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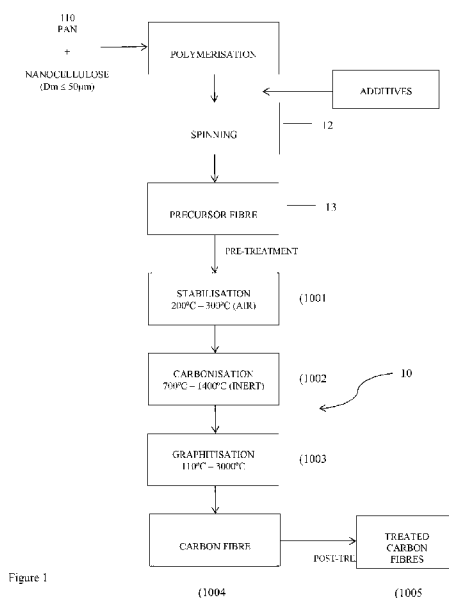


Figure 1

(57) Abstract: A method of producing carbon fibre, the method comprising the steps of (a) spinning precursor fibre filaments from a solution or a dispersion comprising nanocellulose fibrils with a diameter of less than 50 nm and a solvent; and (b) carbonizing the precursor fibre by pyrolysis at an elevated temperature to obtain the carbon fibre.

CARBON FIBRES FROM BIO-POLYMER FEEDSTOCKS

TECHNICAL FIELD

[0001] The present invention relates to production of carbon fibres.

BACKGROUND ART

[0002] Carbon fibres are strong, with an extremely high ratio of strength-to-volume, and are lighter than steel. This makes their use in composites ideally suited to applications where strength, stiffness, lower weight, and outstanding fatigue characteristics are critical requirements. They also can be used when high temperature, chemical inertness and high vibration damping are important. For these reasons, carbon fibre reinforced composites are now used in a wide range of industries, such as lightweight, fuel efficient automobile and aircraft components. The demand for carbon fibre in the automotive sector alone has been projected to more than triple from 3,400 tonnes in 2012 to 12,100 tonnes in 2017.

[0003] To date, high manufacturing costs have meant that the broader uptake of carbon fibre composites has been limited. Carbon fibres are generally made from high grade polyacrylonitrile (PAN), an expensive, petroleum derived polymer that accounts for ~50% of the cost of manufacturing. Approximately 20 % of the production cost is attributed to the energy input that is made significant due to the use of heating processes in carbonisation and graphitisation steps. Consequently, the production cost of carbon fibre could be decreased significantly with the adoption of a lower cost raw material precursor for the carbon and a decrease in the energy input required, such as would be achievable with lower processing temperatures. The use of cheaper textile grade PAN, other less expensive petroleum derived fibres such as polyethylene and polypropylene and other low cost polymers has led to sub-optimal mechanical properties. In many cases such as with thermoplastics including polyethylene (PE) and polypropylene (PP), the precursor polymer fibres are spun from a melt prior to being pyrolysed. The use of plant derived raw materials offers the opportunity for not only bringing down the cost, but also for decoupling from the cost volatility of petroleum in addition to the environmental and supply chain security benefits provided by a renewable and sustainable feedstock. But, while cellulose-derived carbon fibres are known, their share of the market has also been limited by their comparatively poor performance, particularly tensile strength, due to imperfect fibre structure. In addition, extensive pre-processing is typically required, adding significantly to costs. The poor mechanical properties of carbon fibres derived from cellulose may, in part, be derived from the fact that efforts to produce carbon fibres from cellulose to date have employed cellulose materials

composed of agglomerates of smaller diameter primary nanofibrils. The interfaces between primary nanofibrils in an agglomerated fibre can act as conduits for crack propagation, reducing the resistance of the material to mechanical failure under stress. Agglomerates are particularly prolific in cellulose materials derived from higher plants which are also perhaps the most attractive types of cellulose for industrial applications due to their lower cost compared to cellulose from other sources such as bacteria, algae and tunicates. The definition of “higher plants” is well known and includes vascular plants including those that have roots and produce flowers or seeds such as grasses and other members of the superphylum Tracheata. Algae is classified as a “lower plant”. Cellulose materials derived from higher plants and with fibre diameters as small as 50 nm have been used as precursors for carbon fibres however even these fibres are agglomerates of smaller diameter primary fibres that have diameters below 5 nm.

[0004] The use of biopolymers such as plant material for the production of carbon fibres has the potential to both reduce cost and improve the sustainability of the production cycle. Cellulose has a number of significant advantages, such as having a very well-ordered crystal structure and being able to thermally decompose without melting. Natural fibres, such as cotton and ramie, are less desirable for carbonization because of their discontinuous filament structure, and low degree of orientation and impurities arising from the complex structure of natural cellulose sources such as lignin and hemicellulose. New processing techniques are able to make continuous fibres from natural cellulose fibres which have ordered crystalline structures. Cellulose undergoes thermal decomposition without melting. Furthermore, through pyrolysis it forms a strong fibrous carbonaceous material and cellulosic precursors have high thermal conductivity, high purity, mechanical flexibility and low precursor cost although mechanical properties are still inferior to PAN-derived fibres. At present, cellulose derived fibres have low carbon yields and do not have sufficient tensile strength for widespread use. Extensive pre-processing is also typically undertaken, which adds significantly to costs. While cellulosic materials are used as carbon precursors on a large scale, their use is mostly limited to activated carbon as an adsorbant and not as a source for producing carbon fibres.

[0005] Carbon fibres formed by the processing of agglomerated fibrils of cellulose typically result in carbon fibre with poor mechanical properties since the low strength associated with the interface between fibrils in the cellulose agglomerate is typically transferred to the resulting carbon fibre structure. That is, the resulting carbon fibre typically consists of agglomerated carbon fibrils where the bond strength between adjacent fibrils is poor, leading to poor overall mechanical properties in the carbon fibre. Furthermore, carbon fibres produced in a typical carbonisation process typically have significantly reduced volume relative to the cellulose

precursor used such that the diameter of the carbon fibre is less than that of the original cellulose fibre. This is a consequence of the shrinkage that occurs on processing in which much of the non-carbon elements, and even some of the carbon making up the cellulose are removed, leaving the carbon with a much reduced volume. Cellulose has a carbon content of 44.4 % however carbon yields as low as 10-20 % after pyrolysis are well known.

[0006] It will be clearly understood that references to known processes or methods referred to herein does not constitute an admission that the publication forms part of the common general knowledge in the art in Australia or in any other country.

SUMMARY OF INVENTION

[0007] The present invention is directed to production of carbon fibres, which may at least partially overcome at least one of the abovementioned disadvantages or provide the consumer with a useful or commercial choice.

[0008] With the foregoing in view, the present invention in one form, resides broadly in a method of producing carbon fibre, the method comprising the steps of:

- (a) spinning precursor fibre filaments from a solution or a dispersion comprising nanocellulose fibrils with a mean diameter of less than 50 nm; and
- (b) carbonizing the precursor fibre filaments by pyrolysis at an elevated temperature to obtain the carbon fibre.

[0009] In an embodiment of the first aspect, the carbonising results in formation of fibrillar nanostructures such that the mean diameter of the fibrillar nanostructures is less than or equal to the mean diameter of the nanocellulose fibrils.

[0010] In another embodiment of the first aspect, the carbonising results in formation of a first group and a second group of fibrillar nanostructures, wherein the mean diameter of the first group of fibrillar nanostructures is greater than the mean diameter of the nanocellulose fibrils and the mean diameter of the second group of fibrillar nanostructures is less than or equal to the mean diameter of the nanocellulose fibrils.

[0011] In a second aspect, there is provided a method of producing carbon fibre, the method comprising the steps of:

- (a) spinning precursor fibre filaments from a solution or a dispersion comprising nanocellulose fibrils; and

(b) carbonising the precursor fibre filaments by pyrolysis at an elevated temperature to obtain the carbon fibre;

wherein the carbonising results in formation of fibrillar nanostructures such that the mean diameter of the fibrillar nanostructures is greater than the mean diameter of the nanocellulose fibrils.

[0012] In an embodiment, the nanocellulose fibrils have a mean diameter of less than 40 nm and preferably less than 30 nm, more preferably less than 20 nm.

[0013] In another embodiment, the nanocellulose fibrils have a mean diameter of less than 10 nm, preferably less than 8 nm and more preferably less than 5 nm.

[0014] Preferably, the nanocellulose fibrils are derived from higher plants.

[0015] It will be appreciated that references to a specific fibril or fibre diameter do not mean that all of the fibres or fibrils within a sample of material have a diameter of specifically that value. Rather, samples of material typically contain a distribution of fibril/fibre diameters and the diameter value quoted refers to a mean value of the diameter.

[0016] The diameter of fibrils and fibres is typically measured using imaging methods such as scanning electron microscopy (SEM) or transmission electron microscopy (TEM) in which a number of fibres/fibrils within a population are measured in order that a reasonable estimate of the mean diameter can be developed. Therefore, the mean diameter may be calculated on a number-average basis.

[0017] In some embodiments the solution or dispersion of the first or second aspect may comprise an aqueous medium. The applicant has realised that providing a carbon fibre which is formed from spinning precursor fibre filaments from an aqueous dispersion of nanocellulose fibrils (without the addition of any other additional polymer) and carbonising those precursor fibres is highly advantageous in that it alleviates the need for using organic solvents such as dimethyl formamide (DMF). Organic solvents are typically used in prior art processes for forming carbon fibres known in the art. In at least some embodiments, the present invention presents a significant economic advantage over prior art methods in providing a method for producing carbon fibres that reduces and preferably alleviates the need to use organic solvents.

[0018] In alternative embodiments, the precursor fibre filaments are composite fibre filaments comprising nanocellulose fibrils and further comprising another polymer. The

nanocellulose fibrils may be dispersed in a polymer melt. The polymer may comprise one or more polymers including, but not limited to the following: Polyacrylonitrile (PAN), Polyethylene (PE), Lignin, Polypropylene, Polyacrylonitrile-methyl acrylate copolymers (PAN-MA), poly[acrylonitrile-co-itaconic acid] copolymers, poly[acrylonitrile-co-acrylamide] copolymers, Pitch, and other established carbon fibre precursors. The polymers may also include polyolefins, including polyethylene, polypropylene, polymethylpentene, polybutene, polyisobutylene and Polyesters such as Polyhydroxyalkanoates (PHAs), Polylactic acid (PLA) and Polycaprolactone (PCL).

[0019] Using this approach, the use of low cost nanocellulose fibrils in combination with other more expensive polymer fibres such as PAN can lower the cost of carbon fibre production and decrease reliance on petrochemical derived raw materials. Alternatively, the use of nanocellulose fibrils with favourable mechanical properties in combination with other polymers that would otherwise have insufficient mechanical properties to be used in certain applications may result in carbon fibres with improved mechanical properties over carbon fibres derived from the polymers had the nanocellulose fibrils not been present. This results from the superior mechanical properties provided by the carbon derived from nanocellulose fibrils. In some cases, the lower limit of fibre diameter that can be drawn from a polymer melt is limited by the mechanical properties of the melt since small diameter polymer melts are more fragile and prone to breakage than larger polymer melt fibres. A polymer melt with poor mechanical properties may be unable to produce small fibre diameters during melt spinning demanded by many applications. The addition of nanocellulose fibrils to a polymer melt may provide additional strength to the melt, reinforcing it and enabling finer fibres to be spun. This approach then may enable the adoption of polymer alternatives to PAN that would otherwise not be viable without the use of the nanocellulose fibrils.

[0020] In some embodiments, the precursor fibre filaments comprising the polymer melt described above may be spun by wet spinning nanocellulose fibrils/polymer blends in organic solvents. The organic solvents may be selected from solvents including, but not limited to Dimethylformamide (DMF) or Dimethyl Sulfoxide (DMSO). Such spinning is known as organic wet spinning.

[0021] In an alternative embodiment, the precursor fibre filaments may be spun by melt spinning polymers such as lignin and/or polyethylene blended with nanocellulose fibrils. The addition of lignin to the nanocellulose fibrils improves melt spinnability and processability of the

produced carbon fibres because lignin is melt processable in its own right, with melt flow assisting fibrillary alignment, and, having a high aromatics content, promoting cross-linking.

[0022] The applicant has realised that using lignin, one of the world's most abundant biomolecules with a carbon content of more than 60%, for producing carbon fibres may present significant benefits particularly with a view towards reducing costs for production of carbon fibres on a large scale.

[0023] In a further alternative embodiment, the precursor fibre filaments may be spun by spinning of continuous fibres from an aqueous dispersion of the nanocellulose fibrils.

[0024] In an embodiment, the precursor fibre filaments may be impregnated with a carbonization enhancing additive such as an organo-silicone additive.

