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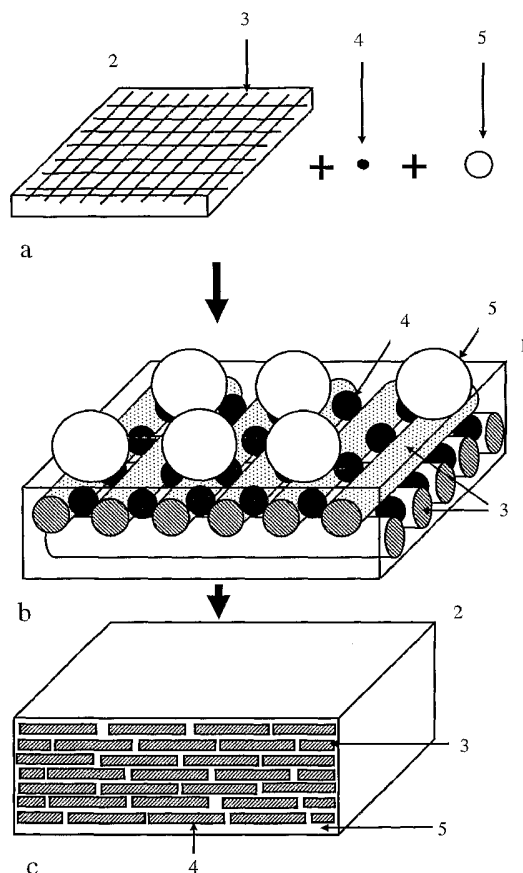
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[Continued on next page]

(54) Title: IMPROVED BIOCOMPOSITE MATERIAL



(57) Abstract: A biocomposite material (1) and methods of production thereof are described. The biocomposite material (1) exhibits a physical stiffness, strength and toughness comparable to known glass fibre composites while its composition makes it inherently impermeable to water. A general formulation for the biocomposite material (1) is given by the expression:  $\text{Cel}_{(1-x-y)} \text{HPI}_x \text{HPO}_y$  where "Cel" represents cellulose fragments (2), "HPI" represents hydrophilic binders (4), "HPO" represents hydrophobic binders (5) and (x) and (y) quantify the percentage by weight of the hydrophilic (4) and hydrophobic binders (5) present within a material, respectively. The described properties of the biocomposite material (1) are achieved when (x) is within the range of from 0.05 to 0.55 and (y) is within the range of from 0.05 to 0.65.



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1 **Improved Biocomposite Material**

2

3 The present invention relates to the field of  
4 biocomposite materials and in particular to biocomposite  
5 materials produced through the extraction of cellulose  
6 from plants.

7

8 The use of plant based long fibres such as hemp, flax,  
9 kanaf, cotton, jute, sisal and coconut fibre mats as  
10 reinforcement for polymer matrices such as polypropylene  
11 and epoxy resins are well known to those skilled in the  
12 art. These composites utilise fibres which are typically  
13 several centimetres long and hundreds of micrometers wide  
14 (usually in the form of bundles of several bast fibre  
15 cells). Primarily these plant based long fibres have  
16 found applications in the automotive industry, but only  
17 for non-structural applications such as door liners and  
18 parcel shelves, due in part to the poor surface finish  
19 achieved with these materials, but mainly because of  
20 their reduced toughness when compared to glass fibre  
21 reinforced polymers (GFRP). These materials are also  
22 known to exhibit inherent problems with water absorption  
23 and odour release.

1  
2 Shorter plant fibres, mainly derived from wood pulp, have  
3 also been used by those skilled in the art as  
4 reinforcements for plastics. Traditional materials made  
5 from these fibres include Formica, medium density fibre  
6 board (MDF) and high density fibre board (HDF). However,  
7 these materials suffer from similar problems to the long  
8 plant fibre composites, being either brittle and water  
9 proof (e.g. Formica) or alternatively tough but water  
10 absorbent (e.g. MDF).

11  
12 Recently it has been discovered that high performance  
13 materials can be produced by impregnating mats of  
14 fibrillated wood pulp fibres with phenolic resin (see  
15 Nakagaito et al "The Effect Of Morphological Changes From  
16 Pulp Fiber Towards Nano-Scale Fibrillated Cellulose On  
17 The Mechanical Properties Of High-Strength Plant Fibre  
18 Composites" Applied Physics A: Materials Science &  
19 Processing Vol. 78 Page 547-552 (2004) and Yano et al  
20 "Bio-Composites Produced From Plant Microfiber Bundles  
21 With A Nanometer Unit Web-Like Network" Journal Materials  
22 Science Vol. 39 Page 1635-1638 (2004)). The fibrillation  
23 of the wood fibres acts to partially separate cellulose  
24 microfibrils within the cell walls so that the wood  
25 fibres become more absorbent and the surface 'roughened'  
26 so that there is a greater surface area for interaction  
27 with other fibres and binders. In general these  
28 materials are stiff and strong but only achieve toughness  
29 equal to or greater than glass fibre if the resin content  
30 is kept to less than 3%, so resulting in a highly  
31 hygroscopic material which losses strength as it absorbs  
32 water. Also the method of manufacturing the materials,  
33 which involves impregnating sheets of dry fibres with

1 dilute resin and then stacking many thin (<0.5mm) sheets  
2 of impregnated material on top of one another and hot  
3 pressing at high pressure, is a very time consuming  
4 process, taking over 100 hours. This severely increases  
5 manufacturing time compared to GFRP and so greatly limits  
6 the potential range of applications for these materials.

7  
8 US Patent No. US 4,609,431 in the name of Congoleum  
9 Corporation teaches of a tough, water proof material  
10 produced by mixing lower quantities of wood pulp fibres  
11 (less than 30%) with glass fibres and thereafter  
12 embedding these within a complex of rubber materials and  
13 inorganic fillers. However, these materials exhibit a  
14 lower stiffness than GFRP which limits their applications  
15 to surface finishes. Furthermore, such materials can  
16 only be classified as a partial biocomposite material due  
17 to the significant proportion of GFRP present.

