Abstract: A fibre reinforced material (1) and methods of production thereof are described. The fibre reinforced material (1) comprises a matrix material made from a biocomposite material (3) produced through the extraction of cellulose from plants. Within the biocomposite material (3) are located a plurality of fibres (2). The described material (1) exhibits a physical stiffness, strength and toughness that is greater than that for known carbon fibre reinforced plastics. Furthermore the composition of the material (1) also makes it inherently impermeable to water. This makes the fibre reinforced material (1) ideally suited for making monolithic structures, laminate structures (12) and rod structures for use in a variety of fields, for example as fishing rods.
Improved Fibre Reinforced Material

The present invention relates to the field of fibre reinforced materials and in particular to a fibre reinforced biocomposite material wherein the biocomposite material is produced through the extraction of cellulose from plants.

Carbon fibre reinforced plastics have become widely used in a large number of industrial sectors over the last twenty years. These systems have become highly developed and refined, however there still exist some inherent physical problems with these materials. ...

One of the most significant problems relates to the large difference in stiffness between the carbon fibres and surrounding plastic matrix. Typically, carbon fibres exhibit a Young's modulus value in the range of 150 to 600 GPa whereas the plastic matrix materials, such as epoxy resin, typically have modulus values of between 2 to 8GPa. These differing Young's modulus values cause delamination problems when different layers of the carbon fibre composites are bonded together with resins.
The unidirectional arrangement of carbon fibres within the plastic matrix also results in materials that exhibit very low stiffness and strength at right angles to the fibre direction.

One way to alleviate these problems would be to increase the stiffness of the matrix material. However this needs to be achieved without compromising toughness, otherwise the composite material would become very brittle. The prior art teaches of a number of alternative materials to plastic employed as the matrix as well as alternative materials to carbon fibre being employed as the fibres.

For example, UK Patent Application No. 9930677.1 in the name Balmoral Group Limited teaches of a spherical object made from layers of carbon, glass or mineral fibre reinforced polymers and layers of natural fibre reinforced polymers. The natural fibre-reinforcement described therein is produced by long or intermediate plant fibres such as coir, jute, hemp, wood fibre, sisal, tow, kenaf or straw.

PCT Application No. PCT/SE99/00859 in the name Danogips A/S teaches of a composite material containing wood fibres and carbon fibres. In particular an electrically conductive material is described that comprises a composite that contains 95-100% of carbon fibres and cellulose fibres.

European Patent No. 1,268,198 in the name Dreier teaches of a thermally deformable composite material comprising at least two layers of wood arranged so as to sandwich a
carbon fibre layer while US Patent No. 4,533,598 in the name CasChem Inc. teaches of a composite material comprising resin bonded layers of wood veneer and reinforcing carbon fibres.

UK Patent Publication No. 2343353 teaches of a fishing rod comprising a composite material made from carbon fibre covered at least partly by a layer of woody material, preferably in the form of a bamboo film adhered to the body of the rod.

There have also been investigations carried out in relation to the properties of chitosan-carbon fibre materials. For example, Chinese Patent Application No. 1094066 in the name Auhui University teaches of a medical chitosan film, containing carbon fibres and a method of production of this material.

Finally, Iguchi et al (Journal of Materials Science, 2000, 35, p261-270) describe a material formed by mixing carbon fibres with bacterial cellulose. During production it is found that the cellulose adheres to the carbon fibres, however no mechanical testing of the material produced is reported and the described bacterial cellulose was found to be highly hygroscopic.

It is therefore an object of an aspect of the present invention to provide a fibre reinforced material that exhibits an improved physical stiffness, strength and toughness when compared with carbon fibre reinforced plastics.
It is a further object of an aspect of the present invention to provide a fibre reinforced material that exhibits an improved physical stiffness, strength and toughness when compared with carbon fibre reinforced plastics and which is also inherently impermeable to water.

It is a yet further object of an aspect of the present invention to provide a fibre reinforced material that exhibits the above properties and which can be produced economically on a commercial scale.

For clarity purposes it should be noted that the stiffness of a material is quantified by the Young's modulus exhibited by the material while the toughness of a material is quantified by the amount of energy absorbed per unit volume of the material up to the point of failure. Furthermore, it should be noted that within the following description there are two types of fibres described; cellulose microfibrils that form cell fragments within the biocomposite material and secondary fibres (referred to as fibres) which utilise the biocomposite material as a matrix.

Furthermore, an impermeable material is defined as a material that has a significantly slower rate of water uptake when completely immersed in water when compared to cellulose.

In the following formulations "CeI" represents cellulose fragments, "HPI" represents hydrophilic binders, "HPO" represents hydrophobic binders and x and y quantify the
percentage by weight of the hydrophilic and hydrophobic binders present within a material, respectively.

**Summary of the Invention**

According to a first aspect of the present invention there is provided a fibre reinforced material comprising a biocomposite material reinforced with a plurality of fibres wherein the biocomposite material comprises a plurality of cellulose fragments made up of a network of cellulose microfibrils, a plurality of hydrophilic binders located within the network of cellulose microfibrils and a plurality of hydrophobic binders arranged to interact with the hydrophilic binders so as to encapsulate the plurality of cellulose fragments.

The above arrangement ensures good stress transfer from the biocomposite material to the plurality of fibres, and from the hydrophobic binders through the hydrophilic binders to the cellulose microfibrils, so providing the fibre reinforced material with the desired stiffness, strength and toughness. By arranging the hydrophobic binders so as to encapsulate the cellulose fragments, the fibre reinforced material is also rendered impermeable to water.