[0025] In further embodiments spinning enhancing agents such as polyethylene oxide, polyvinyl alcohol or an amine group containing compound may be added to the solution or the dispersion. Furthermore, such agents may also be added to disrupt hydrogen bonding in the solution or the dispersion thereby resulting in improved elongation and processing of the precursor fibre filaments.

[0026] In a third aspect, the invention provides a method of producing carbon fibre, the method comprising the steps of

(a) homogenising nanocellulose fibrils having a mean diameter of less than 50 nm to form homogenised nanocellulose fibrils;

(b) carbonising the homogenised fibrils by pyrolysis at an elevated temperature to obtain the carbon fibre;

wherein the carbonising results in formation of fibrillar nanostructures such that the mean diameter of the fibrillar nanostructures is greater than the mean diameter of the nanocellulose fibrils.

[0027] The applicant has realised that homogenising the nanocellulose fibrils by way of dispersing nanocellulose fibrils in a solvent followed by drying of the homogenised fibrils by methods such as freeze drying and further carbonisation results in formation of carbon fibres which do not necessarily require the use of expensive polymers such as PAN and the like discussed in previous sections.

[0028] In some embodiments, the nanocellulose fibrils may be pre-treated by a pre-

treatment process such as a halogenation pre-treatment step. The halogenation pre-treatment may comprise contacting the nanocellulose fibrils with a halogen and/or a halogen derivative to form a nanocellulose fibril-halogen mixture and heating the mixture to a heating temperature of at least 80°C for a heating time period of at least 10 minutes; thereby forming halogenated nanocellulose fibrils.

[0029] The halogenation pre-treatment step may be utilised for bromination and/or iodisation and/or chlorination.

[0030] The halogenation step may further comprise the step of irradiating the nanocellulose-halogen mixture under visible and/or ultraviolet and/or infra-red radiation for promoting halogenation of the nanocellulose fibrils.

[0031] A skilled person would readily appreciate that the halogenation pre-treatment step may be used for pre-treating the precursor fibre filaments spun from nanocellulose fibrils as discussed in the first and second aspects. Alternatively, the halogenation pre-treatment step may also be used for pre-treating the nanocellulose fibrils directly in conjunction with the third aspect of the present invention.

[0032] Without wishing to be bound by theory, the applicants theorise that adopting the halogenation pre-treatment step prior to the carbonisation step for the method of the present invention results in higher yields of carbon fibre product relative to the carbon content of the precursor material.

[0033] In an embodiment, the carbonizing step is preceded by a stabilisation step wherein the precursor filaments are heat treated at an intermediate stabilisation temperature. The precursor fibres may be stabilised by heating and stretching in a heating chamber with well controlled gas flow. This stabilisation process is commonly introduced to induce dehydration/dehydrogenation and/or oxidation, thus creating cross-linked “ladder polymer” chains and as a result the T_g of the fibre increases.

[0034] In an embodiment, the process further comprises a graphitization step. In one embodiment, the graphitisation step is carried out at a graphitisation temperature that is equal to or greater than the elevated carbonisation temperature. During graphitisation, the precursor fibre filaments may be oriented in a preferred orientation by mechanical means such as stretching to apply tension. The step of applying tension to the precursor fibre filaments helps in maintaining the fibre filaments in a desirable orientation and/or reduces variation in longitudinal dimension of the fibre filaments.

[0035] In an embodiment, the method further comprises a processing step for enhancing carbon bonding strength in the precursor fibre filaments. Carbon bonding strength may be enhanced by adding metal ions (in solution form such as V^+ ; Cr^{++} ; Mn^+ ; Fe^{++} ; Co^+ ; Ni^{++} ; Cu^+). Addition of metal ions may also be balanced by addition of halogenated compounds such as bromides and chlorides. In one embodiment, the metal ions may be added in the form of adding a metal solution containing one or more compounds or mixtures of compounds including but not limited to chlorides, bromides, iodides, nitrates, sulphates, phosphates with metals including but not limited to Fe, Ni, Co, Cu, Sn, Sb, Mn, Cr, V, Ti. The metal ions are preferably added to the precursor fibre prior to the carbonisation step. In some embodiments, the metal ions may be impregnated into the precursor fibre filaments, for example by contacting the precursor fibre filaments with a solution containing the metal ions.

[0036] In an embodiment, one or more catalysts may be added or applied for catalysing stabilisation and/or carbonisation of the precursor filaments. The catalysts may contain metals or mixtures of metals including but not limited to zinc, gallium, In, Sn, Sb, Bi, Cu, Ni, Co, Fe, Ru, Mn, Cr, V, Ti, Al, Au, Ir, Pt, Zr, Mo, Ag, Ga, Ca, Mg, Be, Sr and non-metals, Na, K, B, S, P, N, Se and may be in the form of oxides, halides, or reduced or partially reduced metals or mixtures of metals.

[0037] In an embodiment, the step of carbonisation comprises slow pyrolysis in which temperature is increased to an initial temperature in the range of 600°C to 1500°C, more preferably 800°C to 1100°C under an inert atmosphere (such as N_2 /Ar atmosphere).

[0038] In an embodiment, the process further comprises a graphitisation wherein the carbonised fibre filaments are graphitised at a graphitisation temperature in the range of 900°C to 3000°C.

[0039] In an embodiment, the carbonisation stage is preceded by a stabilisation stage of heating the precursor filaments at a stabilisation temperature in the range of 150°C to 350°C.

[0040] In an embodiment, the nanocellulose fibrils have an aspect ratio of at least 250. Aspect ratio is the ratio of length to diameter of the fibrils.

[0041] In an embodiment the nanocellulose fibrils are derived from higher plants.

[0042] In one embodiment, the nanocellulose fibrils are derived from plant material in which the amount of hemicellulose in the plant material is greater than the amount of lignin in the plant material.

[0043] In one embodiment, the nanocellulose fibrils are derived from a grass species having C4 anatomy.

[0044] In one embodiment, the nanocellulose fibrils are derived from a drought-tolerant grass species.

[0045] In one embodiment, the nanocellulose fibrils are derived from arid grass species.

[0046] In one embodiment of the present invention, the nanocellulose fibrils are derived from Australian native arid grass known as “spinifex”. Spinifex (also known as ‘porcupine’ and ‘hummock’ grass) is the long-established common name for three genera which include *Triodia*, *Monodia*, and *Symplectrodia* (not to be confused with the grass genus *Spinifex* that is restricted to coastal dune systems in Australia). Hummock grassland communities in arid Australia are dominated by spinifex species of the genus ‘*Triodia*’. There are 69 described species of *Triodia*, which are long-lived and deep rooted allowing root growth to penetrate through tens of metres under the ground. Of the 69 species, abundant species are two soft species called *T. pungens*, *T. shinzii* and two hard species *T. basedowii*, *T. longiceps*. *T. Pungens* has a typical composition of: cellulose 37 %, hemicellulose : 36 %, lignin: 25% and ash 4 %

[0047] The present invention is also directed toward the structure of the carbon fibres that result from the methods of processing described herein. By using a cellulose precursor composed of separated nanofibrils with mean diameter less than 50 nm rather than larger agglomerates of fibrils as discussed earlier in the background section, the carbon fibre formation process described herein has been found to result in carbon fibres in which the individual cellulose nanofibrils may be fused or adhered together to form a carbon fibre of greater diameter than the precursor cellulose nanofibrils, rather than a more loosely bonded agglomerate. This adhesion results in significantly greater bond strength between components in the carbon fibre and the resulting carbon fibres have the appearance of single strands of carbon as opposed to the more fracturous materials obtained with the use of cellulose agglomerates. This results in superior mechanical and electrical properties relative to conventional cellulose-derived carbon fibre. As such, the present invention is directed to carbon fibres formed by processing cellulose fibres of smaller mean diameter in comparison than the mean diameter of the resulting carbon fibre.

[0048] Carbon fibres formed by the processing of agglomerated fibrils of cellulose typically result in carbon fibre with poor mechanical properties since the low strength associated with the interface between fibrils in the cellulose agglomerate is typically transferred to the resulting carbon fibre structure. That is, the resulting carbon fibre typically consists of agglomerated

carbon fibrils where the bond strength between adjacent fibrils is poor, leading to poor overall mechanical properties in the carbon fibre. Furthermore, carbon fibres produced in a typical carbonisation process typically have significantly reduced volume relative to the cellulose precursor used such that the diameter of the carbon fibre is less than that of the original cellulose fibre. The carbon fibres produced from the method of the present invention addresses one or more of the issues such as agglomeration and poor mechanical properties.

[0049] With the foregoing in view, in another aspect the present invention resides in carbon fibres formed from a cellulose precursor where the cellulose precursor comprises nanofibrils with diameter less than 50 nm and wherein the carbon fibres have elongate nanostructures with a mean diameter in the range of 5 nm to 200 nm and a mean length in the range of 5 μm to 500 μm .

[0050] In another aspect, the present invention provides a carbon fibre comprising carbonised nanocellulose fibrils, wherein prior to carbonisation, the nanocellulose fibrils have a mean diameter of less than 50 nm.

[0051] In another aspect, the present invention provides a carbon fibre comprising carbonised nanocellulose fibrils, said carbonised fibrils having a nanostructure with a mean diameter that is greater than mean diameter of the nanocellulose fibrils prior to carbonisation.

[0052] In cases where processing conditions do not promote the fusion of individual nanocellulose fibrils to form a larger diameter carbon fibre or the extent of fusion is limited such that carbon fibres are formed from only a small number of fused nanocellulose fibrils, the diameter of the resulting carbon fibres may be smaller than that of the precursor nanocellulose fibrils.

[0053] With the foregoing in view, in another aspect the present invention resides in carbon fibres formed from a cellulose precursor where the cellulose precursor comprises nanofibrils with mean diameter less than 50 nm and wherein the carbon fibres have a mean diameter smaller than that of the cellulose precursor.

[0054] In another aspect, the invention provides carbon fibres formed from a cellulose precursor where the cellulose precursor comprises nanofibrils with mean diameter of less than 50 nm and wherein the carbon fibres have elongate nanostructures with a mean diameter in the range of 5 nm to 200 nm and a mean length in the range of 5 μm to 20 μm .

[0055] In yet another aspect, the invention provides carbon fibres formed from a cellulose

precursor where the cellulose precursor comprises nanofibrils with mean diameter less than 50 nm and wherein the carbon fibres have elongate nanostructures with a mean diameter of less than 50 nm.

[0056] In another aspect, the invention provides carbon fibres formed from a cellulose precursor where the cellulose precursor comprises nanofibrils with mean diameter less than 50 nm and wherein the carbon fibres comprises a first group and a second group of carbon fibres, wherein the first group of carbon fibres have elongate nanostructures with a mean diameter of less than or equal to 50 nm and the second group of carbon fibres have elongate nanostructures with a mean diameter of more than 50 nm.

[0057] In yet another aspect, the invention provides a carbon fibre comprising halogenated nanocellulose fibrils that have been carbonised to form the carbon fibre.

[0058] In yet another aspect, the invention provides a method of producing carbon fibre, the method comprising the steps of

(a) homogenising lignin in a solution or dispersion; and

(b) carbonising the lignin by pyrolysis at an elevated temperature to obtain the carbon fibre.

[0059] In another aspect, the invention also provides a method of producing carbon fibre, the method comprising the steps of:

(a) spinning precursor fibre filaments from a solution or a dispersion comprising lignin; and

(b) carbonizing the precursor fibre filaments by pyrolysis at an elevated temperature to obtain the carbon fibre.

[0060] The lignin may also be pre-treated before the carbonisation step by the halogenation pre-treatment step described in the previous sections.

[0061] Any of the features described herein can be combined in any combination with any one or more of the other features described herein within the scope of the invention.

[0062] The reference to any prior art in this specification is not, and should not be taken as an acknowledgement or any form of suggestion that the prior art forms part of the common general knowledge.

BRIEF DESCRIPTION OF DRAWINGS

[0063] Various embodiments of the invention will be described with reference to the following drawings, in which:

[0064] Figure 1 is a flow diagram showing a process of producing carbon fibres in accordance with a first embodiment of the present invention.

[0065] Figure 2 is a flow diagram showing a process of producing carbon fibres in accordance with a second embodiment of the present invention.

[0066] Figure 3 is a flow diagram showing a process of producing carbon fibres in accordance with a third embodiment of the present invention.

[0067] Figures 4A, 4B and 4C show Transmission Electron Microscopy (TEM) images of nanocellulose fibrils and pyrolised nanocellulose fibrils obtained in Example 1.

[0068] Figure 5 represents the Raman spectra of freeze dried spinifex nanofibrillated cellulose (NFC) obtained after carbonisation (240 °C under air for 1 h, 800 °C under argon for 2.5 h) in Example 1.

[0069] Figures 6A and 6B show Scanning Electron Microscopy (SEM) images of pyrolised nanocellulose fibrils obtained in Example 1.