18  
19 A further method of forming composite materials is  
20 described by Matsumura et al "Cellulosic Nanocomposites I  
21 Thermally Deformable Cellulose Hexanoates From  
22 Heterogeneous Reaction" J. Applied Polymer Science Vol.  
23 78 Page 2242-2253 (2000). This method involves the  
24 chemical treatment of the surface of wood fibres so as to  
25 cause esterification of the wood fibres. The esterified  
26 fibres are then hot pressed together to form consolidated  
27 sheets. Although these materials are water resistant  
28 they exhibit only limited modulus and strength.

29  
30 The prior art also teaches that it is possible to  
31 completely separate cellulose microfibrils from animal  
32 and bacterial sources which are much smaller and thinner  
33 than the previously discussed plant fibres (being 5-20nm

in diameter), see PCT Application No. PCT/NL92/00206 in the name of DSM N.V. and PCT Application No. PCT/US89/02355 in the name of Brown, respectively. Composite materials made from these animal and bacterial cellulose microfibrils have been shown to exhibit high stiffness and good strength but have inherently low failure strains which results in them being brittle in nature.

Improvements to these composite materials have been achieved by mixing the cellulose microfibrils with low modulus resins/binders so as to produce a tougher composite material. However, the tensile modulus of these composite materials is less than 5 GPa, which is no better than the levels achieved within non-reinforced plastics, and is too low to allow them to be employed within many structural applications.

Within these composite materials it is also desirable to achieve high volume fractions of the cellulose microfibrils within the finished composites. However, this in itself is problematic because even when a few percent, by weight, of free cellulose microfibrils are added to a liquid, the viscosity of the liquid increases dramatically. Indeed the liquid quickly becomes a gel if the cellulose microfibrils begin to interact with one another (at less than 15% microfibril content).

To date the only way to achieve the high volume fractions, which are necessary to produce high stiffness, high strength composite materials, has been to employ a method described by Nakagaito et al "Bacterial Cellulose: The Ultimate Nano-Scalar Cellulose Morphology For The

1 Production Of High-Strength Composites" Applied Physics  
2 A: Materials Science & Processing DOI: 10.1007/s00339-  
3 004-2932-3 (2004). This method involves the formation of  
4 mats of the cellulose microfibrils by precipitation from  
5 water, drying off of the water (or sequential replacement  
6 of the water with an organic solvent) and then  
7 impregnating the resultant material with a resin (often  
8 under high pressure). This is a complex and time  
9 consuming process involving many individual manufacturing  
10 steps and so the composite materials produced by this  
11 route consume large amounts of energy during  
12 manufacturing and therefore are not economical for  
13 commercial scale production.

14

15 It is also known to those skilled in the art that  
16 cellulose microfibrils can be found within almost all  
17 plant cell walls. Indeed Dufresne et al "Mechanical  
18 behaviour of sheets prepared from sugar beet cellulose  
19 microfibrils" J Appl Polym Sci Vol. 64 Page 1185-1194  
20 (1997) teach that these cellulose microfibrils can be  
21 extracted from these plant cells using a combination of  
22 chemical degradation of plant material and high pressure  
23 homogenisation. The cellulose microfibrils can then be  
24 used to produce composite materials, in a similar way to  
25 those described previously in connection with animal and  
26 bacterial cellulose microfibrils, as described in  
27 Dufresne A et al "Cellulose Microfibrils From Potato  
28 Tuber Cells: Processing And Characterisation Of Starch-  
29 Cellulose Microfibril Composites" J. Applied Polymer  
30 Science Vol. 76 Page 208-2092 (2000). To date the  
31 composite materials produced by this method exhibit very  
32 poor mechanical properties with low stiffness and poor  
33 strength. This is partly due to the low upper limit of

1 15% of the cellulose microfibrils that can be mixed with  
2 the liquid resin, before it becomes a solid gel, as  
3 discussed above.

4

5 It is therefore an object of an aspect of the present  
6 invention to provide a biocomposite material that  
7 exhibits a physical stiffness, strength and toughness  
8 comparable to known glass fibre composites but which is  
9 also inherently impermeable to water.

10

11 It is a further object of an aspect of the present  
12 invention to provide a biocomposite material that  
13 exhibits the above properties and which can be produced  
14 economically on a commercial scale.

15

16 For clarity purposes it should be noted that the  
17 stiffness of a material is quantified by the Young's  
18 modulus exhibited by the material while the toughness of  
19 a material is quantified by the amount of energy absorbed  
20 per unit volume of the material up to the point of  
21 failure. Furthermore, an impermeable material is defined  
22 as a material that has a significantly slower rate of  
23 water uptake when completely immersed in water when  
24 compared to cellulose or previously known cellulose  
25 composites.

26

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

32

33



1

2 Summary of the Invention

3

4 According to a first aspect of the present invention  
5 there is provided a biocomposite material comprising a  
6 plurality of cellulose fragments made up of a network of  
7 cellulose microfibrils, a plurality of hydrophilic  
8 binders located within the network of cellulose  
9 microfibrils and a plurality of hydrophobic binders  
10 arranged to interact with the hydrophilic binders so as  
11 to encapsulate the plurality of cellulose fragments.

12

13 The above arrangement ensures good stress transfer from  
14 the hydrophobic binders through the hydrophilic binders  
15 to the cellulose microfibrils so providing the  
16 biocomposite material with the desired stiffness,  
17 strength and toughness. By arranging the hydrophobic  
18 binders so as to encapsulate the cellulose fragments, the  
19 biocomposite material is also rendered impermeable to  
20 water.

21

22 Most preferably the biocomposite material of the first  
23 aspect of the present invention has the general  
24 formulation  $\text{Cel}_{(1-x-y)} \text{HPI}_x \text{HPO}_y$  where  $x$  is within the range  
25 of from 0.05 to 0.55 and  $y$  is within the range of from  
26 0.05 to 0.65.

27

28 According to a second aspect of the present invention  
29 there is provided a biocomposite material that is  
30 impermeable to water comprising a plurality of cellulose  
31 fragments made up of a network of cellulose microfibrils,  
32 a plurality of hydrophilic binders and a plurality of  
33 hydrophobic binders having the general formulation  $\text{Cel}_{(1-x-}$

1     $y) \text{HPI}_x \text{HPO}_y$  where  $x$  is within the range of from 0.05 to  
2    0.55 and  $y$  is within the range of from 0.05 to 0.65.

