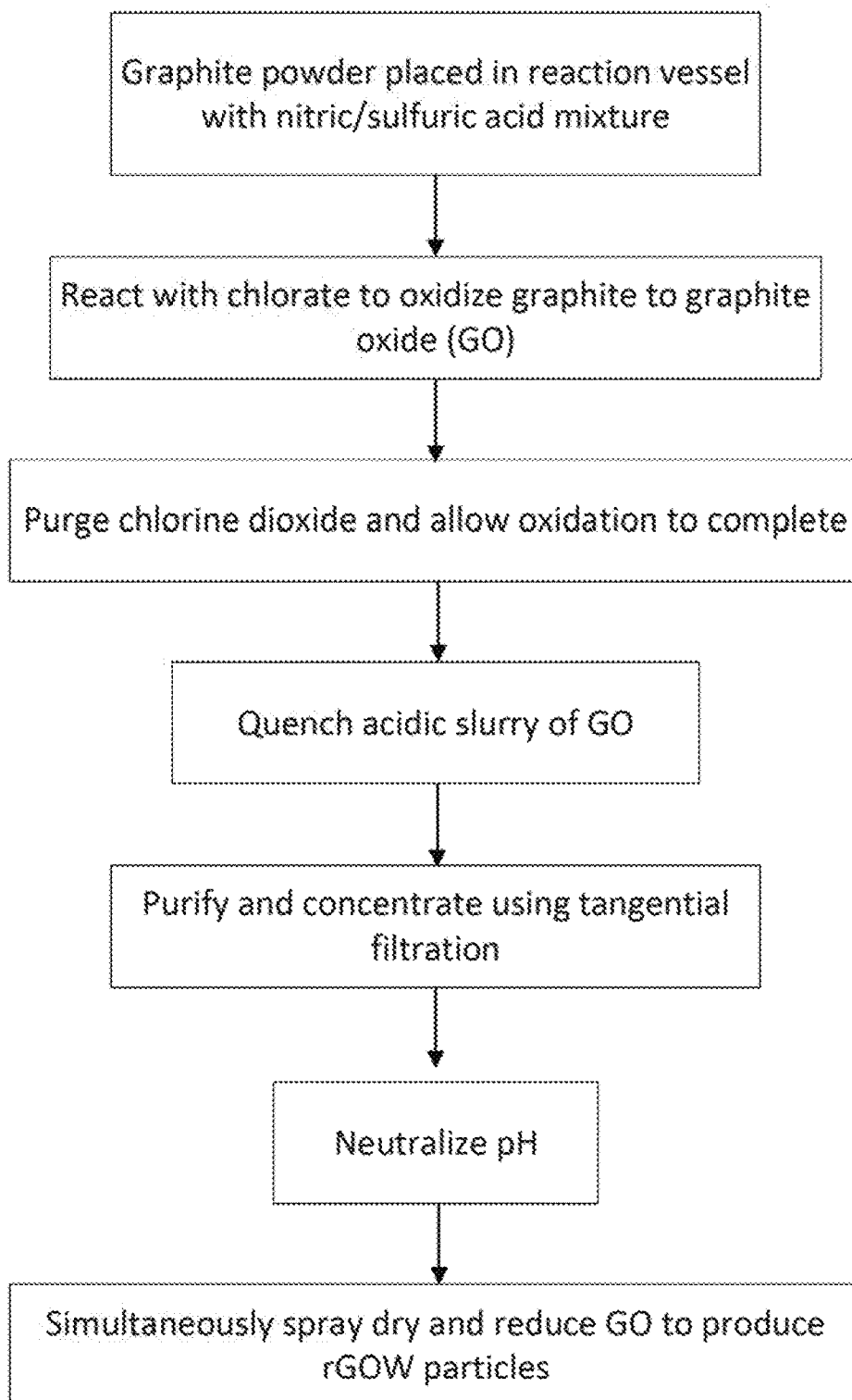


Figure 6



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2020/052459

| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>INV. C08K3/04 C08L23/10<br>ADD.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                   |                                                                                                                               |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
| According to International Patent Classification (IPC) or to both national classification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                   |                                                                                                                               |
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>C08K C08L                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                                                                                                   |                                                                                                                               |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                   |                                                                                                                               |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>EPO-Internal, WPI Data                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                   |                                                                                                                               |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                   |                                                                                                                               |
| Category*                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | Citation of document, with indication, where appropriate, of the relevant passages                                | Relevant to claim No.                                                                                                         |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | EP 2 184 324 A1 (CLARIANT INT LTD [CH])<br>12 May 2010 (2010-05-12)<br>example Comparative Example 21<br>-----    | 1-15                                                                                                                          |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | EP 1 632 529 A1 (BOREALIS TECH OY [FI])<br>8 March 2006 (2006-03-08)<br>paragraph [[0094]]; examples 1-3<br>----- | 1-15                                                                                                                          |
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| X,P                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | EP 3 495 410 A1 (BOREALIS AG [AT])<br>12 June 2019 (2019-06-12)<br>the whole document<br>-----                    | 1-15                                                                                                                          |
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| <div style="display: flex; justify-content: space-between;"> <span><input type="checkbox"/> Further documents are listed in the continuation of Box C.</span> <span><input checked="" type="checkbox"/> See patent family annex.</span> </div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |                                                                                                                   |                                                                                                                               |
| <div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div> |                                                                                                                   |                                                                                                                               |
| Date of the actual completion of the international search<br><br><div style="text-align: center; font-size: 1.2em;">30 April 2020</div>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                   | Date of mailing of the international search report<br><br><div style="text-align: center; font-size: 1.2em;">15/05/2020</div> |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                   | Authorized officer<br><br><div style="text-align: center; font-size: 1.2em;">Balmer, J</div>                                  |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/052459

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date           |
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