[0070] Figure 7 shows thermogravimetric analysis (TGA) data for the cellulose nanofibrils derived from Spinifex grass as per Example 1.

[0071] Figure 8 shows FTIR spectra comparing samples from example 1 at different pyrolysis temperatures and time durations.

[0072] Figure 9 shows pictures of NFC sheets at different stages during carbonisation in accordance with Example 2.

[0073] Figure 10: represents the Raman spectra for carbonised spinifex NFC sheet in accordance with Example 2.

[0074] Figure 11 shows images of samples (including comparative examples) before and after carbonisation in accordance with Example 2.

[0075] Figure 12 represents thermograms of the different samples (including comparative

examples) under nitrogen in accordance with Example 2.

[0076] Figure 13 represents TGA data of samples in accordance with Example 2.

[0077] Figure 14 represents TGA thermograms of the halogen absorbed samples (including comparative samples) in accordance with Example 2.

[0078] Figure 15 shows images of halogen absorbed samples (including comparative examples) before and after carbonisation.

[0079] Figure 16 TGA shows TGA thermograms of lignin and brominated lignin (with 98 wt. % increase) under nitrogen in accordance with Example 3.

[0080] Preferred features, embodiments and variations of the invention may be discerned from the following Detailed Description which provides sufficient information for those skilled in the art to perform the invention. The Detailed Description is not to be regarded as limiting the scope of the preceding Summary of the Invention in any way. The Detailed Description will make reference to a number of drawings as follows:

DESCRIPTION OF EMBODIMENTS

[0081] Referring to Figure 1, a process (100) for producing carbon fibres in accordance with the present invention is illustrated. The process comprises an initial step (110) of uniformly mixing nanofibrillated cellulose (NFC) with diameter of less than 50 nm with PAN in an organic solvent, Dimethylformamide (DMF). The quantity of nanocellulose added may be variable and may range from 2.5 wt% to 25 wt%. The mixture may be subsequently polymerized in a polymerization step (110) to form a composite blend of PAN-nanocellulose. Prior to spinning precursor fibre filaments from the blend, spinning enhancing agents such as polyethylene oxide, polyvinyl alcohol or amine groups may be added to disrupt the hydrogen bonding in the composite blend. Subsequently, the precursor fibre filaments may be obtained by organic solvent based spinning in a spinning step 120.

[0082] The precursor fibres as obtained may be stabilised by heating and stretching in a chamber with well controlled gas flow in a stabilisation step (1001) in which the precursor fibres may undergo oxidation, dehydration and/or dehydrogenation at an elevated temperature that may lie in the range of 200⁰C to 350⁰C for 0.5 to 4 hours by ramping up the temperature of the chamber from room temperature at a ramping rate of 1-5 °C/min. This process creates cross-linked “ladder polymer” chains and the T_g of the precursor fibre increases.

[0083] After stabilising the precursor fibres, carbonisation (1002) of the oxidised fibres can be carried out at temperature of approximately 800°C under inert conditions (Ar/N₂ atmosphere). The carbonisation step is followed by graphitisation (1003) of the carbonised fibres at temperatures ranging from 1100°C to 3000°C while stretching the carbonised fibres to ensure preferred crystalline orientation to form carbon fibres (1004).

[0084] Prior to or during carrying out the stabilisation step (1001), the precursor fibres may be treated with metal ion containing solutions (such as FeCl₃, NiNO₃, CoSO₄ etc) in a pre-treatment step. Addition of such metal ions is associated with increased stabilization rates, increased efficiencies and rates of carbonization, and improved final fibre properties. Control and acceleration of re-dehydration and cyclisation reactions promoted by the metals may be balanced by inhibition of complete carbon oxidation. Halogenated compounds (such as bromides and chlorides) are thought to inhibit complete oxidation and may act synergistically with metal oxides through activated precursors that can then undergo a catalysed dehydrogenation-aromatization reaction with minimal deep oxidation. They may also be involved in addition reactions to the polymer in their own right, which can in turn lead to dehydrogenation (through a dehydrohalogenation and subsequent crosslinking process). In addition, carbon fibre yields (after carbonisation) are typically far less than might be achieved theoretically due to de-polymerization and reactions of backbone carbons to CO, CO₂, organic volatiles, acids, and tars. Efficient catalysts promote the direct carbon to carbon bond formation as opposed to loss of carbon through side reactions that helps in increasing overall yield. In addition to treating with metal ion containing solutions new nanoparticle based catalysts including zinc and iron oxides may also be used for promoting the carbonisation of the treated precursor fibres. These catalysts include doped and binary metal oxides, sulfides and halides based on low cost hosts including iron, titanium, and manganese. These catalysts may be added to the precursor fibres by ultrasonic spray pyrolysis and precipitation.

[0085] Finally, post-formation treatments may also be carried out for enhancing the carbon bonding strength between the resin matrix (eg. PAN) and the NFC to obtain strengthened carbon fibres (1005).

[0086] Referring to Figure 2, a process (200) for producing carbon fibres in accordance with the present invention is illustrated. The process comprises an initial step of adding NFC with diameter of less than 50 nm with polymers such as lignin and/or polyethylene to form a polymerised nanocomposite melt. Precursor fibres are subsequently obtained by melt spinning (220) of the nanocomposite melt.

[0087] The precursor fibres (230) may be further processed in accordance with a halogenation pre-treatment step 235. The halogenation pre-treatment step may comprise forming a mixture of halogen material or a halogen derivative with the precursor fibre and heating the mixture to an elevated temperature. For example, a sample of the precursor fibre 230 may be mixed with a pre-determined quantity of liquid bromine to form a bromine-precursor fibre mixture. The mixture may be introduced and sealed in a heat resistant quartz tube. The contents of the quartz tube may then be subjected to an irradiation step involving irradiating the contents of the tube with simulated solar light. Such an irradiation step promotes halogenation of the precursor fibre. The halogenated precursor fibre is then collected after initially drying the halogenated precursor fibre and subsequently subjected to the processing steps 1001-1005 in accordance with the process described in the first embodiment to obtain carbon fibres.

[0088] Referring to Figure 3, a process (300) for producing carbon fibres in accordance with the present invention is illustrated. The process comprises an initial step of mixing NFC (with diameter of less than 50 nm) with water to form a colloidal dispersion in the form of a NFC hydrogel. Precursor fibre filaments may be spun in an acetone coagulation bath by aqueous dope spinning of the NFC hydrogel.

[0089] The precursor fibres (330) may be further processed in accordance with the processing steps 1001-1005 in accordance with the process described in the first embodiment to obtain carbon fibres

[0090] For a better understanding of embodiments in accordance with the present invention, together with the technical means, the characteristics and the purposes thereof, reference is made to the following examples described in the foregoing passages.

EXAMPLE 1 Pyrolysis of cellulose nanofibrils

[0091] Nanofibrillated cellulose (NFC) derived from spinifex grass with an average diameter of 3.7 ± 1 nm and length of several microns was produced based on the high pressure homogenisation method described in the applicant's previously filed international patent application PCT/AU2014/050368 and incorporated herein by reference. A homogeniser such as EmulsiFlex homogeniser or GEA homogenizer was used for homogenising the NFC.

[0092] Figure 4A illustrates a Transmission Electron Microscopy (TEM) image of the homogenised nanofibrillated cellulose (NFC) derived from spinifex grass before the carbonisation step. After pyrolysis at 350°C, under inert (helium) atmosphere, the fusion of NFC nanofibers occurs to form larger diameter carbon fibres having a diameter of 100 nm (from 3.7

nm NFC diameter to 100 nm carbon fibre diameter) as shown in Figures 4B and 4C. A 24 % residual mass was obtained after pyrolysis at 350 °C. Further, the carbonisation of the freeze dried spinifex NFC was also performed using a higher temperature carbonisation procedure, by stabilising the carbon fibre under air at 240 °C for 60 min then heating to 800 °C at a ramp rate of 5 °C/min followed by holding at 800 °C for 150 min under argon. The measured residual mass was 10 %. The quality of the resulting carbon was assessed based on the Raman spectra, as judged by the degree of disorder which is indicated by the 'D/G ratio'. The peaks of the graphite structure-derived G-band and the defect-derived D-band appear in the vicinities of 1590 cm⁻¹ and 1350 cm⁻¹, respectively as shown in Figure 5. The smaller the value, the more of the graphitic structure was present. As in Figure 2, the D/G ratio for freeze dried sample was 1.10. Figures 6A and 6B show the TEM and SEM images of these carbonised fibres. It can be seen that even at higher temperatures of 800°C, the fibre shape is retained after pyrolysis.

[0093] Thermogravimetric analysis: TGA results showed the onset degradation temperature to be about ~ 266°C for the cellulose nanofibrils (see Figure 7) whereas cellulose nanocrystals from commercial microcrystalline cellulose (MCC, Avicel PH 101 NF) showed decomposition temperature about ~ 330°C.

[0094] Differential scanning calorimetry: As shown in Table 1 below, the plant derived cellulose nanofibrils showed the endothermic transition onset at 297.4°C with the maximum at 337.5°C under inert atmosphere (nitrogen).

Table 1:

Code	Sample	Transitions	temp	Onset	delta H
			(deg C)	(deg C)	(J/g)
N-NFC0	Plant derived NFC (freeze dried)	Endotherm	337.5	297.4	171.1
Zn-NFC0	ZnO-treated plant derived NFC (freeze-dried)	Endotherm	330.3	296.5	139.4

[0095] The catalyst (zinc oxide, 0.3 micron particles) had no significant effect on the lowering the thermal transition.

[0096] The low endotherm for plant derived cellulose nanofibrils can be related to the metal ions present in some plants which might be adsorbed as nutrients during their growth. As the ICP-OES analysis suggested, about 12 mg/kg of zinc was present in the nanofibrils. This metal and other metal ions may act as a natural catalyst and possibly reduce the required amount of external catalyst. Such metal ions may also act as co-catalysts.

[0097] Pyrolysis: The plant derived nanofibrils were subjected to pyrolysis. Figures 4A and 4B compare the morphology of the cellulose nanofibrils before and after pyrolysis. The high aspect ratio nanofibrils can be seen in figure 4A, with average diameter 7 nm (below 20 nm) and the average length of 3.5 microns (below 7 micron).

[0098] As observed from Figure 4B, upon pyrolysis at 350°C for 30 minutes, these small nanofibrils were observed to fuse together and form slightly thicker nanofibrils with diameter below 150 nm and increased length of 10-12 microns. The fusion of adjacent nanofibrils and increment in the length offers an advantage for producing stronger carbon fibres.

[0099] In another sample of the plant derived nanofibrils, zinc oxide was added as a catalyst. Fig 4C depicts a TEM image of a sample of the plant derived nanofibrils (with ZnO) pyrolysed at 350°C for 30 minutes. The fibrillar structure is maintained in the carbon fibre.

[00100] The high aspect ratio of cellulose precursors is vital in (1) Forming percolating network between them, (2) Increased viscosity to facilitate the fibre-spinning (3) forming long pyrolysed carbon fibres.

[00101] The Fourier Transformation Infrared (FTIR) shown in Fig 8 confirms the structural changes (dehydroxylation, oxidation, breakage of glycosidic linkages) and the formation of C=C and C=O bonds which are related to the graphitic structure in the carbon fibres. Based on the peak intensity of C=C bond at 1620 cm⁻¹ the sample pyrolysed at 300 °C for 60 min showed a partial decomposition, whereas the more extensive decomposition for fibres pyrolysed at 350 °C and 400 °C can be seen. A comparative example of a carbon fibre formed from another source of cellulose is also shown.

EXAMPLE 2- Pyrolysis of nanofibrillated cellulose (NFC) paper

[00102] An NFC suspension was obtained after homogenisation in accordance with the process described under example 1. The suspension was freeze-dried by immersing in liquid nitrogen and drying under vacuum in a lyophiliser/freezer-drier in order to obtain dry lyophilizate or fluffy powder of NFC. A thin sheet (paper) was produced from the NFC dispersion by

vacuum filtering using a Büchner funnel fitted with a cellulose acetate membrane filter (pore size: 0.45 μm , diameter: 47 mm. Advantec, Toyo Roshi Kaisha, Ltd, Japan). Prior to filtration, the dispersion was stirred for 24 hours, then filtration was continued until the wet sheet of NFC was formed. The wet sheet was peeled from the filter paper, placed between Teflon sheets and compression-moulded using a hydraulic press with no significant force at 103 °C for one hour, then the sample was removed and conditioned at room temperature and 65% humidity for a week prior to testing. For ease of reference, the sheet of NFC will be referred to as “NFC paper”.

[00103] When the spinifex NFC was made in sheet (paper) form, the residual mass after carbonisation to 800 °C was higher at about 19% on a mass basis. Figure 9 shows the pictures of spinifex NFC sheet, after stabilisation at 240 °C and after carbonisation at 800 °C.