3  
4    Preferably the plurality of hydrophilic binders are  
5    located within the network of cellulose microfibrils and  
6    the plurality of hydrophobic binders are arranged to  
7    interact with the hydrophilic binders so as to  
8    encapsulate the plurality of cellulose fragments.

9  
10    Most preferably the biocomposite material of the first  
11    and second aspects of the present invention exhibits a  
12    stiffness in the range from 5 GPa to 90 GPa.

13  
14    According to a third aspect of the present invention  
15    there is provided a biocomposite material that is  
16    impermeable to water and which exhibits a stiffness in  
17    the range from 5 GPa to 90 GPa.

18  
19    Preferably the biocomposite material of the third aspect  
20    of the present invention comprises a plurality of  
21    cellulose fragments made up of a network of cellulose  
22    microfibrils, a plurality of hydrophilic binders located  
23    within the network of cellulose microfibrils and a  
24    plurality of hydrophobic binders arranged to interact  
25    with the hydrophilic binders so as to encapsulate the  
26    plurality of cellulose fragments.

27  
28    Preferably the biocomposite material of the third aspect  
29    of the present invention has the general formulation  
30     $\text{Cel}_{(1-x-y)} \text{HPI}_x \text{HPO}_y$  where  $x$  is within the range of from 0.05  
31    to 0.55 and  $y$  is within the range of from 0.05 to 0.65

32

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

4

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

8

9 Most preferably the biocomposite material of the various  
10 aspects of the present invention exhibit a bending  
11 strength in the range from 60 MPa to 600 MPa.

12

13 Most preferably the biocomposite material of the various  
14 aspects of the present invention exhibits a stiffness in  
15 the range from 14GPa to 21GPa.

16

17 Most preferably the biocomposite material of the various  
18 aspects of the present invention exhibits a strength in  
19 the range from 200MPa to 300MPa.

20

21 Most preferably the biocomposite material of the various  
22 aspects of the present invention exhibit a toughness in  
23 the range from 3 MJm<sup>-3</sup> to 10 MJm<sup>-3</sup>.

24

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

31

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

4  
5 Alternatively the hydrophobic binders comprises a binder  
6 selected from the group comprising polyurethanes,  
7 phenolic resins, acrylics and siloxanes.

8  
9 According to a fourth aspect of the present invention  
10 there is provided a monolithic structure comprising two  
11 or more layers wherein at least one layer comprises a  
12 biocomposite material in accordance with any of the first  
13 to third aspects of the present invention.

14  
15 The formation of a monolithic layered structure provides  
16 a structure within which the mechanical properties can be  
17 gradated, as appropriate. As curing results in there  
18 being no distinct interfaces between the layers, these  
19 monolithic structures experience no compromise to their  
20 mechanical properties.

21  
22 Optionally the monolithic structure comprises at least  
23 one layer of a plastic material. Preferably the plastic  
24 material comprises a carbon fibre reinforced material.

25  
26 According to a fifth aspect of the present invention  
27 there is provided a laminate structure comprising two or  
28 more layers wherein at least one layer comprises a  
29 biocomposite material in accordance with any of the first  
30 to fourth aspects of the present invention.

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

4  
5 Preferably the laminate structure comprises one or more  
6 layers of resin located between the two or more layers of  
7 the structure.

8  
9 Preferably the one or more layers of resin comprise a  
10 hydrophobic resin such as epoxy or polyurethane.

11  
12 According to a sixth aspect of the present invention  
13 there is provided a tube, suitable for use in a fishing  
14 rod, the tube comprising a biocomposite material in  
15 accordance with the first to fifth aspects of the present  
16 invention.

17  
18 According to a seventh aspect of the present invention  
19 there is provided a method of producing cellulose  
20 fragments, comprising a network of cellulose  
21 microfibrils, from a plant material comprising the steps  
22 of:

- 23 1) Producing a first pulp of the plant material;
- 24 2) Mixing a first pulp with a bleach solution so that a  
25 quantity of pectins and hemicelluloses present within  
26 the plant material are dissolved within a resultant  
27 solution;
- 28 3) Producing a second pulp by removing the bleach from the  
29 resultant solution; and
- 30 4) Reducing the water content present within the second  
31 pulp.

32

1 Optionally the first pulp is filtered and washed in water  
2 before mixing with the bleach solution;

3

4 Preferably the step of producing the first pulp comprises  
5 the steps of:

6 1) Heating the plant material so as to soften the plant  
7 material;

8 2) Filtering any resultant liquid from the softened plant  
9 material; and

10 3) Blending the resultant residue with water.

11

12 Optionally the step of producing the first pulp further  
13 comprises chopping of the plant material before heating.

14

15 Preferably the plant material is heated to temperature  
16 between 85°C and 120°C at atmospheric pressure.

17

18 Optionally the blended resultant residue and water is  
19 allowed to stand for a period of at least one day.

20 Optionally a micro-organism is added to the blended  
21 resultant residue so as to aid the breakdown of the plant  
22 material. The micro-organism optionally comprises  
23 bacterium or yeast.

24

25 Preferably the mixture of the first pulp and the bleach  
26 solution is allowed to stand for a period of at least  
27 thirty minutes so as to form the resultant solution.  
28 This has been found to have the effect of aiding the  
29 reduction of the particle size produced.

30

31 Preferably the step of producing a second pulp comprises  
32 washing and filtering the resultant solution so as to  
33 remove the bleach and so produce a second residue.

1  
2 Optionally the step of producing the second pulp further  
3 comprises the step of homogenising the second residue.

4  
5 Preferably the second residue is homogenised by mixing  
6 the second residue within a high shear mixing process.  
7 Alternatively the second residue is homogenised by  
8 pressurising the second residue at a pressure between 500  
9 and 1000 bar.

10  
11 Alternatively, the step of producing a second pulp  
12 comprises homogenising the resultant solution and then  
13 washing and filtering the homogenised resultant solution  
14 so as to remove the bleach.