Most preferably the biocomposite material of the first aspect of the present invention has the general formulation $\text{Cel}(i_{x-y})\text{HPI}_x\text{HPO}_y$ where $x$ is within the range of from 0.01 to 0.55 and $y$ is within the range of from 0.05 to 0.65.
According to a second aspect of the present invention, there is provided a fibre reinforced material that is impermeable to water comprising a biocomposite material reinforced with a plurality of fibres wherein the biocomposite material comprises a plurality of cellulose fragments made up of a network of cellulose microfibrils, a plurality of hydrophilic binders and a plurality of hydrophobic binders having the general formulation Cel(i_x, y) HPI_x HPO_y where x is within the range of from 0.01 to 0.55 and y is within the range of from 0.05 to 0.65.

Preferably the plurality of hydrophilic binders are located within the network of cellulose microfibrils and the plurality of hydrophobic binders are arranged to interact with the hydrophilic binders so as to encapsulate the plurality of cellulose fragments.

Most preferably the fibre reinforced material of the first and second aspects of the present invention exhibits a stiffness in the range from 5GPa to 90GPa.

According to a third aspect of the present invention, there is provided a fibre reinforced material comprising a biocomposite material reinforced with a plurality of fibres wherein the fibre reinforced material is impermeable to water and which exhibits a stiffness in the range from 5GPa to 90GPa.

Preferably the biocomposite material of the third aspect of the present invention comprises a plurality of cellulose fragments made up of a network of cellulose microfibrils, a plurality of hydrophilic binders located within the network of cellulose microfibrils and a
plurality of hydrophobic binders arranged to interact with the hydrophilic binders so as to encapsulate the plurality of cellulose fragments.

Preferably the biocomposite material has the general formulation $\text{Cel(i}_{-x-y})\text{HPI}_x\text{HPO}_y$ where $x$ is within the range of from 0.01 to 0.55 and $y$ is within the range of from 0.05 to 0.65.

Preferably the plurality of fibres of the various aspects of the present invention are arranged in a randomly orientated manner. Alternatively, the plurality of fibres of the various aspects of the present invention are arranged in a unidirectional manner.

Most preferably the plurality of fibres comprise fibres selected from a group comprising carbon fibre, carbon nanotubes, aramid fibres, glass fibres, hemp fibres and flax fibres.

Most preferably the cellulose fragments of the various aspects of the present invention are arranged in a randomly orientated manner.

Most preferably the material of the various aspects of the present invention exhibit a tensile strength in the range from 60 MPa to 1 GPa.

Most preferably the material of the various aspects of the present invention exhibit a bending strength in the range from 60 MPa to 600 MPa.
Most preferably the material of the various aspects of the present invention exhibits a stiffness in the range from 14 GPa to 40 GPa.

Most preferably the material of the various aspects of the present invention exhibits a strength in the range from 200 MPa to 600 MPa.

Most preferably the material of the various aspects of the present invention exhibits a toughness in the range from 2 MJm\(^{-3}\) to 10 MJm\(^{-3}\).

Preferably the hydrophilic binders comprise a hydrophilic or substantially hydrophilic polymer. The hydrophilic polymer may comprise a hemicellulose, an acrylic resin or alternatively a partially hydrolysed polyvinyl acetate. Optionally the hydrophilic polymer comprises a biological hydrophilic polymer e.g. gelatine and guar gum.

Optionally the hydrophobic binders comprise a hydrophobic polymer. The hydrophobic polymer may comprise an epoxy such as a bisphenol-A or a modified bisphenol A epoxy.

Alternatively the hydrophobic binders comprises a binder selected from the group comprising polyurethanes, phenolic resins, acrylics and siloxanes.

According to a fourth aspect of the present invention there is provided a monolithic structure comprising two or more layers wherein at least one layer comprises a reinforced fibre material in accordance with any of the first to third aspects of the present invention.
The formation of a monolithic layered structure provides a structure within which the mechanical properties can be gradated, as appropriate. As curing results in there being no distinct interfaces between the layers, these monolithic structures experience no compromise to their mechanical properties.

 Optionally the monolithic structure comprises at least one layer of a plastic material. Preferably the plastic material comprises a carbon fibre reinforced material.

 According to a fifth aspect of the present invention there is provided a laminate structure comprising two or more layers wherein at least one layer comprises a fibre reinforced material in accordance with any of the first to fourth aspects of the present invention.

 Optionally the laminate structure comprises at least one layer of a plastic material. Preferably the plastic material comprises a carbon fibre reinforced material.

 Optionally the laminate structure comprises one or more layers of resin located between the two or more layers of the structure.

 Optionally the one or more layers of resin comprise a hydrophobic resin such as epoxy or polyurethane.

 According to a sixth aspect of the present invention there is provided a tube, suitable for use in a fishing rod, the tube comprising a fibre reinforced material in accordance with the first to fifth aspects of the present invention.
According to a seventh aspect of the present invention there is provided a method of producing a fibre reinforced material that is impermeable to water comprising the steps of:

1) Producing a biocomposite paste comprising a plurality of cellulose fragments a plurality of hydrophilic binders, and a plurality of hydrophobic binders;

2) Incorporating a plurality of fibres within the biocomposite paste; and

3) Fixing the combined plurality of fibres and the biocomposite paste.

Preferably the step of producing a biocomposite paste comprises the steps of:

1) Producing the plurality of cellulose fragments, comprising a network of cellulose microfibrils;

2) Incorporating the plurality hydrophilic binders within the plurality of cellulose fragments; and

3) Encapsulating the plurality of cellulose fragments and the plurality of hydrophilic binders within the plurality of hydrophobic binders.