[00104] This NFC in sheet form gave a D/G ratio of about 1.05 in the Raman spectra (Figure 10). When compared with existing literature, such a low D/G ratio after carbonisation was only obtained for cellulose from tunicates, which are marine animals. For cellulose from plant based materials, the D/G ratio is typically higher, at between 1.20 to 1.46.

[00105] The carbonisation of spinifex NFC was compared with other forms and sources of cellulose such as commercially available microcrystalline cellulose (MCC, derived from wood sources, Avicel PH-101 NF (Farm grade), with a particle size of 50 μm (purchased from FMC biopolymers, Philadelphia, United States)), sulphuric acid hydrolysed cellulose nanocrystals (CNC, with an average diameter of 6.9 ± 35 nm and length of 244.5 ± 54 nm) and Whatman filter paper (derived from cotton), as shown in Figure 11.

[00106] Figure 12 shows thermograms of the samples heated under nitrogen to 800 °C. It can be seen that spinifex nanofibrillated cellulose (NFC) exhibited higher residual mass (%) than others, at 18% on a mass basis.

[00107] Table 2 compares the residual mass (%) values obtained from thermogravimetry under nitrogen and carbonisation under air to 240 °C and then under argon to 800 °C. It can be seen that higher residual mass (%) was observed for sheets made from spinifex NFC.

Table 2: Residual mass (%) from thermogravimetry and pyrolysis tests.

Sample	Residual mass (%) from TGA at 800 °C	Residual mass (%) measured from carbonisation in furnace to 800 °C
Whatman filter paper (Cotton)	8	13
Microcrystalline cellulose Avicel PH-101 (Wood)	12	13
Sulphuric acid hydrolysed cellulose nanocrystals (CNC)	12	14
Homogenized Spinifex NFC (sheet)	19	19-22

Halogenation of NFC paper

[00108] Halogenation of NFC paper was carried out.

UV light promoted bromination of NFC

[00109] A weighed amount (40 mg) of NFC was taken into a quartz tube. Liquid bromine (about 1.1 mmol) was added and the tube was sealed with a Teflon coated rubber septum. The tube was then irradiated under a sun simulator (PLS-SXE300) at 120 °C for 1-2 h. Bromination was observed as a colour change from white to dark-red and then black for cellulose and from brown to black for lignin. These samples were then dried under vacuum at room temperature. To quantify bromination, the percentage weight increase was calculated with reference to the initial weight.

Iodine Absorption

[00110] For iodine absorption, NFC paper was weighed and closed in sample vials with 50 mg iodine beads, and heated at 100 °C for 30 min to generate fuming iodine and then left for 24 h.

[00111] For bromine absorption cellulose papers were immersed in 2 mL of bromine in sample vials at room temperature for 24 h. After absorption, all the samples were purged with nitrogen overnight (15 h). The percentage weight increase was calculated with reference to the initial weight.

[00112] Cellulose samples including NFC were brominated via photo-irradiation under an air atmosphere as described above. With 12.4 wt. % increase after bromination, the brominated

spinifex NFC sheet showed higher residual mass following TGA to 800 °C compared with the un-modified NFC sheet (Figure 13).

[00113] Similarly halogen (iodine and bromine) absorbed NFC sheets showed higher residual masses in both TGA and under carbonisation to higher temperatures. Figure 9 shows the TGA thermogram for the halogen absorbed samples compared with neat spinifex NFC. In Figure 9, “I-absorbed WMFP” denotes iodine-absorbed Whatman filter paper, “I-absorbed NFC” denotes iodine-absorbed Spinifex nanofibrillated cellulose, “Br-absorbed WMFP” denotes bromine absorbed Whatman filter paper and “Br-absorbed NFC” denotes bromine-absorbed Spinifex nanofibrillated cellulose.

[00114] Figure 10 represents a visual comparison of various cellulosic materials before and after carbonation (240 °C under air 1 h and heated to 800 °C under argon at 5 °C/min ramp rate). (1) denotes iodine-absorbed Whatman filter paper, (2) denotes iodine-absorbed spinifex NFC, (3) denotes bromine-absorbed Whatman filter paper and (4) denotes bromine-absorbed spinifex NFC. The residual mass (%) with reference to initial amount of cellulose is listed in Table 3.

Table 3: Residual mass % from TGA and after carbonisation of halogen absorbed samples

Sample	Residual mass (%) from TGA at 800 °C	Residual mass (%) measured from carbonisation to 800 °C in furnace (with reference to initial cellulose)
Whatman filter paper (Cotton)	8	13
Spinifex NFC sheet	19	22
Iodine absorbed Whatman filter paper (Cotton)	23	19
Iodine absorbed spinifex NFC sheet	31	30
Bromine absorbed Whatman filter paper (Cotton)	36	33
Bromine absorbed spinifex NFC sheet	46	41

[00115] It can be seen that both iodine and bromine absorbed spinifex NFC samples showed higher residual mass (%). We observed in the TGA that the absorption of halogens facilitated early mass loss, assumed to be due to dehydrohalogenation in these samples. The halogen-absorbed cellulose samples showed no significant difference with respect to the degree of disorder (D/G ratio), which ranged between 1.09 to 1.15 for these samples.

EXAMPLE 3- Bromination of Lignin

[00116] Kraft alkali lignin was purchased from Sigma Aldrich (Castle Hill, Australia) and used as received.

[00117] Another component of lignocellulosics, lignin was also brominated under halogenating conditions as discussed under example 3. After the bromination, the weight percentage increase was about 98 % which accounted for the bromine adding to the lignin molecules. Figure 11 compares the TGA thermograms of neat lignin and brominated lignin. An early stage weight loss (which began at around 200 °C) for brominated lignin may likely be related to the loss of bromine species such as HBr. When normalised by the initial lignin mass, the residual mass is about 46 % which is similar to that of neat lignin at 43%. A similar observation was made when they were carbonised to 800 °C (see Figure 17 and Table 4). The D/G ratio calculated from Raman spectra was 1.20 for both lignin and brominated lignin.

Table 4: Residual mass (%) lignin and brominated lignin after TGA analysis and carbonisation (for brominated lignin, values are normalised with reference to initial lignin mass)

Sample	Residual mass (%) from TGA at 800 °C under nitrogen	Residual mass (%) measured from carbonisation in furnace until 800 °C
Lignin	43	48
Brominated lignin	46	46

EXAMPLE 4- Wet spinning of PAN/nanocellulose precursor fibre filaments

[00118] Wet spinning of PAN/fibre blends in a solvent such as DMF is known. An amount of the nanocellulose fibrils obtained from Example 1 may be uniformly mixed with PAN in a solvent such as DMF to produce a PAN/nanocellulose blend fibre blend as precursor fibre filaments. It is expected that the addition of nanocellulose may result in improvement in the

thermal stabilization of carbon fibres produced from such precursor fibres. The amount of nanocellulose is variable and may be altered systematically in accordance with the properties as desired in the precursor fibre filament.

[00119] Dispersions of NFC, CNC and MCC in PAN dissolved in an organic solvent DMF (sourced from EMD chemicals, Saudi Arabia) were prepared for use in subsequent electrospinning trials. In order to minimize the moisture content, cellulose samples and PAN were vacuum-dried at 50 °C for 12 hours and PAN polymer was subsequently dissolved in dimethylformamide (DMF) at 50 °C by stirring. A dispersion of freeze-dried cellulose sample in DMF was stirred for 1.5 hours then subjected to ultrasonication at 20 % amplitude for three minutes (using the Q500 Sonicator). This procedure was repeated twice until a stable dispersion of nanoparticles in DMF was obtained. The cellulose dispersion was subsequently added to the PAN polymer solution to give a final mass concentration of 1 wt% cellulose (relative to PAN mass) in the blend and these combined dispersions were then mixed by stirring for one hour at room temperature with a magnetic stirrer. To ensure a high level of mixing prior to electrospinning, the composite solutions were mixed for a further three minutes with an ultrasonic probe at 20 % amplitude, followed by magnetic stirring for a further two hours at room temperature.

[00120] An alternative precursor consisting of NFC dispersed in PVA polymer dissolved in water was prepared for subsequent electrospinning. PVA polymer was dissolved in water by stirring at 80 °C for four hours to form a 10 wt. % PVA solution then a dispersion of NFC in water was added to the PVA solution at room temperature to give a mass concentration of 1 wt% NFC in the final dispersion. The mixture was stirred for one hour then subjected to ultrasonication at 20 % amplitude for three minutes (using the Q500 Sonicator) followed by stirring for another two hours at room temperature to obtain a homogeneous dispersion. The final mixture was degassed before electrospinning.

[00121] The electrospinning apparatus consisted of a syringe pump, syringe needle, high voltage power supply and a collector, which was fabricated using an aluminium foil strip. Each solution was loaded into a syringe and the positive electrode was clipped onto the syringe needle with 0.5 mm diameter. The flow rate of the PAN dispersions was held at 1.5 mm/hour, at an applied voltage of 20 kV and tip to collector distance of 13 cm, while the parameters for the PVA solutions were 0.5 mm/hour, 22 kV, and 13 cm respectively. In order to compare the effect of nanocellulose on the morphology and properties of polymer, a blank sample of each polymer was also electrospun as a control. Solutions were electrospun horizontally onto the target. After

electrospinning, the collected composite nanofibers were dried in vacuum oven at 60 °C for 8 hours.

[00122] Samples of the electrospun precursor fibres were initially stabilized by heating to 240 °C in air at a rate of 3 °C/min, followed by a 60 minute isotherm at 240 °C. The stabilized fibres were then carbonized by heating at a rate of 5 °C/min, followed by a 150 minute isotherm at the final temperature of 800 °C in an argon atmosphere.

[00123] Figure 18 compares the TGA thermograms of electrospun neat polyacrylonitrile, PAN composite fibres spun with 1 wt. % of different cellulose particles (MCC, CNC and NFC) and neat spinifex NFC. TGA thermograms for neat polyacrylonitrile and its composites with 1 wt. % of MCC (microcrystalline cellulose) represented as PAN/1-MCC, CNC (sulphuric acid hydrolysed cellulose nanocrystals) represented as PAN/1-CNC and NFC (spinifex nanofibrillated cellulose NFC) represented as PAN/1-NFC.

[00124] Figure 19 shows the PAN and PAN/cellulose composite fibers before and after carbonisation as listed under the column samples under Table 5. Table 5 indicates the retained residual mass (%) with spinifex NFC than other cellulose after high temperature carbonisation.

Table 5: Residual mass (%) from PAN/cellulose composite fibers after TGA analysis and carbonisation

Sample	Residual mass (%) from TGA at 800 °C under nitrogen	Residual mass (%) measured from carbonisation in furnace until 800 °C
Polyacrylonitrile (PAN)	36	53
PAN with 1 wt% of MCC (PAN/1-MCC)	37	46
PAN with 1 wt% of CNC (PAN/1-CNC)	37	46
PAN with 1 wt% of NFC (PAN/1-NFC)	37	54

[00125] Unlike for the other forms of cellulose, the overall mass yield in the presence of NFC is very similar to that of PAN alone.

[00126] Figure 20 shows the Raman spectra obtained from the carbonised fibres of PAN and PAN/cellulose composites. The D/G ratio for NFC incorporated PAN is significantly lower than

for the others, at 1.20 compared to >1.4 for the PAN and PAN/CNC composite. It is possible that this is related to fusion induced by xylans in the hemicellulosic part of the NFC, as well as potentially the orientation of PAN molecules along the cellulose fibres facilitating crosslinking of sorts. Therefore, the addition of NFC may be improving the degree of order in PAN without affecting the yield.

Polyacrylonitrile /brominated spinifex NFC (cast films)

[00127] Figure 21 compares the TGA thermograms of cast films of neat polyacrylonitrile PAN and its composite with 1.13 wt. % brominated spinifex nanofibrillated cellulose (where 1 wt. % accounts for NFC and 0.13 wt. % account for bromine in PAN). Bromination of the PAN/NFC film was carried out by the halogenation method described in previous examples including example 1. The presence of the brominated cellulose has resulted in a significant increase in mass yield after thermal treatment to 800 °C.

[00128] Figure 22 shows the cast films of PAN and PAN/brominated spinifex NFC before and after carbonisation. The retained mass (%) was calculated and is listed in Table 6.

Table 6: Residual mass (%) from PAN/brominated cellulose composite films after TGA analysis and carbonisation

Sample	Residual mass (%) from TGA at 800 °C under nitrogen	Residual mass (%) measured from carbonisation in furnace to 800 °C
PAN	35	54
PAN with 1.13 wt. % brominated NFC	47	54

EXAMPLE 3- Melt spinning of Polyethylene/nanocellulose precursor fibre filaments

[00129] Melt spinning of polymers such as polyethylene is known for making carbon fibres. An amount of the nanocellulose as obtained from example 1 may be uniformly mixed with the polyethylene to form a nanocomposite melt. Precursor fibre filaments can be spun from the nanocomposite melt. Once again, it is expected that addition of the nanocellulose may improve the properties of the carbon fibres produced from the precursor fibre filaments of example 3.