15  
16 Preferably the step of reducing the water content present  
17 within the second pulp comprises pressing the second  
18 pulp.

19  
20 Most preferably the pressing of the second pulp results  
21 in the second pulp comprising at least 40% water by  
22 weight.

23  
24 According to an eighth aspect of the present invention  
25 there is provided a method of producing a biocomposite  
26 material that is impermeable to water comprising the  
27 steps of:

- 28 1) Producing a plurality of cellulose fragments,  
29 comprising a network of cellulose microfibrils;  
30 2) Incorporating a plurality hydrophilic binders within  
31 the plurality of cellulose fragments; and

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

Most preferably the step of producing the plurality cellulose fragments comprises the method of the seventh aspect of the present invention.

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

- 1) Re-hydrating the cellulose fragments with a first emulsion 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 so as to produce a composite paste material;
- 3) Applying pressure to the composite paste material;
- 4) Removing water from the composite paste material; and
- 5) Curing the dried composite paste material.

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



1 Most preferably the surfactant is non-ionic.

2

3 Alternatively the production of the second emulsion  
4 comprises the steps of:

5 1) Obtaining a sample of the second pulp;

6 2) Homogenising the sample so as to reduce the plurality  
7 of cellulose fragments to individual cellulose fibrils  
8 and microfibrils; and

9 3) Mixing the hydrophobic binders with the homogenised  
10 sample.

11

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

14 Most preferably the ratio is between 10:1 and 5:1.

15

16 Preferably the step of removing water further comprises  
17 air drying the composite paste material at a temperature  
18 below 120°C. Optionally the step of removing water from  
19 the composite paste material comprises applying a vacuum  
20 to the paste.

21

22 Preferably the curing of the dried composite paste  
23 material comprises a first curing of the dried composite  
24 paste material at a temperature within the range from  
25 ambient to 180°C but ideally in the range 80-160°C.

26

27 Optionally the curing of the dried composite paste  
28 material further comprises a second curing of the dried  
29 composite paste material at a temperature within the  
30 range 120-180°C.

31

32

33

1 Specific Description

2

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

7

8 Figure 1 presents a series of schematic representations  
9 of the structure of a biocomposite material in accordance  
10 with aspects of the present invention;

11

12 Figure 2 presents a schematic representation of the  
13 chemical structure of a cellulose fragment employed  
14 within the biocomposite material of Figure 1;

15

16 Figure 3 presents a flow chart of the method for  
17 producing the biocomposite material of Figure 1;

18

19 Figure 4 presents a flow chart of the method for  
20 producing cellulose fragments as employed within the  
21 method of Figure 3;

22

23 Figure 5 presents a schematic representation of a  
24 monolithic structure in accordance with an aspect of the  
25 present invention; and

26

27 Figure 6 presents a schematic representation of a  
28 laminate structure in accordance with an aspect of the  
29 present invention;

30

31 A detailed description of a biocomposite material 1 in  
32 accordance with aspects of the present invention shall  
33 now be described with reference to Figure 1 and 2.

1  
2 From Figure 1 the biocomposite material 1 can be seen to  
3 comprise a plurality of cellulose fragments 2 in the form  
4 of a network of cellulose microfibrils 3. The cellulose  
5 fragments 2 can be seen to be infiltrated with a  
6 hydrophilic (or substantially hydrophilic) binder 4 and  
7 encapsulated within a hydrophobic binder 5. In practice  
8 the cellulose fragments 2 can range from comprising a mix  
9 of individual cellulose microfibrils (typically ~20nm in  
10 diameter) to sections of cellulose cells typically ~50  $\mu\text{m}$   
11 in length and breadth and less than 1  $\mu\text{m}$  in thickness  
12 themselves made up of a number of cellulose microfibrils  
13 3. A schematic representation of the chemical structure  
14 of cellulose is presented in Figure 2.

15  
16 In the present embodiment the hydrophilic binder 4  
17 comprises partially hydrolysed polyvinyl acetate.  
18 Partially hydrolysed polyvinyl acetate is known by those  
19 skilled in the art to be a substantially hydrophilic  
20 polymer that readily forms micelles in water. The  
21 diameter and nature of the partially hydrolysed polyvinyl  
22 acetate particles is such that they locate within the  
23 cellulose fragment 2, as shown in Figure 1(b).

24  
25 In the present embodiment the hydrophobic binder 5  
26 comprises an epoxy resin. Cured epoxy resins are known  
27 by those skilled in the art to be hydrophobic in nature.  
28 The uncured epoxy resin is therefore formed into micelles  
29 with a typical diameter of ~0.5 - 2  $\mu\text{m}$ . The diameter and  
30 nature of the epoxy particles is such that these  
31 particles cannot locate within the cellulose fragments 2.  
32 In the cured material, Figure 1(c), the polymer particles  
33 fuse and the epoxy interacts with the partially

1 hydrolysed polyvinyl acetate with the result that there  
2 is a transfer of stress from the cured epoxy matrix via  
3 the partially hydrolysed polyvinyl acetate to the  
4 cellulose fragments 2. This interaction provides the  
5 composite material with the physical parameters as  
6 detailed in Table 1 below which relates in particular to  
7 a material that comprises 25% partially hydrolysed  
8 polyvinyl acetate by weight and 25% epoxy by weight and  
9 in which the cellulose fragments are randomly orientated  
10 throughout the composite material. For comparison  
11 purposes Table 1 also includes typical results for  
12 alternative materials known to those skilled in the art  
13 i.e. GFRP and so called waterproof hemp (hemp with a 30%  
14 polypropylene fibre content).

15  
16 A further function of the epoxy is that it effectively  
17 encapsulates the cellulose fragments 2 and hence the  
18 partially hydrolysed polyvinyl acetate located therein,  
19 so rendering the biocomposite material 1 impermeable to  
20 water.

21  
22 The precise physical properties of the biocomposite  
23 material 1 outlined in Table 1 can be varied by altering  
24 the relative proportion by weight of both the partially  
25 hydrolysed polyvinyl acetate and the epoxy. It has been  
26 found that a biocomposite material that is impermeable to  
27 water can be produced when the partially hydrolysed  
28 polyvinyl acetate comprise between 5% and 55% of the  
29 total weight of the material while the epoxy can be  
30 varied within a range of 5% to 65% of the total weight of  
31 the material. It has been possible to produce these  
32 biocomposite materials in samples in excess of 4mm thick.