Preferably the step of incorporating the plurality hydrophilic binders within the cellulose fragments comprises:

1) Re-hydrating the cellulose fragments with a first emulsion/dispersion comprising the hydrophilic binders so as to produce a paste; and

2) Removing excess water and excess hydrophilic binders from the paste.
Preferably the step of encapsulating the plurality of cellulose fragments and the plurality of hydrophilic binders comprises:

1) Producing a second emulsion comprising the plurality of hydrophobic binders;
2) Mixing the second emulsion with the paste containing the hydrophilic binder.

Preferably the production of the second emulsion involves mixing the hydrophobic binders with a surfactant and water.

Most preferably the surfactant is non-ionic.

Preferably the ratio of the hydrophobic binders to the water within the second emulsion is between 10:1 and 1:5.
Most preferably the ratio is between 10:1 and 5:1.

Optionally the step of incorporating the plurality of fibres within the biocomposite paste comprises pre-impregnating the plurality of fibres with a curable resin. Preferably the curable resin comprises epoxy.

Most preferably the step of fixing the combined plurality of fibres and the biocomposite paste comprises the steps of:

1) Applying pressure to the combined plurality of fibres and the biocomposite paste;
2) Removing water from the combined plurality of fibres and the biocomposite paste;
3) Curing the dried combined plurality of fibres and the biocomposite paste.
Preferably the step of removing water comprises air drying the combined plurality of fibres and the biocomposite paste at a temperature below 120°C. Optionally the step of removing water from combined plurality of fibres and the biocomposite paste comprises applying a vacuum to the paste.

Preferably the curing of the dried combined plurality of fibres and the biocomposite paste comprises a first curing of the dried combined plurality of fibres and the biocomposite paste at a temperature within the range from ambient to 180°C but ideally in the range 80-160°C.

Optionally the curing of the dried combined plurality of fibres and the biocomposite paste further comprises a second curing of the dried combined plurality of fibres and the biocomposite paste at a temperature within the range 120-180°C.

Specific Description

Aspects and advantages of the present invention will become apparent upon reading the following detailed description and upon reference to the following drawings in which:

Figure 1 presents a schematic representation of the structure of a fibre reinforced material in accordance with an aspect of the present invention;

Figure 2 presents a schematic representation of the biocomposite material of the fibre reinforced material of Figure 1;
Figure 3 presents a schematic representation of the chemical structure of cellulose present within the biocomposite material of Figure 2.

Figure 4 presents a flow chart of the method for producing the fibre reinforced material of Figure 1;

Figure 5 presents a flow chart of the method for producing cellulose fragments as employed within the method of Figure 4;

Figure 6 presents a schematic representation of a monolithic structure in accordance with an aspect of the present invention; and

Figure 7 presents a schematic representation of laminate structures in accordance with an aspect of the present invention.

A detailed description of a fibre reinforced material 1 in accordance with aspects of the present invention shall now be described with reference to Figures 1 and 2.

From Figure 1, the fibre reinforced material 1 can be seen to comprise a plurality of carbon fibres 2 located within a biocomposite material 3. A schematic representation of the biocomposite material 3 is shown in Figure 2. It can be seen that the biocomposite material 3 itself comprises a plurality of cellulose fragments 4 in the form of a network of cellulose microfibrils 5. The cellulose fragments 4 are infiltrated with a hydrophilic (or substantially hydrophilic) binder 6 and
encapsulated within a hydrophobic binder 7. In practice
the cellulose fragments 4 can range from comprising a mix
of individual cellulose microfibrils (typically ~20 nm in
diameter) to sections of cellulose cells typically ~50 µm
in length and breadth and less than 1 µm in thickness
themselves made up of a number of cellulose microfibrils
5. A schematic representation of the chemical structure
of cellulose is presented in Figure 3.

In the present embodiment the hydrophilic binder 6
comprises partially hydrolysed polyvinyl acetate. Partially hydrolysed polyvinyl acetate is known by those
skilled in the art to be a substantially hydrophilic
polymer that readily forms micelles in water. The
diameter and nature of the partially hydrolysed polyvinyl
acetate particles is such that they locate within the
cellulose fragment 3, as shown in Figure 2 (b).

In the present embodiment the hydrophobic binder 7
comprises an epoxy resin. Cured epoxy resins are known
by those skilled in the art to be hydrophobic in nature.
The uncured epoxy resin is therefore formed into micelles
with a typical diameter of ~0.5 - 2 µm. The diameter and
nature of the epoxy particles is such that these
particles cannot locate within the cellulose fragments 4.

In the cured fibre reinforced material 1 of Figure 1, the
polymer particles fuse and the epoxy interacts with the
partially hydrolysed polyvinyl acetate with the result
that there is a transfer of stress from the cured epoxy
matrix via the partially hydrolysed polyvinyl acetate to
the cellulose fragments 4. In a similar manner, as the
biocomposite material 3 fuses, it binds to the carbon
fibres thereby ensuring a further transfer of stress during mechanical loading from the biocomposite material to the carbon fibres.

A further function of the epoxy is that it effectively encapsulates the cellulose fragments and hence the partially hydrolysed polyvinyl acetate located therein, so rendering the reinforced fibre material impermeable to water.

The above described interactions provide the fibre reinforced material with the physical parameters as detailed in Table 1 below for composite material with randomly aligned carbon fibres. In particular, the properties outlined in Table 1 relate to a material that comprises 4% partially hydrolysed polyvinyl acetate by weight and 38% epoxy by weight, 8% carbon fibre by weight and in which the cellulose fragments are randomly orientated throughout the composite material. For comparison purposes Table 1 also includes typical results for a randomly orientated carbon fibre reinforced plastic.