EXAMPLE 4- Continuous spinning of precursor fibre filaments from a nanocellulose dispersion

[00130] An aqueous dispersion or suspension of the nanocellulose from example 1 may be prepared by suspending the nanocellulose fibrils in water to obtain a transparent suspension/dispersion. The suspensions may be spun in an acetone coagulation bath from a needle (such as ϕ 0.95 mm) set on syringes (such as ϕ 6.5 and 35 mm). Different sizes of syringes may be used for control the spinning rate. The syringes may be pushed by a syringe pump at rates of 2.3- 73.6 mm/min. Consequently, the spinning rates of the precursor fibre filaments may be controlled over the ranges of 0.1-100 and 0.1-10 m/min, respectively.

EXAMPLE 5- Carbonisation of precursor fibre filaments

[00131] Precursor fibre filaments as produced in any one of Examples 2-4 may be stabilised by heating and stretching the fibre filaments in a chamber with well controlled gas flow. Stabilisation creates cross-linked “ladder polymer” chains and the T_g of the fibre increases; the fibres are then carbonized ($\sim 800^\circ\text{C}$). This is followed by graphitization at temperatures ranging from 1100°C to 3000°C while stretching to ensure a preferred crystalline orientation. Finally, post-formation treatments may also be carried out to enhance the carbon bonding strength between the epoxy resin matrix (PAN-Example 2 or PE-Example 3) and the nanocellulose. The process may have rate limitations in the low temperature thermostabilization where the rate of fibre dehydration/dehydrogenation/oxidation is relatively slow (requiring residence times of up to 4 hours) and must be balanced against other processes.

[00132] Metal ion containing solutions (such as FeCl_3 , NiNO_3 and CoSO_4) may also be used to treat the precursor fibres during the stabilization process. Without wishing to be bound by theory, it is hypothesized that addition of such ions may be associated with increased stabilization rates, increased efficiencies and rates of carbonization, and improved final fibre properties. Control and acceleration of re-dehydration and cyclisation reactions promoted by the metal ion may be balanced by inhibition of complete carbon oxidation. Halogenated compounds (such as bromides and chlorides) may be used for inhibiting complete oxidation and/or for promoting dehydrogenation through a dehydrohalogenation process. It is also theorised that the halogenated compounds can act synergistically with metal oxides through activated precursors that can then undergo a catalysed dehydrogenation-aromatization reaction with minimal deep oxidation. Using efficient catalysts that promote the direct carbon to carbon bond formation as opposed to loss of carbon through side reactions also helps in increasing yield in the as formed carbon fibre derived from the precursor fibre filaments.

EXAMPLE 6- Preparing Catalysts and additives for precursor fibre filaments

[00133] The precursor fibres obtained from Examples 2 and 3 may be pre-treated with a number of specific metal cations found active in dehydropolycondensation reactions from several salts (halogen and non-halogen anions) including the transition metal cations (V^{+} ; Cr^{++} ; Mn^{+} ; Fe^{++} ; Co^{+} ; Ni^{++} ; Cu^{+}).

[00134] In addition to salt pretreated preparations, further nanoparticulate catalysts starting with known catalysts such as zinc and iron oxides and partially reduced compounds including doped and binary metal oxides, sulfides, and halides based on low cost hosts including iron, titanium, and manganese may also be added. These compounds may be in the form of nanoparticles with functionalized surfaces. Such catalysts may be impregnated or incorporated by preparatory methods such as ultrasonic spray pyrolysis and precipitation.

[00135] In the present specification and claims (if any), the word ‘comprising’ and its derivatives including ‘comprises’ and ‘comprise’ include each of the stated integers but does not exclude the inclusion of one or more further integers.

[00136] Reference throughout this specification to ‘one embodiment’ or ‘an embodiment’ means that a particular feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, the appearance of the phrases ‘in one embodiment’ or ‘in an embodiment’ in various places throughout this specification are not necessarily all referring to the same embodiment. Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more combinations.

[00137] In compliance with the statute, the invention has been described in language more or less specific to structural or methodical features. It is to be understood that the invention is not limited to specific features shown or described since the means herein described comprises preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims (if any) appropriately interpreted by those skilled in the art.

CLAIMS

1. A method of producing carbon fibre, the method comprising the steps of:
 - (a) spinning precursor fibre filaments from a solution or a dispersion comprising nanocellulose fibrils with a mean diameter of less than 50 nm; and
 - (b) carbonizing the precursor fibre filaments by pyrolysis at an elevated temperature to obtain the carbon fibre.

2. A method of producing carbon fibre, the method comprising the steps of:
 - (a) spinning precursor fibre filaments from a solution or a dispersion comprising nanocellulose fibrils; and
 - (b) carbonising the precursor fibre filaments by pyrolysis at an elevated temperature to obtain the carbon fibre;

wherein the carbonising results in formation of fibrillar nanostructures such that the mean diameter of the fibrillar nanostructures is greater than the mean diameter of the nanocellulose fibrils.

3. A method in accordance with claim 1 wherein the carbonising results in formation of fibrillar nanostructures such that the mean diameter of the fibrillar nanostructures is less than or equal to the mean diameter of the nanocellulose fibrils.

4. A method in accordance with claim 1 wherein the carbonising results in formation of a first group and a second group of fibrillar nanostructures, wherein the mean diameter of the first group of fibrillar nanostructures is greater than the mean diameter of the nanocellulose fibrils and the mean diameter of the second group of fibrillar nanostructures is less than or equal to the mean diameter of the nanocellulose fibrils.

5. A method in accordance with any one of the preceding claims wherein the precursor fibre filaments further comprises lignin.

6. A method in accordance with any one of the preceding claims wherein the solution or the dispersion comprises an aqueous medium.

7. A method in accordance with any one of claims 1 to 5 wherein the solution or the dispersion comprises an organic solvent.

8. A method in accordance with claim 7 wherein the precursor fibre filaments are a composite fibre comprising nanocellulose fibrils and further comprising a polymer such that the polymer is at least partially soluble in the organic solvent.
9. A method in accordance with any one of the preceding claims wherein spinning enhancing agents are added to the solution or the dispersion.
10. A method in accordance with any one of the preceding claims comprising the step of adding an agent for disrupting hydrogen bonding in the solution or the dispersion for improved elongation and processing of the precursor fibre filaments.
11. A method of producing carbon fibre, the method comprising the steps of
- (a) homogenising nanocellulose fibrils to form homogenised nanocellulose fibrils ;
 - (b) carbonising the homogenised fibrils by pyrolysis at an elevated temperature to obtain the carbon fibre;
- wherein the carbonising results in formation of fibrillar nanostructures such that the mean diameter of the fibrillar nanostructures is greater than the mean diameter of the nanocellulose fibrils.
12. A method in accordance with claim 11 wherein the nanocellulose fibrils have a mean diameter of less than 50 nm.
13. A method in accordance with any one of the preceding claims wherein the nanocellulose fibrils are pre-treated by a pre-treatment process comprising a halogenation step.
14. A method in accordance with claim 13 wherein the halogenation step further comprises:
- contacting the nanocellulose fibrils with a halogen and/or a halogen derivative to form a nanocellulose fibril-halogen mixture and
 - heating the mixture to a heating temperature of at least 80°C for a heating time period of at least 10 minutes; thereby forming halogenated nanocellulose fibrils.
15. A method in accordance with claim 14 wherein the halogenation step further comprises irradiation of the nanocellulose-halogen mixture under visible and/or ultraviolet and/or infra-red radiation for promoting halogenation of the nanocellular fibrils.

16. A method in accordance with any one of claims 14 or 15 wherein weight percentage (wt%) of halogen in the halogenated nanocellulose fibrils is in the range of 2-50 wt. %.
17. A method in accordance with claim 11 wherein the homogenisation step further comprises homogenising lignin and the nanocellulose fibrils to form a nanocellulose-lignin mixture and wherein the carbonising step comprises carbonising the nanocellulose-lignin mixture.
18. A method in accordance with claim 16 wherein the homogenised nanocellulose-lignin mixture is halogenated in accordance with claims 14 to 16 prior to the carbonisation step.
19. A method in accordance with any one of the preceding claims wherein the nanocellulose fibrils have a mean diameter of less than 40 nm and preferably less than 30 nm, more preferably less than 20 nm.
20. A method in accordance with any one of the preceding claims wherein the nanocellulose fibrils have a mean diameter of less than 10 nm, preferably less than 8 nm and more preferably less than 5 nm.
21. A method in accordance with any one of the preceding claims wherein the nanocellulose fibrils are derived from higher order plants.
22. A method in accordance with any one of the preceding claims wherein the nanocellulose fibrils are derived from Spinifex grass.
23. A method in accordance with claim 21 wherein the higher plants comprises lignin and hemicellulose and wherein the amount of lignin is less than the amount of hemicellulose.
24. A method in accordance with any one of the preceding claims comprising addition of additives for increasing the rate of stabilisation and/or carbonization and/or for improving physical properties of the carbon fibres.
25. A method in accordance with claim 24 wherein the additive comprises a catalyst.
26. A method in accordance with any one of the preceding claims wherein the carbonizing step is preceded by a stabilisation step wherein the precursor filaments are dehydrated/dehydrogenated/oxidised at stabilisation temperature.
27. A method in accordance with any one of the preceding further comprising a graphitisation step wherein graphitisation of the carbonised fibres is carried out at a

graphitisation temperature that is equal to or greater than the elevated carbonisation temperature and wherein during graphitisation, the carbonised fibre is oriented in a preferred orientation.

28. A method in accordance with any one of the preceding claims further comprising a processing step for enhancing carbon bonding strength in the carbonised fibre.

29. A method in accordance with claim 28, wherein the processing step comprises the step of adding strengthening agents.

30. A method in accordance with any one of the preceding claims further comprising the step of adding one or more catalysts for catalysing stabilisation and/or carbonisation of the precursor filaments.

31. A method in accordance with any one of the preceding claims wherein the step of carbonisation comprises slow pyrolysis of the precursor fibre in which temperature is increased to an initial temperature in the range of 700°C to 1400°C, more preferably 800°C to 1100°C under an inert atmosphere for carbonisation of the precursor fibre.

32. A method in accordance with claim 31 further comprising a step of graphitisation of the carbonised filaments, wherein graphitisation is carried out at a temperature in the range of 1100°C to 3000°C.

33. A method in accordance with any one of the preceding claims wherein the carbonisation step is preceded by a stabilisation step, wherein the precursor fibres are dehydrated/dehydrogenated/oxidised at oxidising stabilisation temperature in the range of 200°C to 300°C.

34. A method in accordance with any one of the preceding claims comprising the step of applying tension to the precursor fibre filaments during the carbonisation step to maintain the fibre filaments in a desirable orientation and/or reduce variation in the longitudinal dimension of the fibre filaments.

35. A carbon fibre produced by a method in accordance with any one of the preceding claims.

36. A carbon fibre comprising carbonised nanocellulose fibrils, wherein prior to carbonisation, the nanocellulose fibrils have a mean diameter of less than 50 nm.

37. A carbon fibre in accordance with claim 35 wherein the nanocellulose fibrils have a mean

diameter of less than 40 nm and preferably less than 30 nm, more preferably less than 20 nm.

38. A carbon fibre comprising carbonised nanocellulose fibrils, said carbonised nanocellulose fibrils having a nanostructure with a mean diameter that is greater than mean diameter of the nanocellulose fibrils prior to carbonisation.

39. A carbon fibre in accordance with claim 37 wherein the mean diameter of the carbonised fibrils is at least 5 nm and more preferably at least 100 nm, even more preferably up to 200 nm.

40. Carbon fibres formed from a cellulose precursor where the cellulose precursor comprises nanofibrils having a mean diameter less than 50 nm and wherein the carbon fibres have elongate nanostructures with a mean diameter in the range of 5 nm to 200 nm and a mean length in the range of 5 μ m to 20 μ m.

41. Carbon fibres formed from a cellulose precursor wherein the cellulose precursor comprises nanofibrils with mean diameter less than 50 nm and wherein the carbon fibres have elongate nanostructures with a mean diameter of less than 50 nm.

42. Carbon fibres formed from a cellulose precursor where the cellulose precursor comprises nanofibrils with mean diameter less than 50 nm and wherein the carbon fibres comprise a first group and a second group of carbon fibres, wherein the first group of carbon fibres have elongate nanostructures with a mean diameter of less than or equal to 50 nm and the second group of carbon fibres have elongate nanostructures with a mean diameter of more than 50 nm.