1 Methods for producing the biocomposite material 1 shall  
2 now be described in detail, a flow chart for which is  
3 presented in Figure 3.

4

5 The first stage of this process involves the production  
6 of the cellulose fragments 2, comprising a network of  
7 cellulose microfibrils 3 which provides the framework for  
8 the biocomposite material 1. The production of the  
9 cellulose fragments 2 is achieved by the following  
10 process, a flow chart for which is provided in Figure 4:

11

- 12 1) A plant material is coarsely chopped into a plurality  
13 of pieces. In this particular example the plant  
14 material comprises chopped carrot.
- 15 2) The coarsely chopped carrot is then hydrothermally  
16 treated, at a temperature between 85-120°C at  
17 atmospheric pressure, until it begins to soften.  
18 Optionally steam and pressures above atmospheric  
19 pressures may be utilised to soften the carrots.
- 20 3) The resultant cooking liquid is then drained off from  
21 the softened coarsely chopped carrot.
- 22 4) Fresh water is then added to the residue material and  
23 this material is then processed in high speed blender  
24 for approximately 3-5 minutes so as to increase the  
25 available surface area of the material.
- 26 5) Optionally, the material can then be immediately used  
27 as described below. Alternatively, the material can be  
28 allowed to stand for a period of time before use with  
29 or without the addition of a micro-organism e.g.  
30 bacteria or yeast. Such additional steps further  
31 assist in the breakdown of the carrot material.
- 32 6) The resultant pulp produced by the blending process may  
33 then be filtered and washed with clean water.

- 1 7) Next the residue produced within the previous stage is  
2 mixed with a concentrated bleach solution and  
3 thereafter allowed to stand for 30 minutes, although  
4 longer time periods may be employed. The addition of  
5 bleach acts to kill of any unwanted micro-organisms  
6 while ensuring that a significant quantity of the  
7 pectins and hemicelluloses present within the original  
8 carrot material is dissolved within the resultant  
9 solution.
- 10 8) The bleach is then removed by washing and filtering.  
11 Thereafter, water is added to the residue which is then  
12 homogenised by passing through a high shear in-line  
13 mixer or a high shear batch mixer. This involves the  
14 passing of the residue through a fine mesh under high  
15 shearing conditions so as to break down the cellular  
16 material in the residue so as to produce a pulp  
17 containing a range of cellulose fragments i.e. sized  
18 from individual cellulose microfibrils (on a scale of  
19 20nm in diameter) up to sections of cellulose cells  
20 typically 50  $\mu\text{m}$  in length and breadth and less than 1  
21  $\mu\text{m}$  in thickness depending on the precise processing  
22 conditions.
- 23 9) It is then required to reduce the water content within  
24 the resultant pulp. This is achieved by wrapping the  
25 pulp in a fine meshed bag and then pressing within a  
26 standard mechanical press. The resulting pressed pulp  
27 provides the required cellulose fragments 2 and in  
28 particular comprises 1-30% cellulose by weight, and so  
29 behaves as a solid, feeling dry to the touch. It is  
30 essential that there remains enough water present  
31 within the cellulose fragments 2 so as to prevent the  
32 cellulose fragments 2 from interacting too strongly and  
33 therefore forming a rigid solid.

1  
2 Although the above stage employs carrot plant material, a  
3 range of alternative plant materials may equally well be  
4 employed in order to obtain cellulose fragments 2,  
5 comprising the network of cellulose microfibrils 3.  
6 These include, but are not limited to turnip, swede,  
7 apple, sugar beet, beetroot and onions.

8  
9 As an alternative to hydrothermally treating the coarsely  
10 chopped carrot, as outlined within step 2 above, the  
11 chopped carrot may simply be heated in a microwave or  
12 infrared heater until the required softening occurs.

13  
14 As an alternative to the homogenisation process of step 8  
15 above, the homogenised filtrate may be produced by  
16 subjecting the filtrate to a single pass through a high  
17 pressure homogeniser (at between 500-1000 bar).

18  
19 In a further alternative to the above step 8 a sample of  
20 the homogenised pulp is taken before the water content  
21 within the pulp is reduced by pressing. This sample of  
22 pulp is then available for employment within a later  
23 stage of the process, as described in detail below.

24  
25 The second stage of the process for producing the  
26 biocomposite material 1 involves the incorporation of a  
27 hydrophilic (or substantially hydrophilic) binder 4  
28 within the cellulose fragments 2. This can be achieved  
29 by the following process:

30  
31 1) The cellulose fragments 2, comprising a network of  
32 cellulose microfibrils 3 are re-hydrated with an  
33 emulsion or a particulate suspension of hydrophilic

1 matrix material, namely PVA which exhibits high strains  
2 to failure (greater than 6%) and a low modulus of  
3 between 200-1000 MPa when formed into a solid.  
4 Depending upon the particular requirements of the  
5 biocomposite material 1 the emulsion produced at this  
6 stage can comprise between 5 and 60% resins (and/or  
7 glues) by weight and between 40 and 95% water. For the  
8 biocomposite material detailed within Table 1 the  
9 proportion of total resin (and/or glues) by weight was  
10 within the range of 45-55%.

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

17  
18 Although the above stage employs PVA as the hydrophilic  
19 binder any other hydrophilic binding material that can be  
20 incorporated within the cellulose fragments 2 may equally  
21 well be employed. Suitable alternative hydrophilic  
22 binding materials include acrylic resins and biological  
23 hydrophilic polymers such as gelatines and gaur gum.

24  
25 The final stage of the process for producing the  
26 biocomposite material 1 involves the encapsulation of the  
27 cellulose fragments 2 and the PVA particles with a  
28 hydrophobic binder 5. This can be achieved by the  
29 following process:

30  
31 1) An emulsion is formed by adding an epoxy resin to water  
32 through the employment of a non-ionic surfactant (e.g.  
33 Triton®-X octyl phenol ethoxylate). Typically the



1 ratio of the epoxy particles to water is between 10:1  
2 and 1:5. For the biocomposite material detailed in  
3 Table 1 the ratio of the epoxy particles to water was  
4 1:1.