The physical properties of the fibre reinforced material outlined in Table 1 and 2 can be varied by altering the relative proportion by weight of the partially hydrolysed polyvinyl acetate, the epoxy or the carbon fibres. It has been found that a fibre reinforced material that is impermeable to water can be produced when the partially hydrolysed polyvinyl acetate comprise between 1% and 55% of the total weight of the material while the epoxy can be varied within a range of 5% to 65% of the total weight of the material. It has been possible to produce these
fibre reinforced materials in samples in excess of 4mm thick.

It will be appreciated by those skilled in the art that the carbon fibres can be replaced with alternative high modulus, strength reinforcing fibres including, but not limited to, carbon nanotubes aramid fibres, glass fibres, hemp fibres, flax fibres. Furthermore, the orientation of the carbon fibres 2 shown in Figure 1 are for exemplary purposes only. It will be appreciated that a variety of orientation of the carbon fibres may be employed i.e. long or short individual fibres, bundles of fibres or woven clothes made out of the fibres. The function of the secondary reinforcing fibres is to confer increased stiffness and strength upon the final dried and cured mixture.

A method for producing the fibre reinforced material 1 shall now be described in detail, a flow chart for which is presented in Figure 4.

The first stage of the process involves the production of a bicomposite paste. In the first instance this involves the production of the cellulose fragments 4, comprising a network of cellulose microfibrils 5 which provides the framework for the biocomposite material 3. The production of the cellulose fragments 4 is achieved by the following process, a flow chart for which is provided in Figure 5:

1) A plant material is coarsely chopped into a plurality of pieces. In this particular example the plant material comprises chopped carrot.
2) The coarsely chopped carrot is then hydrothermally treated, at a temperature between 85-120°C at atmospheric pressure, until it begins to soften. Optionally steam and pressures above atmospheric pressures may be utilised to soften the carrots.

3) The resultant cooking liquid is then drained off from the softened coarsely chopped carrot.

4) Fresh water is then added to the residue material and this material is then processed in high speed blender for approximately 3-5 minutes so as to increase the available surface area of the material.

5) Optionally, the material can then be immediately used as described below. Alternatively, the material can be allowed to stand for a period of time before use with or without the addition of a micro-organism e.g. bacteria or yeast. Such additional steps further assist in the breakdown of the carrot material.

6) The resultant pulp produced by the blending process may then be filtered and washed with clean water.

7) Next the residue produced within the previous stage is mixed with a concentrated bleach solution and thereafter allowed to stand for 30 minutes, although longer time periods may be employed. The addition of bleach acts to kill of any unwanted micro-organisms while ensuring that a significant quantity of the pectins and hemicelluloses present within the original carrot material is dissolved within the resultant solution.

8) The bleach is then removed by washing and filtering. Thereafter, water is added to the residue which is then homogenised by passing through a high shear in-line mixer or a high shear batch mixer. This involves the passing of the residue through a fine mesh under high
shearing conditions so as to break down the cellular material in the residue so as to produce a pulp containing a range of cellulose fragments i.e. sized from individual cellulose microfibrils (on a scale of 20nm in diameter) up to sections of cellulose cells typically 50 µm in length and breadth and less than 1 µm in thickness depending on the precise processing conditions.

It is then required to reduce the water content within the resultant pulp. This is achieved by wrapping the pulp in a fine meshed bag and then pressing within a standard mechanical press. The resulting pressed pulp provides the required cellulose fragments and in particular comprises 1-30% cellulose by weight, and so behaves as a solid, feeling dry to the touch. It is essential that there remains enough water present within the cellulose fragments so as to prevent the cellulose fragments from interacting too strongly and therefore forming a rigid solid.

Although the above stage employs carrot plant material, a range of alternative plant materials may equally well be employed in order to obtain cellulose fragments, comprising the network of cellulose microfibrils. These include, but are not limited to turnip, swede, apple, sugar beet, beetroot and onions.

As an alternative to hydrothermally treating the coarsely chopped carrot, as outlined within step 2 above, the chopped carrot may simply be heated in a microwave or infrared heater until the required softening occurs.
As an alternative to the homogenisation process of step 8 above, the homogenised filtrate may be produced by subjecting the filtrate to a single pass through a high pressure homogeniser (at between 500-1000 bar).

In a further alternative to the above step 8 a sample of the homogenised pulp is taken before the water content within the pulp is reduced by pressing. This sample of pulp is then available for employment within a later stage of the process, as described in detail below.

The second stage of the process for producing the biocomposite paste involves the incorporation of a hydrophilic (or substantially hydrophilic) binder 6 within the cellulose fragments 4. This can be achieved by the following process:

1) The cellulose fragments 4, comprising a network of cellulose microfibrils 5 are re-hydrated with an emulsion or a particulate suspension of hydrophilic matrix material, namely PVA which exhibits high strains to failure (greater than 6%) and a low modulus of between 200-1000 MPa when formed into a solid. Depending upon the particular requirements of the biocomposite material 3 the emulsion produced at this stage can comprise between 1 and 60% resins (and/or glues) by weight and between 40 and 95% water. For the fibre reinforced material detailed within Table 1 the proportion of total resin (and/or glues) by weight was 42%.

2) The final step of this stage involves any excess water and PVA material that has not penetrated into the cellulose matrix being removed. This is achieved by
pressing the material (under a significant pressure) over a filter means. A soft smooth paste is then produced.

Although the above stage employs PVA as the hydrophilic binder any other hydrophilic binding material that can be incorporated within the cellulose fragments 4 may equally well be employed. Suitable alternative hydrophilic binding materials include acrylic resins and biological hydrophilic polymers such as gelatines and gaur gum.