43. A carbon fibre comprising halogenated nanocellulose fibrils, wherein said halogenated nanocellulose fibrils are carbonised to form the carbon fibre.

44. A method of producing carbon fibre, the method comprising the steps of

- (a) homogenising lignin in a solution or dispersion; and
- (b) carbonising the lignin by pyrolysis at an elevated temperature to obtain the carbon fibre.

45. A method in accordance with claim 44 comprising a pre-treatment step preceding the carbonising step, the pre-treatment step comprising a halogenation step.

46. A method in accordance with claim 45, wherein the halogenation step further comprises:
contacting the lignin with a halogen and/or a halogen derivative to form a lignin-halogen

mixture and

heating the mixture to a heating temperature of at least 80°C for a heating time period of at least 10 minutes thereby forming halogenated lignin.

47. A method of producing carbon fibre, the method comprising the steps of:

(a) spinning precursor fibre filaments from a solution or a dispersion comprising lignin; and

(b) carbonizing the precursor fibre filaments by pyrolysis at an elevated temperature to obtain the carbon fibre.

48. A method in accordance with claim 47 comprising a pre-treatment step preceding the carbonising step, the pre-treatment step comprising a halogenation step.

49. A method in accordance with claim 48 wherein, the halogenation step further comprises:

contacting the precursor fibre elements with a halogen and/or a halogen derivative to form a fibre filament-halogen mixture and

heating the mixture to a heating temperature of at least 80°C for a heating time period of at least 10 minutes; thereby forming halogenated precursor fibre filaments.