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

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

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

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

17

18 A further improvement in the stiffness and strength of  
19 the biocomposite material 1 can be achieved by employing  
20 a second post drying curing cycle in an oven at between  
21 120-180°C.

22

23 Although the above stage employs an epoxy (e.g.  
24 bisphenol-A or a modified bisphenol A epoxy) as the  
25 hydrophobic binding material any other hydrophobic  
26 binding material that acts to encapsulate the cellulose  
27 fragments 2 and the hydrophilic binders 4 may equally  
28 well be employed. Suitable alternative hydrophobic  
29 binding materials include but are not limited to  
30 polyurethanes, phenolic resins, acrylics and siloxanes.

31

32 The step of the removing the residual water from the  
33 thick smooth paste may be achieved through the

1 application of a vacuum, in conjunction with, or as an  
2 alternative to the process of air drying.

3

4 An alternative method for producing the cellulose  
5 fragments 2' from carrots shall now be described. The  
6 alternative method comprises the steps of:

7

- 8 1) Hydro thermally treating whole carrots at a  
9 temperature between 85°C and 120°C at atmospheric  
10 pressure until they soften. Optionally steam and  
11 pressures above atmospheric pressure may be used  
12 to soften the carrots.
- 13 2) The resultant cooking liquid is then drained off  
14 from the carrots.
- 15 3) Fresh water is then added to the residue material  
16 and this material is then processed in a high  
17 shear mixer for a period of between 5 minutes and  
18 4 hours, although longer process times are  
19 possible.
- 20 4) The resultant residue produced by the shear mixing  
21 process can be taken to the next stage immediately  
22 or alternatively the material can be left to stand  
23 in a container, ideally for 12 - 14 days although  
24 shorter or longer times are possible. Optionally  
25 when left to stand a micro-organism (e.g. bacteria  
26 or yeast) can be added to the residue, as  
27 previously described.
- 28 5) Optionally the resultant residue is then filtered  
29 and washed with clean water.
- 30 6) The residue produced within the previous stage is  
31 then mixed with a bleaching solution ideally of  
32 the concentration 0.5% and is allowed to stand for  
33 up to 15 hours. This ensures that an effective

1           quantity of pectins and hemicellulose present  
2           within the original carrot material is dissolved  
3           within the resultant solution.

4       7) A number of options are available at this stage.  
5           The first option is to remove the bleach by  
6           filtering and washing the resultant solution.  
7           Optionally, if further reduction in the particle  
8           size of the material is desired then further  
9           processing of the material can take place either  
10          using a high shear mixer or through a high-  
11          pressure homogeniser. A final alternative is to  
12          initially homogenise the residue and to thereafter  
13          remove the bleach by filtering and washing the  
14          resultant solution. In practice the resultant  
15          biocomposite material appears to relatively  
16          independent of the particular order of this step  
17          of the process.

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

22  
23   An alternative for forming the hydrophobic polymer  
24   emulsion comprises the employment the sample taken of  
25   pulp produced from the high pressure homogeniser. This  
26   process involves the steps of:

- 27  
28   1) Passing the sample through the homogeniser a number of  
29       times so as to reduce the cellulose fragments to  
30       individual cellulose fibrils and microfibrils. This  
31       material is then retained in liquid form.  
32   2) The epoxy particles are then mixed directly with this  
33       liquid so as to produce an emulsion comprising the

1 epoxy particles and the cellulose fibrils and  
2 microfibrils. Similar ratios to those previously  
3 described are again employed.

4

5 An alternative for forming the hydrophilic polymer  
6 solution comprises the employment of the sample taken of  
7 the pulp from the homogeniser. This process involves the  
8 step of:

9

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

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

19

20 A number of examples of uses of the described  
21 biocomposite materials 1 shall now be described.

22

23 In the first instance the biocomposite material 1 can be  
24 used to produce a monolithic structure 6 through which  
25 the mechanical properties are graded. Essentially a  
26 multi layer structure can be formed within which there  
27 exist no internal interfaces to compromise the overall  
28 structure. This is achieved by laying down a layer of  
29 the uncured material with the correct formulation for the  
30 mechanical properties required (this layer can be several  
31 mm thick) before a second layer of uncured material with  
32 a different mechanical property is laid down on top of  
33 the first. Repeating this step a number of times results

1 in structure with different mechanical properties layers.  
2 Once the required number of layers has been reached the  
3 composite material is then pressed and cured to form the  
4 monolithic structure 6, as appropriate. It will be  
5 readily apparent that each of the layers may in fact  
6 exhibit the same, or similar, mechanical properties.

7  
8 By way of example this method can be employed to produce  
9 a ski in which an extremely tough layer 7 is initially  
10 prepared, upon which a stiffer layer 8 is then laid,  
11 followed by a layer of intermediate properties 9 at the  
12 core with a layer of stiff 8 and then tough material 7  
13 completing the structure. Such a structure is presented  
14 schematically in Figure 5.

15

16 Alternatively, the biocomposite material 1 can be used  
17 within a more conventional lamination process so as to  
18 form a laminate structure 10, see Figure 6. The laminate  
19 structure 10 can be employed to produce thick flat items  
20 such as skis, snow boards, surf boards, skate boards etc  
21 or tubular items such as fishing rods, bicycle frames,  
22 ski poles, sail spars, masts etc. This is achieved by  
23 dipping pre-formed sheets of the biocomposite material 1  
24 in a hydrophobic resin 11, stacking the sheets on top of  
25 one another and thereafter pressing under high pressure.  
26 When the hydrophobic resin 11 has cured the laminate  
27 structure 10 is removed from the press and if necessary  
28 given an extra coating surface of a finishing material.