The final stage of the process for producing the biocomposite paste involves the encapsulation of the cellulose fragments 4 and the PVA particles with a hydrophobic binder 7. This can be achieved by the following process:

1) An emulsion is formed by adding an epoxy resin to water through the employment of a non-ionic surfactant (e.g. Triton®-X octyl phenol ethoxylate). Typically the ratio of the epoxy particles to water is between 10:1 and 1:5. For the fibre reinforced material detailed in Table 1 the ratio of the epoxy particles to water was 1:1.

2) The emulsion is then added to the soft smooth paste produced within the second stage of the process so as to produce a thick smooth paste of uncured wet materials.

It is at this stage that the carbon fibres 2 are added to the biocomposite paste. In practice individual fibres or bundles of carbon fibres 2 are mixed with the paste either mechanically or by hand laying into the paste.
Once fully mixed the final stage of the process can take place. If the carbon fibres to be mixed with the biocomposite paste are in the form of fibre bundles, or bundles within a woven cloth then it has been found to be advantageous to the production of the fibre reinforced material to pre-impregnate the carbon fibres with a synthetic and uncured resin.

In order to fix the combined carbon fibres and biocomposite paste the following steps are carried out:

1) Pressure is applied to the thick smooth paste so as to ensure that the cellulose fragments are forced together and that there is some mixing of the materials at the nanoscopic level.

2) Residual water is then removed from the thick smooth paste by air drying at a temperature up to 110°C.

3) The dried material is then subjected to post drying curing in an oven at between 80-160°C.

A further improvement in the stiffness and strength of the biocomposite material can be achieved by employing a second post drying curing cycle in an oven at between 120-180°C.

Although the above stage employs an epoxy (e.g. bisphenol-A or a modified bisphenol A epoxy) as the hydrophobic binding material any other hydrophobic binding material that acts to encapsulate the cellulose fragments and the hydrophilic binders may equally well be employed. Suitable alternative hydrophobic binding materials include but are not limited to polyurethanes, phenolic resins, acrylics and siloxanes.
The step of the removing the residual water from the thick smooth paste containing the carbon fibres 2 may be achieved through the application of a vacuum, in conjunction with, or as an alternative to the process of air drying.

An alternative method for producing the cellulose fragments 4 from carrots shall now be described. The alternative method comprises the steps of:

D Hydrothermally treating whole carrots at a temperature between 85°C and 120°C at atmospheric pressure until they soften. Optionally steam and pressures above atmospheric pressure may be used to soften the carrots.

2) The resultant cooking liquid is then drained off from the carrots.

3) Fresh water is then added to the residue material and this material is then processed in a high shear mixer for a period of between 5 minutes and 4 hours, although longer process times are possible.

4) The resultant residue produced by the shear mixing process can be taken to the next stage immediately or alternatively the material can be left to stand in a container, ideally for 12 - 14 days although shorter or longer times are possible. Optionally when left to stand a micro-organism (e.g. bacteria or yeast) can be added to the residue, as previously described.

5) Optionally the resultant residue is then filtered and washed with clean water.
The residue produced within the previous stage is then mixed with a bleaching solution ideally of the concentration 0.5% and is allowed to stand for up to 15 hours. This ensures that an effective quantity of pectins and hemicellulose present within the original carrot material is dissolved within the resultant solution.

A number of options are available at this stage. The first option is to remove the bleach by filtering and washing the resultant solution. Optionally, if further reduction in the particle size of the material is desired then further processing of the material can take place either using a high shear mixer or through a high-pressure homogeniser. A final alternative is to initially homogenise the residue and to thereafter remove the bleach by filtering and washing the resultant solution. In practice the resultant bicomposite material appears to be relatively independent of the particular order of this step of the process.

The water content within the resultant pulp is then reduced, as previously described, so as to provide the required cellulose fragments which preferably comprises 1% - 30% cellulose by weight.

An alternative for forming the hydrophilic polymer solution comprises the employment of the sample taken of the pulp from the high pressure homogeniser. This process involves the step of:

1. Passing the sample through the homogeniser a number of times so as to reduce the cellulose fibrils and
microfibrils. This material is retained in the liquid form.

2. The hydrophilic polymer (e.g. PVA) is then mixed directly with this liquid to form a solution comprising PVA particles and the cellulose fibrils and microfibrils. This is then used as previously described.

An alternative for forming the hydrophobic polymer emulsion comprises the employment of the sample taken of pulp produced from the high pressure homogeniser. This process involves the steps of:

1) Passing the sample through the homogeniser a number of times so as to reduce the cellulose fragments 4 to individual cellulose fibrils and microfibrils. This material is then retained in liquid form.

2) The epoxy particles are then mixed directly with this liquid so as to produce an emulsion comprising the epoxy particles and the cellulose fibrils and microfibrils. Similar ratios to those previously described are again employed.

A number of examples of uses of the described fibre reinforced materials 1 shall now be described.

In the first instance the fibre reinforced material 1 can be used to produce a monolithic structure 8 through which the mechanical properties are graded. Essentially a multi layer structure can be formed within which there exist no internal interfaces to compromise the overall structure. This is achieved by laying down a layer of the uncured composite material 1 containing carbon fibres
2 with the correct formulation for the mechanical properties required (this layer can be several mm thick) before a second layer of uncured material 1 with a different mechanical property (produced by using a different ratio of constituents) is laid down on top of the first. Repeating this step a number of times results in a structure with different mechanical property layers. Once the required number of layers has been reached the composite material is then pressed and cured to form the monolithic structure 8, as appropriate. It will be readily apparent that each of the layers may in fact exhibit the same, or similar, mechanical properties. Alternatively, biocomposite layers in the absence of carbon fibres may be incorporated within the monolithic structure 8.