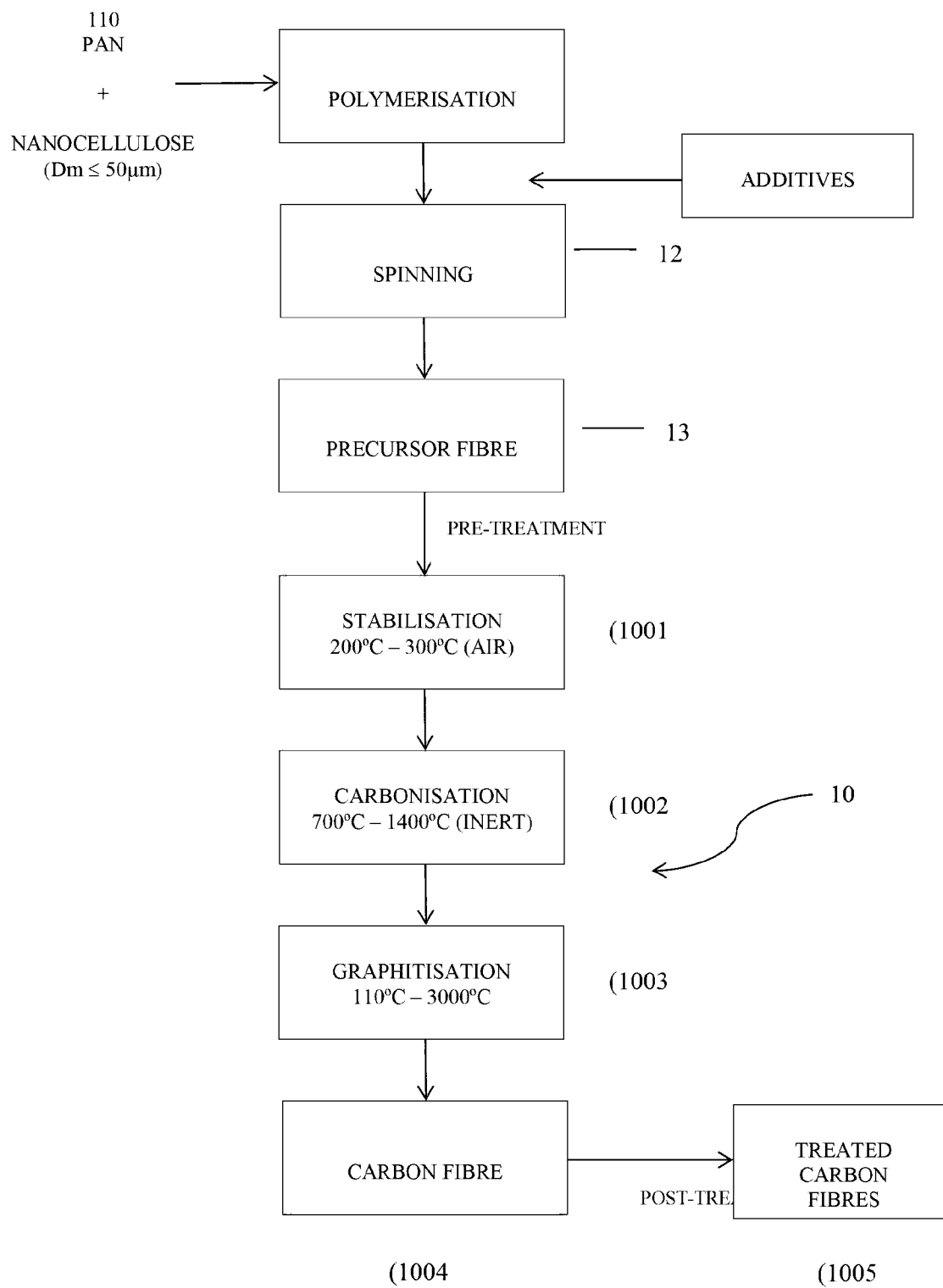


Figure 1

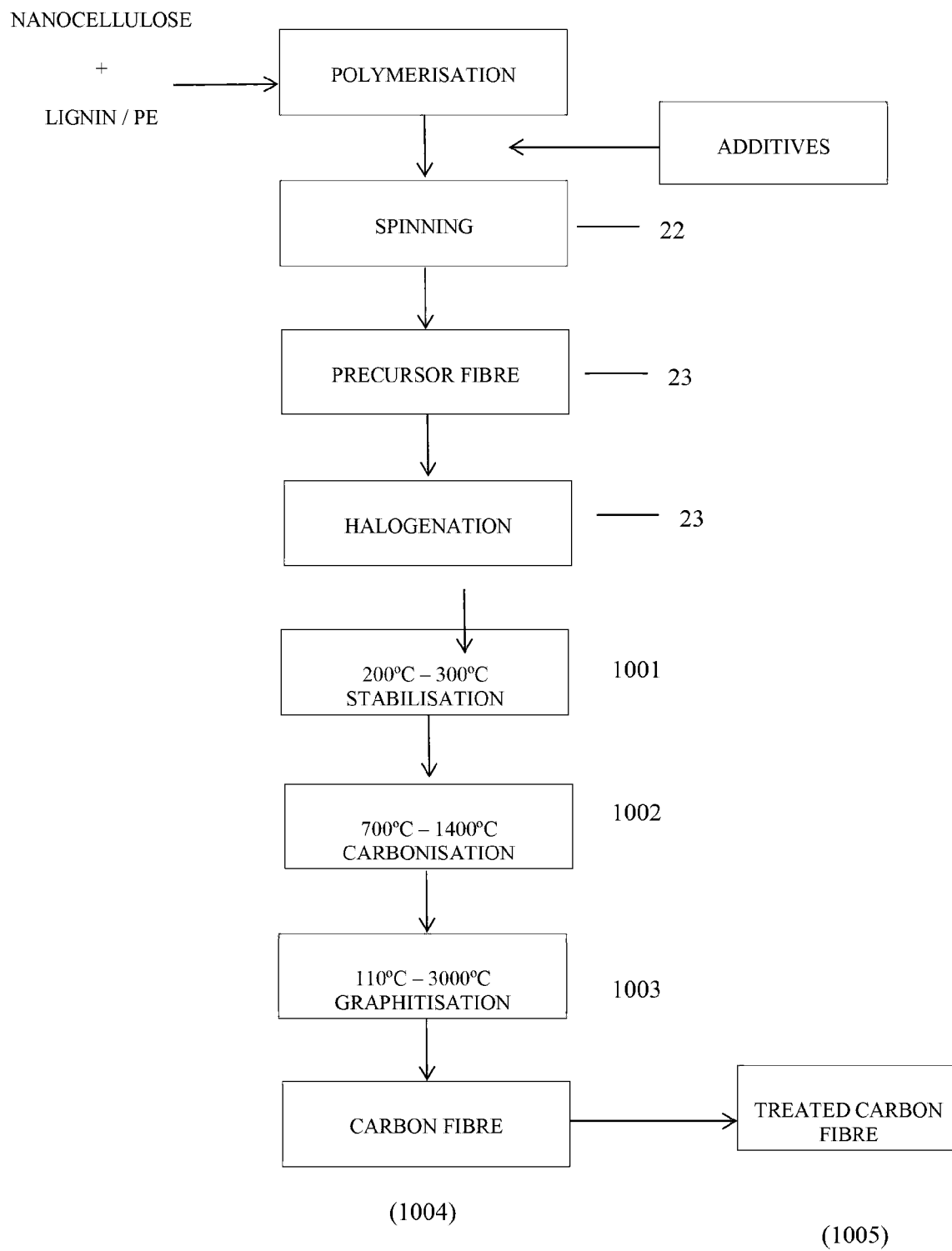


Figure 2

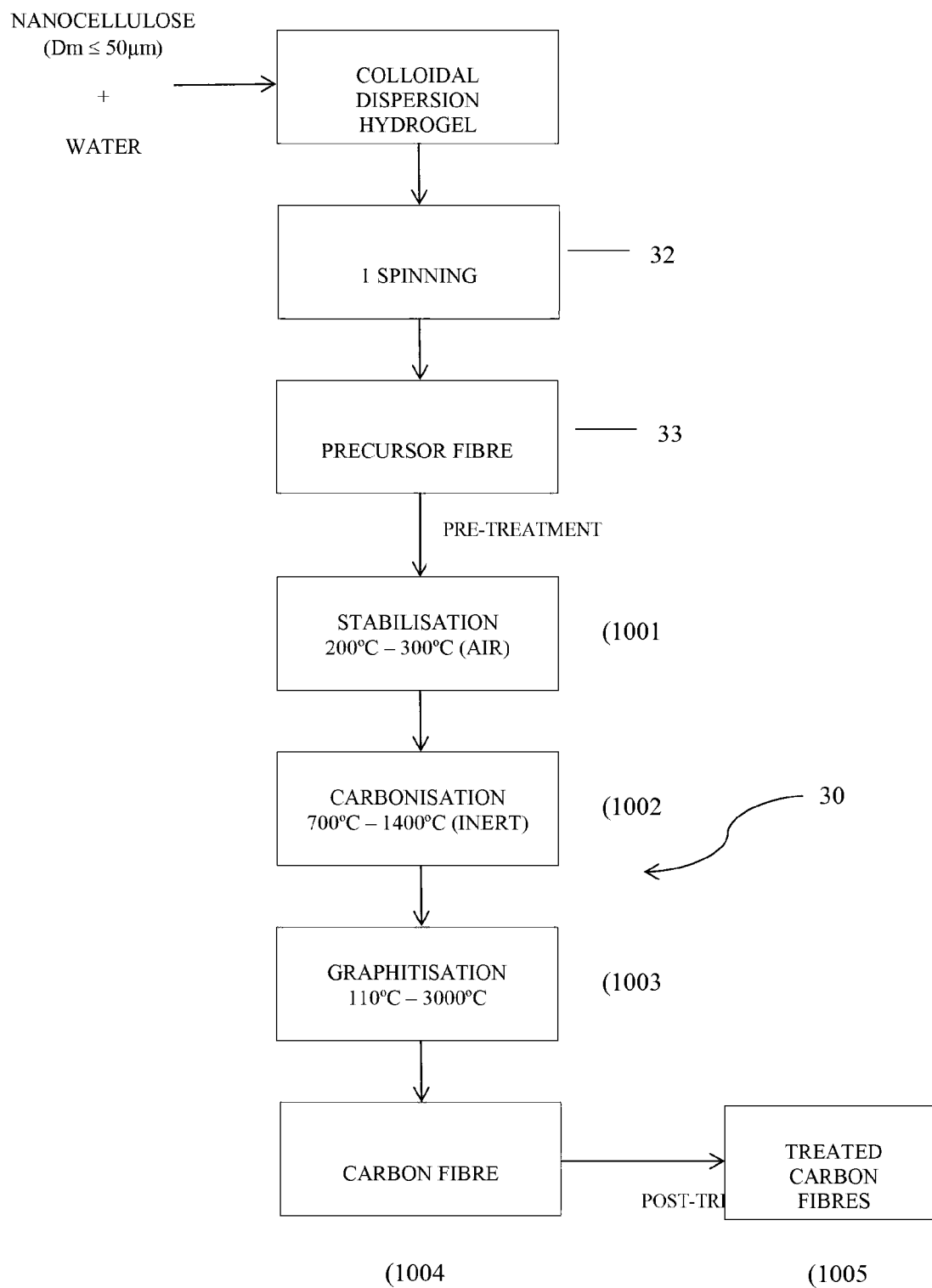


Figure 3



Figure 4A

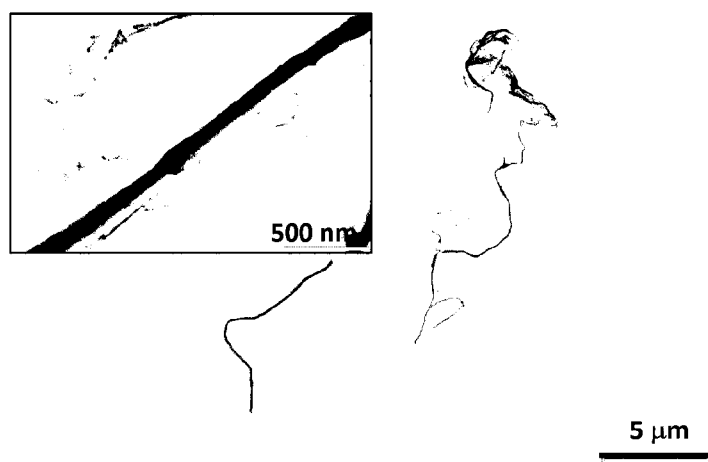


Figure 4B

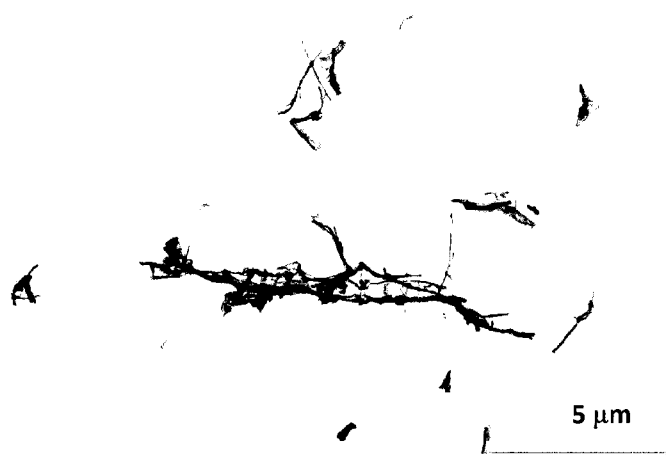


Figure 4C

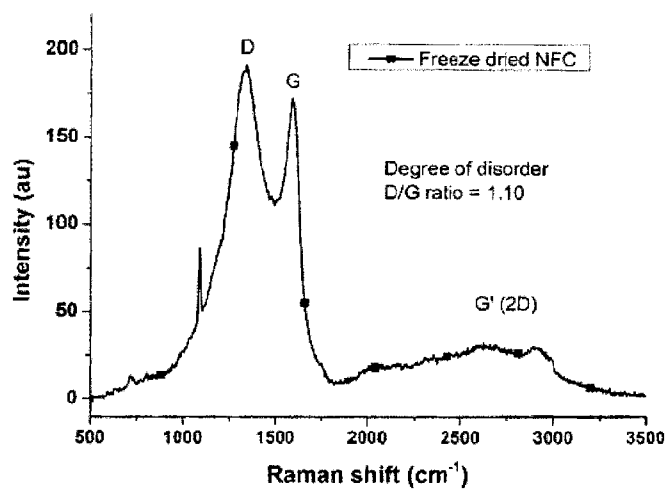


Figure 5

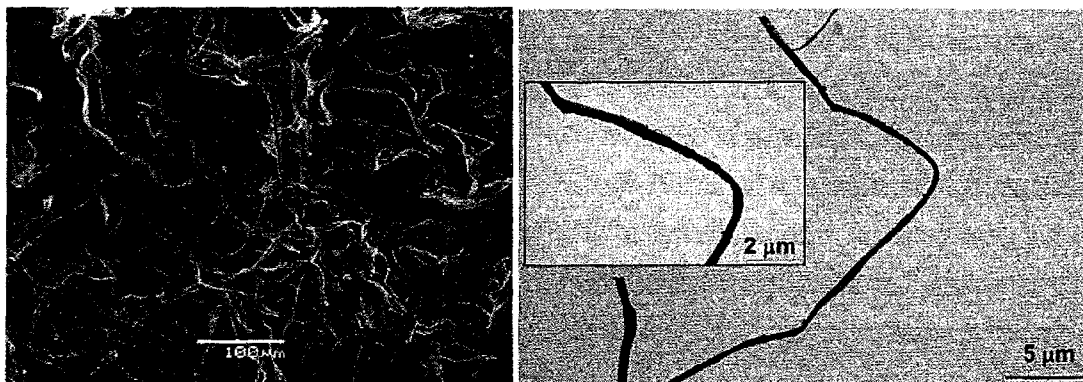


Figure 6A

Figure 6B

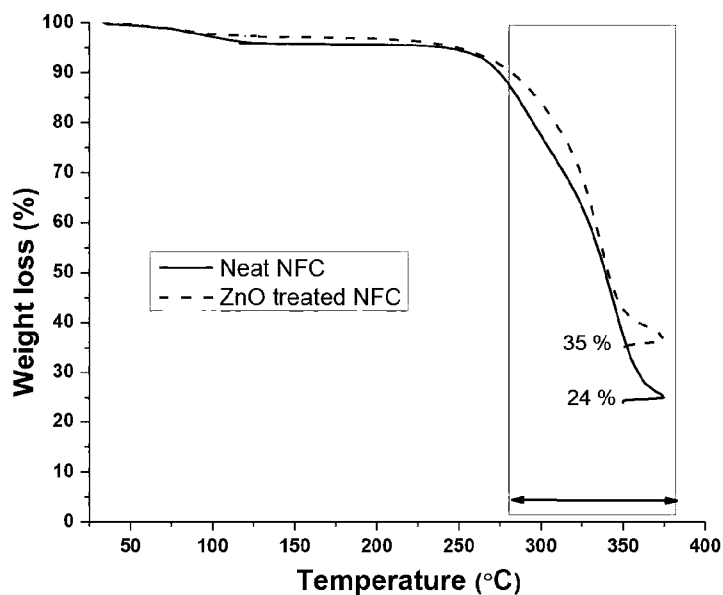


Figure 7

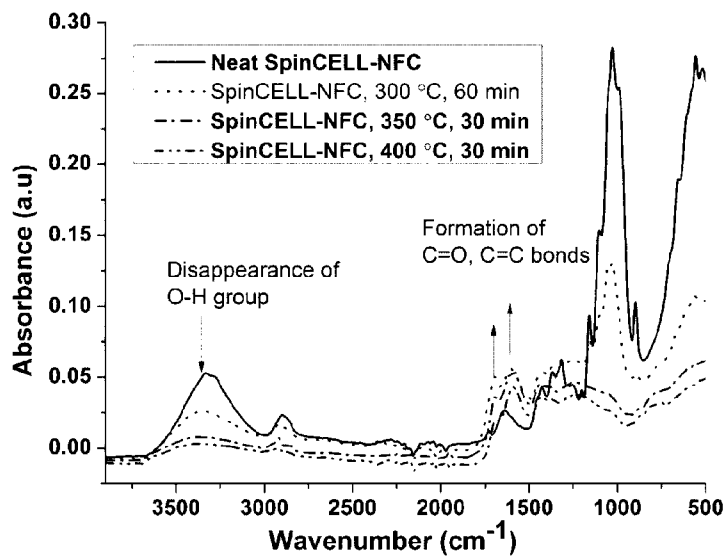


Figure 8

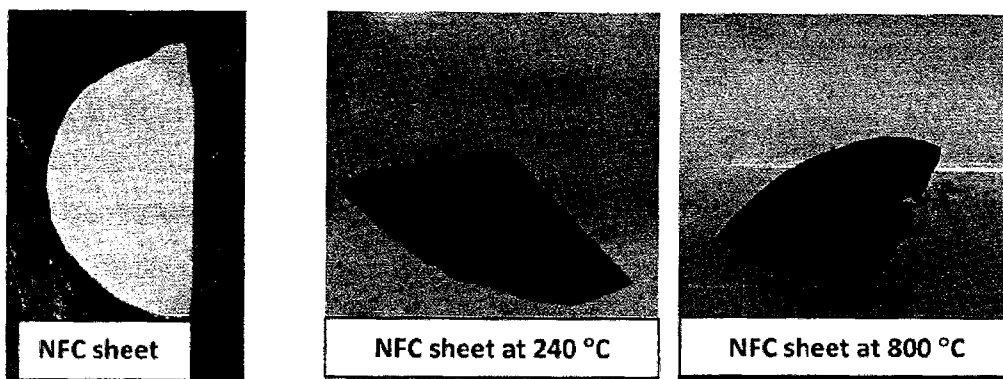


Figure 9

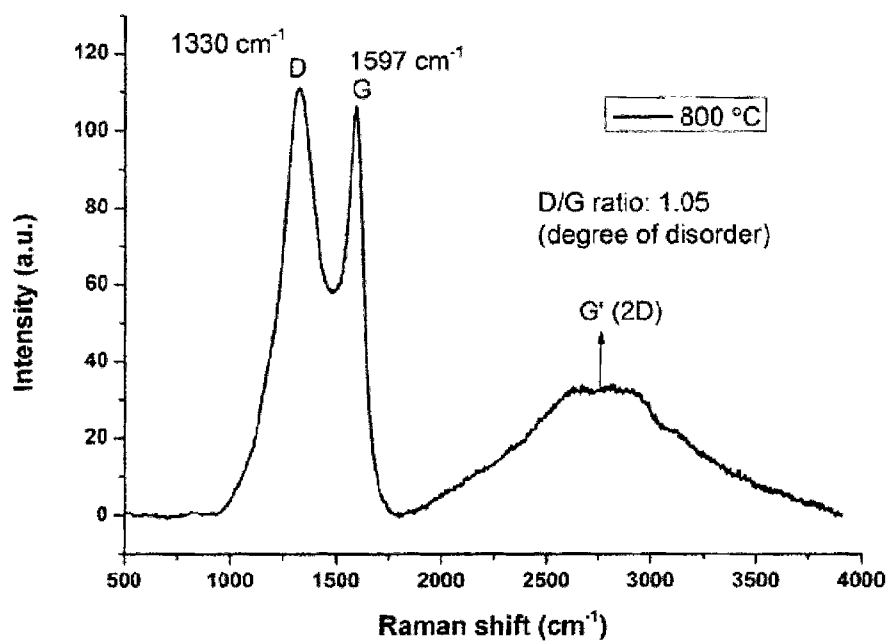


Figure 10

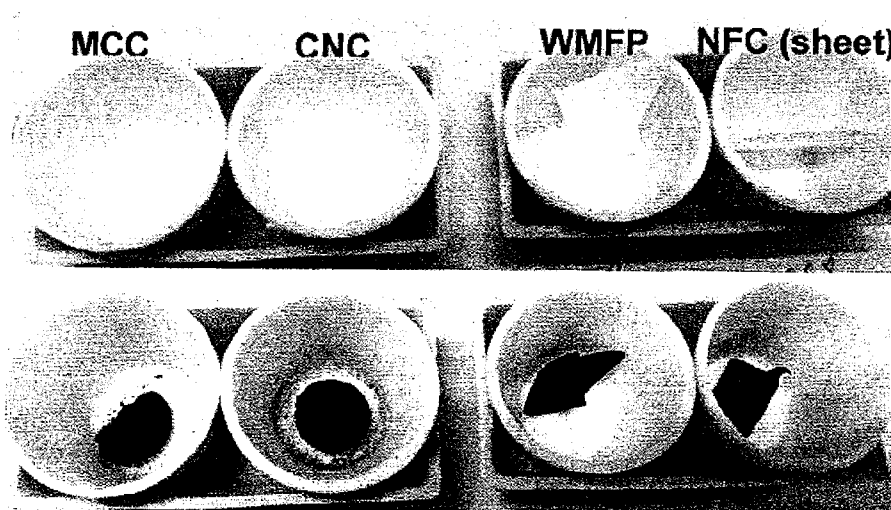


Figure 11

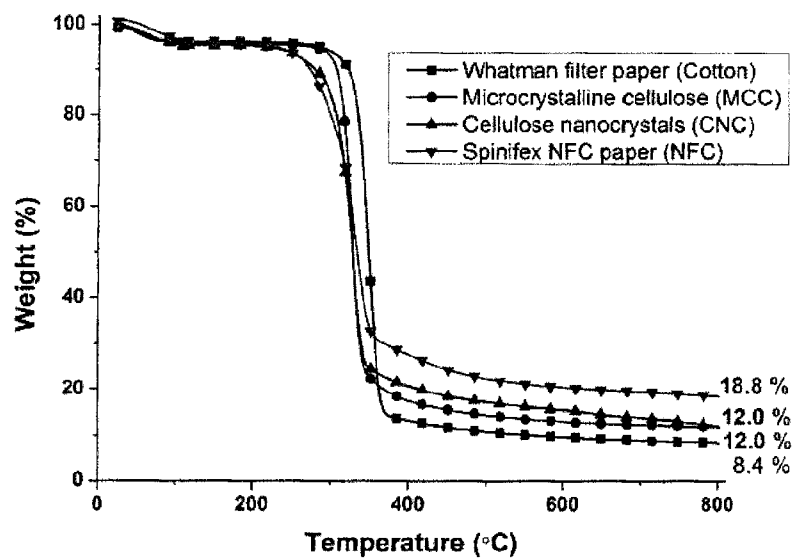


Figure 12

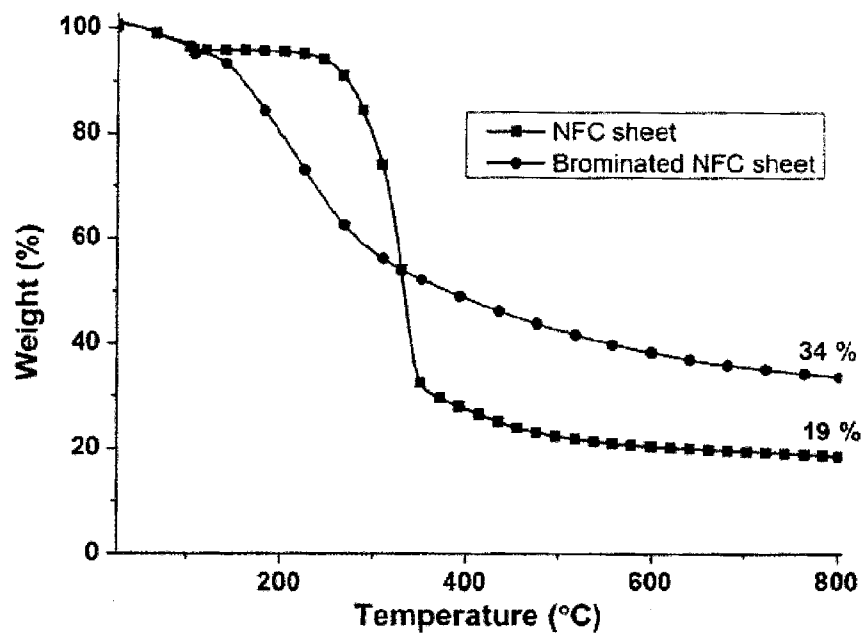


Figure 13

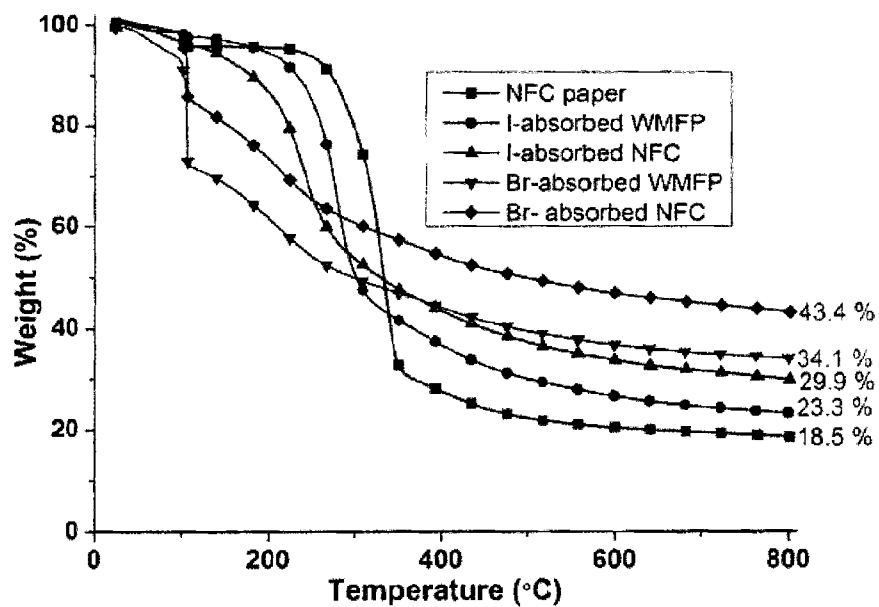


Figure 14

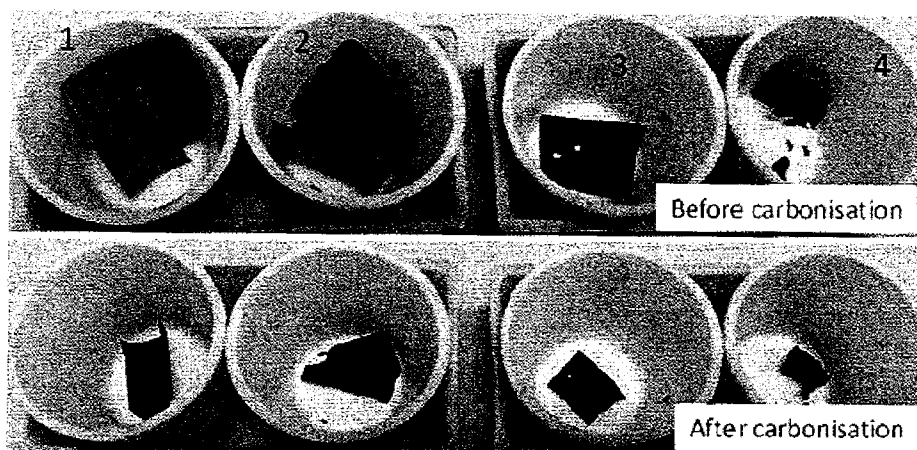


Figure 15

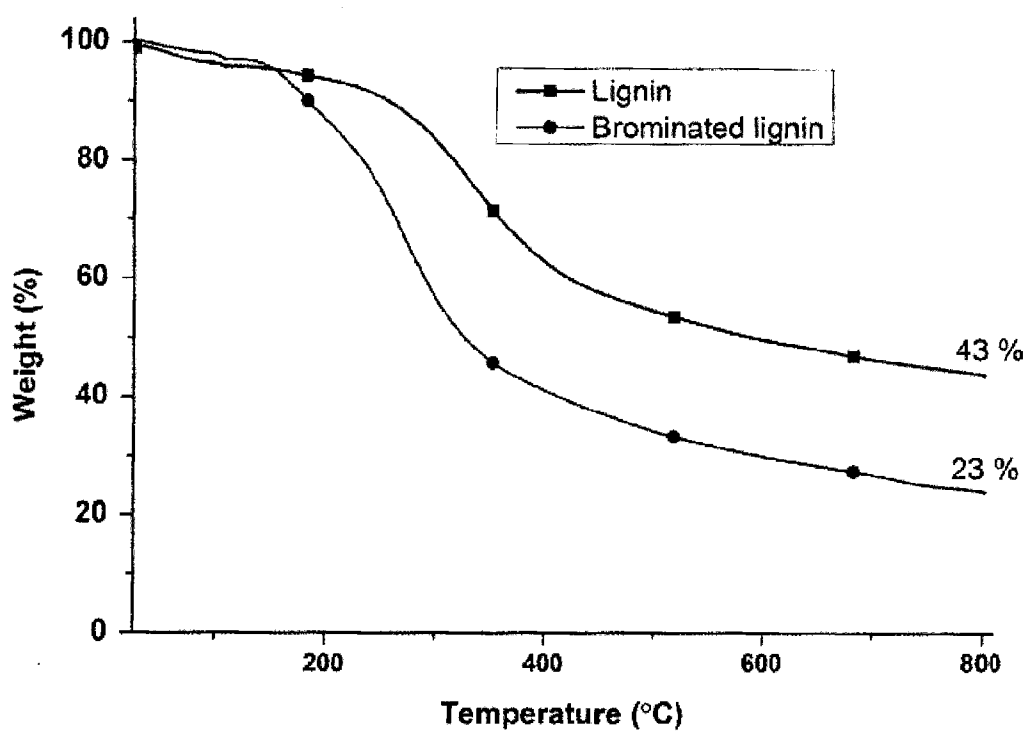


Figure 16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2015/050074

A. CLASSIFICATION OF SUBJECT MATTER

D01F 9/12 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

EPOQUE X-FULL: databases: TXPEA, TXPEB, TXPEC, TXPEE, TXPEF, TXPEH, TXPEI, TXPEP, TXPEPEA, TXPES, TXPUSE0A, TXPUSE1A, TXPUSEA, TXPUSEB, TXPW0EA, WPIAP, EPODOC; keywords: carbon fibre, hemicellulose, nanocellulose, cellulose, lignin, filament, fibril, spin, spun, homogenize, disperse, mix, halogen, bromine, iodine, chlorine, carbonize, pyrolyze, diameter, etc.. Espacenet and AusPat searches with applicant and inventor names; Espacenet and Google Patent searches with keywords: carbon fibre, nano, diameter, spin, nanocellulose, fibril, cellulose nanofiber, microfibrillated cellulose, etc..

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 7 May 2015		Date of mailing of the international search report 07 May 2015	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au		Authorised officer Hong Yu AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262837946	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2015/050074
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2011-026731 A (TORAY IND INC) 10 February 2011 Abstract, examples 1, 11, para. [0020], [41] of English specification retrieved on 30 April 2015 from J-PlatPat website	1, 5-10, 19-37
Y	Abstract, examples 1, 11, para. [0020], [41] of English specification retrieved on 30 April 2015 from J-PlatPat website	13-16, 43
Y	GB 1454629 A (COAL INDUSTRY (PATENTS) LIMITED) 03 November 1976 page 1, lines 75-90, examples	13-16, 43, 45-46, 48-49
Y	GB 1356569 A (COAL INDUSTRY (PATENTS) LIMITED) 12 June 1974 page 2, lines 100-112, examples	13-16, 43, 45-46, 48-49
Y	US 3552922 A (ISHIKAWA ET AL.) 05 January 1971 Abstract, Figures, examples	13-16, 43, 45-46, 48-49
X	US 3723609 A (MANSMANN ET AL.) 27 March 1973 Abstract, example 1	44, 47