29

30 It will be apparent to those skilled in the art that the  
31 laminate structure 10 may comprise one or more layers of  
32 materials already known in the art e.g. plastics and/or  
33 carbon fibre reinforced plastic materials. A known

1 problem of prior art laminate structures that comprise  
2 carbon fibre reinforced plastic materials is the large  
3 difference in stiffness between the fibres and plastic.  
4 Carbon fibres have Young's modulus in the range 150-  
5 600GPa where as plastic materials such as epoxy resin,  
6 typically have moduli of between 2-8GPa. This can cause  
7 problems of delamination when different layers of carbon  
8 fibre composites are bonded together with resins.  
9 Furthermore, it also means that unidirectional carbon  
10 fibre materials have very low stiffness and strength at  
11 right angles to the fibre direction.

12  
13 Incorporation of one or more layers of the biocomposite  
14 material 1 provides a means for alleviating this problem.  
15 The advantage of using the biocomposite material to form  
16 the laminate structure is that it can increase stiffness,  
17 strength and toughness in certain directions, for certain  
18 orientations of the layers. For example a laminate made  
19 from a layer of unidirectional carbon fibres in epoxy  
20 resin and a layer of biocomposite material has higher  
21 stiffness and strength, when tested in tension in the  
22 direction of the carbon fibre axis, than a laminate made  
23 from two layers of carbon-epoxy with fibre directions at  
24 right angles. Although the stiffness is lower when the  
25 laminate is tested in tension at right angles to the  
26 carbon fibre axis, the stiffness in this direction is  
27 still more than adequate for certain applications e.g.  
28 hollow tubular rods where the highest stiffness is  
29 required along the axis of the rod, with just sufficient  
30 stiffness and strength in the hoop direction to prevent  
31 crushing and ovalisation during mechanical loading of the  
32 rod.

33

1 The above described laminate structure may be formed in a  
2 number of ways. The first method comprises applying a  
3 layer of biocomposite paste to a pre-cured layer of high  
4 stiffness fibre reinforced composite. The biocomposite  
5 paste layer is then dried and cured by heating. Pressure  
6 need not be applied to the laminate during curing, but  
7 can be advantageous in reducing imperfections in the  
8 cured biocomposite. Several layers can be built up by  
9 this method (e.g. composite/paste/composite/paste) before  
10 drying and curing, or each paste layer can be cured first  
11 before the addition of further layers.

12  
13 An alternative method involves applying an uncured high  
14 stiffness fibre reinforced plastic to a layer of cured  
15 biocomposite material 1. The high stiffness fibre  
16 reinforced plastic is then cured. Pressure may need to  
17 be applied to the laminate during curing. Several layers  
18 can be again be built up employing this method (e.g.  
19 paste/composite/paste/composite) before drying and  
20 curing, or each paste layer of paste and composite can be  
21 cured first before the addition of further layers.

22  
23 A further alternative method comprises the pressing of  
24 layers of precured biocomposite material 1 and high  
25 stiffness fibre reinforced plastic together with an  
26 adhesive. Pressure is sustained until the adhesive has  
27 cured.

28  
29 The biocomposite material 1 is also found to increase the  
30 toughness of carbon fibre structures when applied as a  
31 surface finish i.e. a lamination of carbon fibre-  
32 biocomposite. This is because certain formulations of  
33 the biocomposite material 1 have higher failure strains

1 than the carbon fibre, while still retaining good  
2 strength.

3

4 A further example application of the biocomposite  
5 material 1 is in the production of tubular sections which  
6 are suitable for use within a fishing rod. The  
7 biocomposite material 1 is initially prepared as  
8 described above. Before curing however the biocomposite  
9 material 1 is placed into a porous mould or a mould which  
10 contains a porous liner (e.g. ceramic, clay or open  
11 celled foam) and formed round a waxed tapered mandrel of  
12 the required dimensions. The biocomposite material 1 is  
13 then air dried to remove water. Next the tapered tube of  
14 the biocomposite material 1 is removed from the mandrel  
15 and preferably heated to a temperature of around 120°C.  
16 Finally the tube is post cured at temperatures of up to  
17 180°C.

18

19 The biocomposite material described above exhibits  
20 several unique features over those materials described in  
21 the prior art. In the first instance the biocomposite  
22 material exhibits stiffness and tensile strength  
23 parameters that are favourably comparable with any  
24 previously described material. In addition these  
25 parameters are achieved without any compromise on the  
26 toughness of the material and so the described composite  
27 material is not brittle like many of the previously  
28 described biocomposite materials. Typically the  
29 composite materials produced exhibit a bending strength  
30 in the range of 60 MPa to 600 MPa.

31

32 Furthermore, the described material has the significant  
33 advantage that it is also impermeable to water so



1 allowing its range of applications to be extensively  
2 increased. In particular, the described material may be  
3 employed to produce skis, snow boards, surf boards, skate  
4 boards etc or tubular items such as fishing rods, bicycle  
5 frames, ski poles, sail spars, masts. However it is  
6 envisaged that wherever there is a requirement for a  
7 strong flat material, that is impermeable to water, then  
8 the described biocomposite material would provide an  
9 ideal solution.

10  
11 Since the described extraction process of cellulose  
12 fragments from the plant material requires relatively  
13 little energy the method of manufacture is more amenable  
14 to be employed on a commercial scale. In addition, the  
15 manufacturing process is less complex than those  
16 previously described in the art to produce composites  
17 from wood fibres or bacterial cellulose. A particular  
18 advantage to the described method is that it does not  
19 require the employment of an organic solvent.

20  
21 As a result a new composite material with a unique  
22 combination of physical properties has been produced from  
23 a sustainable resource and manufactured by a relatively  
24 low energy, non polluting process. In fact the  
25 biocomposite material produced appears to be many times  
26 tougher than any waterproof cellulose based composite  
27 produced to date.

28  
29 The foregoing description of the invention has been  
30 presented for purposes of illustration and description  
31 and is not intended to be exhaustive or to limit the  
32 invention to the precise form disclosed. The described  
33 embodiments were chosen and described in order to best

1 explain the principles of the invention and its practical  
2 application to thereby enable others skilled in the art  
3 to best utilise the invention in various embodiments and  
4 with various modifications as are suited to the  
5 particular use contemplated. Therefore, further  
6 modifications or improvements may be incorporated without  
7 departing from the scope of the invention as defined by  
8 the appended claims.