By way of example this method can be employed to produce a ski in which an extremely tough layer 9 is initially prepared, upon which a stiffer layer 10 is then laid, followed by a layer of intermediate properties 11 at the core with a layer of stiff 10 and then tough material 9 completing the structure. Such a structure is presented schematically in Figure 6.

Alternatively, the fibre reinforced material 1 can be used within a more conventional lamination process so as to form a laminate structure 12, see Figure 7a. The laminate structure 12 can be employed to produce thick flat items such as skis, snow boards, surf boards, skate boards etc or tubular items such as fishing rods, bicycle frames, ski poles, sail spars, masts etc. This is achieved by dipping pre-formed sheets of the fibre reinforced material 1 in a hydrophobic resin 13, stacking
the sheets on top of one another and thereafter pressing under high pressure. When the hydrophobic resin 13 has cured the laminate structure 12 is removed from the press and if necessary given an extra surface coating of a finishing material.

It will be apparent to those skilled in the art that the laminate structure 12 may comprise one or more layers of materials already known in the art e.g. plasties, carbon fibre reinforced plastic materials and non fibre reinforced biocomposite materials.

As discussed above, a known problem of prior art laminate structures that comprise carbon fibre, reinforced plastic materials are the large difference in stiffness between the fibres and the plastic. This can cause problems of delamination when different layers of carbon fibre composites are bonded together with resins.

Incorporation of one or more layers of the fibre reinforced material 1, without the addition of a separate glue layer 13, provides a means for alleviating this problem (see Figure 7b). The advantage of using the fibre reinforced material 1 to form the laminate structure 15 is that it can increase stiffness, strength and toughness in certain directions, for certain orientations of the layers. For example a laminate made from a layer of unidirectional carbon fibres in epoxy resin 14 and a layer of fibre reinforced material 1, see Figure 7 (b), has been found to exhibit a higher stiffness and strength, when tested in tension in the direction of the carbon fibre of the epoxy layer 14, than a laminate
made from two layers of carbon-epoxy with fibre directions at right angles.

The above described laminate structures 15 may be formed in a number of ways. The first method comprises applying a layer of biocomposite paste containing carbon fibres to a pre-cured layer of a known high stiffness fibre reinforced composite. The biocomposite paste layer is then dried and cured by heating. Pressure need not be applied to the laminate during curing, but can be advantageous in reducing imperfections in the fibre reinforced material 1. Several layers can be built up by this method (e.g. composite/material 1/composite/material 1) before drying and curing, or each material 1 layer can be cured first before the addition of further layers.

An alternative method involves applying an uncured high stiffness fibre reinforced plastic to a layer of the fibre reinforced material 1. The high stiffness fibre reinforced plastic is then cured. Pressure may need to be applied to the laminate during curing. Several layers can be again be built up employing this method (e.g. material 1/composite/material 1/composite) before drying and curing, or each material 1 layer and composite layer can be cured first before the addition of further layers.

A further alternative method comprises the pressing of layers of fibre reinforced material 1 and high stiffness fibre reinforced plastic together with an adhesive. Pressure is sustained until the adhesive has cured.

The fibre reinforced material 1 is also found to increase the toughness of carbon fibre structures when applied as
A surface finish i.e. a lamination of carbon fibre-biocomposite. This is because certain formulations of the biocomposite material have higher failure strains than the carbon fibre, while still retaining good strength.

A further example application of the fibre reinforced material is in the production of tubular sections which are suitable for use within a fishing rod. The fibre reinforced material is initially prepared as described above. Before curing however the biocomposite paste and carbon fibres mixture of material is placed into a porous mould or a mould which contains a porous liner (e.g. ceramic, clay or open celled foam) and formed round a waxed tapered mandrel of the required dimensions. The material is then air dried to remove water. Next the tapered tube of the fibre reinforced material is removed from the mandrel and preferably heated to a temperature of around 120°C. Finally the tube is post cured at temperatures of up to 180°C.

An alternative method for the production of tubular sections comprises the employment of pre impregnated (prepreg) carbon fibre. The prepreg carbon fibre is cut to size and then rolled onto a tapered biocomposite tube produced in a similar manner to that described above. Heat shrink tape is then wrapped around the carbon fibre/biocomposite tapered tube. The final stage then involves placing the carbon fibre/biocomposite tapered tube in an oven so as to cure the prepreg carbon fibre.

In an alternative embodiment an additional layer of biocomposite material can be formed around the outside of
the hybrid composite tubes so as to give a strong tough outer layer.

The fibre reinforced materials described above exhibits several unique features over those materials described in the prior art. The first advantage of the reinforced fibre material 1 over conventional carbon-epoxy composites and laminates resides in the fact that the biocomposite has much greater stiffness, strength and toughness than the normal synthetic polymers (e.g. epoxy resin) that are used to make fibre reinforced composites. Therefore the resulting fibre reinforced materials 1 are stiffer, stronger and tougher than conventional systems. This is particularly important with regard to the stiffness and strength of material 1 with unidirectional carbon fibres, when tested at right angles to the carbon fibre axis. In this case the composites are found to be up to ten times stiffer and three times stronger than the equivalent carbon-epoxy composites tested at right angles to the long axis of the carbon fibres.

The advantage of this material over the mixtures of carbon and wood fibres described earlier is that the biocomposite used here has higher stiffness and strength than wood based systems and in addition is more water resistant. In addition these parameters are achieved without any compromise on the toughness of the material and so the described fibre reinforced material is not brittle like many of the known biocomposite based materials. Typically the composite materials 1 exhibit a bending strength in the range of 60 MPa to 600 MPa.
Furthermore, the described material has the significant advantage that it is also impermeable to water so allowing it to be employed within a range of applications. In particular, the described material may be employed to produce skis, snow boards, surf boards, skate boards etc or tubular items such as fishing rods, bicycle frames, ski poles, sail spars, masts. However it is envisaged that wherever there is a requirement for a strong flat material, that is impermeable to water, then the described fibre reinforced material would provide an ideal solution.