Y	Abstract, example 1	45-46, 48-49
X	WO 2012/156441 A1 (FRAUNHOFER-GESELLSCHAFT ZUR FORDERUNG DER ANGEWANDTEN FORSCHUNG E.V.) 22 November 2012 Abstract, examples, claims	44, 47
Y	Abstract, examples, claims	45-46, 48-49
X	WO 2013/112100 A1 (INNVENTIA AB) 01 August 2013 Abstract, page 5, lines 4-5, example 4	44, 47
Y	Abstract, page 5, lines 4-5, example 4	45-46, 48-49
A	US 3461082 A (OTANI ET AL.) 12 August 1969 Abstract, columns 2-3	1-49

Form PCT/ISA/210 (fifth sheet) (July 2009)

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Supplemental Box**Continuation of: Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

Claims 1-12, 13-35(in part), 36-39 are directed to a method of producing carbon fibre, and a carbon fibre. The feature of the specific dimensions of precursor fibre material of nanocellulose fibrils prior to its carbonization to form carbon fibre is specific to this group of claims.

Claims 40-42 are directed to carbon fibres. The feature of the specific dimensions of elongate nanostructures of carbon fibre is specific to this group of claims.

Claims 13-16(in part), 43, 45-46(in part), 48-49(in part) is directed to a carbon fibre. The feature of pretreating nanocellulose fibrils with halogenation is specific to this group of claims.

Claims 17-35(in part), 44, 45-46(in part), 47, 48-49(in part) are directed to a method of producing carbon fibre. The feature of homogenizing or spinning a solution of precursor fibre material of lignin is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all or part of the claimed inventions is nanocellulose fibrils as precursor fibre material of carbon fibre. However this feature does not make a contribution over the prior art because it is disclosed in D1 (see Abstract).

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

The International Searching Authority believes that a search and examination for the 2nd to 4th inventions will not involve more than negligible additional search and examination effort over that for the first invention and so no additional search fee is required in order to search and examine that invention.

INTERNATIONAL SEARCH REPORT		International application No.	
Information on patent family members		PCT/AU2015/050074	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
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		MX 2013013208 A	06 Feb 2014
		US 2014194603 A1	10 Jul 2014
		US 2015037241 A1	05 Feb 2015
		WO 2012156443 A1	22 Nov 2012
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2015/050074	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
WO 2013/112100 A1	01 August 2013	AR 089759 A1	17 Sep 2014
		AU 2013212731 A1	17 Jul 2014
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		DE 1646779 B2	25 Jan 1973
		GB 1111299 A	24 Apr 1968
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			