Since the described extraction process of cellulose fragments from the plant material requires relatively little energy the method of manufacture is more amenable to be employed on a commercial scale. In addition, the manufacturing process is less complex than those previously described in the art to produce composites from wood fibres or bacterial cellulose. A particular advantage to the described method is that it does not require the employment of an organic solvent.

As a result the fibre reinforced material exhibits a unique combination of physical properties can be produced from a sustainable resource and manufactured by a relatively low energy, non polluting process. In fact the fibre reinforced material produced appears to be many times tougher than any waterproof cellulose based reinforced composite produced to date.

The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the
invention to the precise form disclosed. The described embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilise the invention in various embodiments and with various modifications as are suited to the particular use contemplated. Therefore, further modifications or improvements may be incorporated without departing from the scope of the invention as defined by the appended claims.
Table 1 - Mechanical properties of composite 1 with randomly orientated carbon fibres, compared to a carbon-epoxy composite with randomly aligned carbon fibres

<table>
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<tr>
<th>Material</th>
<th>Stiffness (Young’s Modulus, GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Toughness (Energy absorbed to failure, MJ/m³)</th>
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<tr>
<td>Carbon Fibre Reinforced Biocomposite Material</td>
<td>20</td>
<td>240</td>
<td>2.5</td>
</tr>
<tr>
<td>Carbon Fibre Reinforced Plastic</td>
<td>7.2</td>
<td>125</td>
<td>1.25</td>
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1) A fibre reinforced material (1) comprising a biocomposite material (3) reinforced with a plurality of fibres (3) wherein the biocomposite material (1) comprises a plurality of cellulose fragments (4) made up of a network of cellulose microfibrils (5), a plurality of hydrophilic binders (6) located within the network of cellulose microfibrils (5) , and a plurality of hydrophobic binders (7) arranged to interact with the hydrophilic binders (6) so as to encapsulate the plurality of cellulose fragments (4).

2) A fibre reinforced material (1) as claimed in Claim 1 wherein the biocomposite material (3) has the general formulation Cel_{(1-x-y)} HPI_{x} HPO_{y} where x is within the range of from 0.01 to 0.55 and y is within the range of from 0.05 to 0.65.

3) A fibre reinforced material (1) as claimed in Claim 1 or Claim 2 wherein the fibre reinforced material (1) exhibits a stiffness in the range from 5GPa to 90GPa.

4) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the plurality of fibres (2) are arranged in a randomly orientated manner.

5) A fibre reinforced material (1) as claimed in any of Claims 1 to 3 wherein the plurality of fibres (2) are arranged in a unidirectional manner.
6) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the plurality of fibres (2) comprise fibres selected from a group comprising carbon fibre, carbon nanotubes aramide fibres, glass fibres, hemp fibres and flax fibres.

7) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the cellulose fragments (4) are arranged in a randomly orientated manner.

8) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the material (1) exhibits a tensile strength in the range from 60 MPa to 1 GPa.

9) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the material (1) exhibit a bending strength in the range from 60 MPa to 600 MPa.

10) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the material (1) exhibits a stiffness in the range from 14 GPa to 40 GPa.

11) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the material (1) exhibits a strength in the range from 200 MPa to 600 MPa.

12) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the material (1)
exhibits a toughness in the range from 2 MJm$^{-3}$ to 10 MJm$^{-3}$.

13) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the hydrophilic binders (6) comprises a hydrophilic or substantially hydrophilic polymer.

14) A fibre reinforced material (1) as claimed in Claim 13 wherein the hydrophilic polymer comprises a hemicellulose, an acrylic resin or a partially hydrolysed polyvinyl acetate.

15) A fibre reinforced material (1) as claimed in Claim 13 wherein the hydrophilic polymer comprises a biological hydrophilic polymer.

16) A fibre reinforced material (1) as claimed in any of the preceding claims wherein the hydrophobic binders (7) comprises a hydrophobic polymer.

17) A fibre reinforced material (1) as claimed in Claim 16 wherein the hydrophobic polymer comprises an epoxy.

18) A fibre reinforced material (1) as claimed in Claim 16 wherein the hydrophobic binders comprises a binder selected from the group comprising polyurethanes, phenolic resins, acrylics and siloxanes.

19) A monolithic structure comprising two or more layers (9, 10, 11) wherein at least one layer comprises a
reinforced fibre material (1) as claimed in any of Claims 1 to 18.

20) A monolithic structure as claimed in Claim 19 wherein the monolithic structure comprises at least one layer of a plastic material.

21) A monolithic structure as claimed in Claim 20 wherein the plastic material comprises a carbon fibre reinforced material.

22) A laminate structure (12) comprising two or more layers (1, 14) wherein at least one layer comprises a fibre reinforced material (1) as claimed in any of Claims 1 to 18.

23) A laminate structure (12) as claimed in Claim 22 wherein the laminate structure .(12) comprises at least one layer of a plastic material (14).

24) A laminate structure (12) as claimed in Claim 23 wherein the plastic material (14) comprises a carbon fibre reinforced material.

25) A laminate structure (12) as claimed in any of Claims 22 to 24 wherein the laminate structure (12) comprises one or more layers of resin (13) located between the two or more layers (1, 14) of the structure.

26) A laminate structure (12) as claimed in Claim 25 wherein the one or more layers of resin (13) comprise a hydrophobic resin.
21) A tube, suitable for use in a fishing rod, the tube comprising a fibre reinforced material (1) as claimed in any of Claims 1 to 18.

28) A method of producing a fibre reinforced material (1) that is impermeable to water comprising the steps of:
1) Producing a biocomposite paste comprising a plurality of cellulose fragments, (4) a plurality of hydrophilic binders (6), and a plurality of hydrophobic binders (7);
2) Incorporating a plurality of fibres (2) within the biocomposite paste; and
3) Fixing the combined plurality of fibres (2) and the biocomposite paste.

29) A method of producing a fibre reinforced material (1) as claimed in Claim 28 wherein the step of producing a biocomposite paste comprises the steps of:
1) Producing the plurality of cellulose fragments (4), comprising a network of cellulose microfibrils (5);
2) Incorporating the plurality hydrophilic binders (6) within the plurality of cellulose fragments (4); and
3) Encapsulating the plurality of cellulose fragments (4) and the plurality of hydrophilic binders (6) within the plurality of hydrophobic binders (7).
A method of producing a fibre reinforced material (1) as claimed in Claim 29 wherein the step of incorporating the plurality hydrophilic binders (6) within the cellulose fragments (4) comprises:

1) Re-hydrating the cellulose fragments (4) with a first emulsion/dispersion comprising the hydrophilic binders (6) so as to produce a paste; and

2) Removing excess water and excess hydrophilic binders (6) from the paste.

A method of producing a fibre reinforced material (1) as claimed in Claim 29 or Claim 30 wherein the step of encapsulating the plurality of cellulose fragments (4) and the plurality of hydrophilic binders (6) comprises:

1) Producing a second emulsion comprising the plurality of hydrophobic binders (7);

2) Mixing the second emulsion with the paste containing the hydrophilic binders (6).

A method of producing a fibre reinforced material (1) as claimed in Claim 31 wherein the production of the second emulsion involves mixing the hydrophobic binders (7) with a surfactant and water.

A method of producing a fibre reinforced material (1) as claimed in Claim 32 wherein the surfactant is non-ionic.

A method of producing a fibre reinforced material (1) as claimed in Claim 32 or Claim 33 wherein the
ratio of the hydrophobic binders (6) to the water within the second emulsion is between 10:1 and 1:5.

35) A method of producing a fibre reinforced material (1) as claimed in Claim 34 wherein the ratio is between 10:1 and 5:1.

36) A method of producing a fibre reinforced material (1) as claimed in any of Claims 28 to 35 wherein the step of incorporating the plurality of fibres (2) within the biocomposite paste comprises pre-impregnating the plurality of fibres (2) with a curable resin.

37) A method of producing a fibre reinforced material (1) as claimed in Claim 36 wherein the curable resin comprises epoxy.

38) A method of producing a fibre reinforced material (1) as claimed in any of Claims 28 to 37 wherein the step of fixing the combined plurality of fibres (2) and the biocomposite paste comprises the steps of:

1) Applying pressure to the combined plurality of fibres (2) and the biocomposite paste;
2) Removing water from the combined plurality of fibres (2) and the biocomposite paste; and
3) Curing the dried combined plurality of fibres (2) and the biocomposite paste.

39) A method of producing a fibre reinforced material (1) as claimed in Claim 38 wherein the step of removing water comprises air drying the combined
40) A method of producing a fibre reinforced material (1) as claimed in Claim 38 wherein the step of removing water from combined plurality of fibres (2) and the biocomposite paste comprises applying a vacuum to the paste.

41) A method of producing a fibre reinforced material (1) as claimed in any of Claims 38 to 40 wherein the curing of the dried combined plurality of fibres (2) and the biocomposite paste comprises a first curing of the dried combined plurality of fibres (2) and the biocomposite paste at a temperature within the range from ambient to 180°C.

42) A method of producing a fibre reinforced material (1) as claimed in Claim 41 wherein the first curing of the dried combined plurality of fibres (2) and the biocomposite paste is at a temperature within the range from 80 to 160°C.

43) A method of producing a fibre reinforced material (1) as claimed in either of Claims 41 or 42 wherein the curing of the dried combined plurality of fibres (2) and the biocomposite paste further comprises a second curing of the dried combined plurality of fibres (2) and the biocomposite paste at a temperature within the range from 120 to 180°C.
Figure 1
Produce a biocomposite paste comprising cellulose fragments, a plurality of hydrophilic binders and a plurality of hydrophobic binders

Incorporate a plurality of secondary fibres within the biocomposite paste

Fix the combined secondary fibres and biocomposite paste

Figure 4
Produce first pulp comprising plant material

Leave pulp to stand
Use pulp immediately
Add microorganisms

Mix with bleach solution

Produce second pulp by removing bleach

Reduce water content within second pulp

Figure 5
### INTERNATIONAL SEARCH REPORT

**International application No**

PCT/GB2007/000903

### A. CLASSIFICATION OF SUBJECT MATTER

**INV.** C08L1/00  B32B5/10

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)

C08L  DOI F  D21C  B32B

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 practical, search terms used)

EPO-Internal , WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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### D

Further documents are listed in the continuation of Box C

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  *A* document defining the general state of the art which is not considered to be of particular relevance
  
  *E* earlier document but published on or after the international filing date
  
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  *D* document referring to an oral disclosure, use, exhibition or other means
  
  *P* document published prior to the international filing date but later than the priority date claimed

*X* 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

*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

*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

*F* document member of the same patent family

Date of the actual completion of the international search

14 June 2007

Date of mailing of the international search report

28/06/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel (+31-70) 340-2040, TX 31 651 epo nl, Fax (+31-70) 340-3016

Authorized officer

Lux, Rudolf
**INTERNATIONAL SEARCH REPORT**

**Information on patent family members**

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