1 Table 1

2

Material	Stiffness (Young's Modulus GPa)	Tensile Strength (MPa)	Toughness (Energy Absorbed to failure MJm <sup>-3</sup> )
Biocomposite Material	18	250	10
GFRP e.g. Chopped Strand Mat	12	160	4
Waterproof Hemp (30% Polypropylene fibre content)	7	50	1

3

## 1 Claims

2

3 1) A biocomposite material (1) comprising a plurality  
4 of cellulose fragments (2) made up of a network of  
5 cellulose microfibrils (3), a plurality of  
6 hydrophilic binders (4) located within the network  
7 of cellulose microfibrils (3) and a plurality of  
8 hydrophobic binders (5) arranged to interact with  
9 the hydrophilic binders (4) so as to encapsulate the  
10 plurality of cellulose fragments (2).

11

12 2) A biocomposite material (1) as claimed in Claim 1  
13 wherein the material has the general formulation:

14 
$$\text{Cel}_{(1-x-y)} \text{HPI}_x \text{HPO}_y$$

15 where x is within the range of from 0.05 to 0.55 and  
16 y is within the range of from 0.05 to 0.65.

17

18 3) A biocomposite material (1) that is impermeable to  
19 water comprising a plurality of cellulose fragments  
20 (2) made up of a network of cellulose microfibrils  
21 (3), a plurality of hydrophilic binders (4) and a  
22 plurality of hydrophobic binders (5) having the  
23 general formulation  $\text{Cel}_{(1-x-y)} \text{HPI}_x \text{HPO}_y$  where x is  
24 within the range of from 0.05 to 0.55 and y is  
25 within the range of from 0.05 to 0.65.

26

27 4) A biocomposite material (1) as claimed in Claim 3  
28 wherein the hydrophilic binders (4) are located  
29 within the network of cellulose microfibrils (3) and  
30 the plurality of hydrophobic binders (5) are  
31 arranged to interact with the hydrophilic binders  
32 (4) so as to encapsulate the plurality of cellulose  
33 fragments (2).

- 1 5) A biocomposite material (1) as claimed in any of the  
2 preceding claims wherein the material exhibits a  
3 stiffness in the range from 5 GPa to 90 GPa.  
4
- 5 6) A biocomposite material (1) that is impermeable to  
6 water and which exhibits a stiffness in the range  
7 from 5 GPa to 90 GPa.  
8
- 9 7) A biocomposite material (1) as claimed in Claim 6  
10 wherein the material comprises a plurality of  
11 cellulose fragments (2) made up of a network of  
12 cellulose microfibrils (3), a plurality of  
13 hydrophilic binders (4) located within the network  
14 of cellulose microfibrils (3) and a plurality of  
15 hydrophobic binders (5) arranged to interact with  
16 the hydrophilic binders (4) so as to encapsulate the  
17 plurality of cellulose fragments (2).  
18
- 19 8) A biocomposite material (1) as claimed in either of  
20 claims 6 or 7 wherein the material has the general  
21 formulation  $\text{Cel}_{(1-x-y)} \text{HPI}_x \text{HPO}_y$  where x is within the  
22 range of from 0.05 to 0.55 and y is within the range  
23 of from 0.05 to 0.65.  
24
- 25 9) A biocomposite material (1) as claimed in any of the  
26 preceding claims wherein the cellulose fragments are  
27 arranged in a randomly orientated manner.  
28
- 29 10) A biocomposite material (1) as claimed in any of the  
30 preceding claims wherein the material of the  
31 exhibits a tensile strength in the range from 60 MPa  
32 to 1 GPa.

11) A biocomposite material (1) as claimed in any of the preceding claims wherein the material exhibits a bending strength in the range from 60 MPa to 600 MPa.

12) A biocomposite material (1) as claimed in any of the preceding claims wherein the material exhibits a stiffness in the range 14GPa-21GPa.

13) A biocomposite material (1) as claimed in any of the preceding claims wherein the exhibits a strength in the range 180MPa-300MPa.

14) A biocomposite material (1) as claimed in any of the preceding claims wherein the material exhibits a toughness in the range from 3 MJm<sup>-3</sup> to 10 MJm<sup>-3</sup>.

15) A biocomposite material (1) as claimed in any of the preceding claims wherein the hydrophilic binders (4) comprise a hydrophilic or substantially hydrophilic polymer.

16) A biocomposite material (1) as claimed in Claim 15 wherein the hydrophilic polymer comprise a polymer selected from the group comprising hemicellulose, an acrylic resin, a partially hydrolysed polyvinyl acetate and a biological hydrophilic polymer

17) A biocomposite material (1) as claimed in Claim 16 wherein the biological hydrophilic polymer comprises gelatine or guar gum.

1 18) A biocomposite material (1) as claimed in any of the  
2 preceding claims wherein the hydrophobic binders (5)  
3 comprise a hydrophobic polymer.  
4

5 19) A biocomposite material (1) as claimed in Claim 18  
6 wherein the hydrophobic polymer comprises an epoxy.  
7

8 20) A biocomposite material (1) as claimed in Claim 18  
9 wherein the hydrophobic binders (5) comprises a  
10 binder selected from the group comprising  
11 polyurethanes, phenolic resins, acrylics and  
12 siloxanes.  
13

14 21) A monolithic structure (6) comprising two or more  
15 layers (7, 8, 9) wherein at least one of the two or  
16 more layers comprise a biocomposite material (1) as  
17 claimed in any of the preceding claims.  
18

19 22) A laminate structure (10) comprising two or more  
20 layers wherein at least one of the two or more  
21 layers comprise a biocomposite material (1) as  
22 claimed in any of the preceding claims.  
23

24 23) A laminate structure (10) as claimed in Claim 22  
25 wherein the structure further comprises one or more  
26 layers of resin (11) located between the two or more  
27 layers.  
28

29 24) A laminate structure (10) as claimed in Claim 23  
30 wherein the one or more layers of resin (11)  
31 comprise a hydrophobic resin.  
32

1 25) A laminate structure (10) as claimed in Claim 24  
2 wherein the hydrophobic resin comprises epoxy or  
3 polyurethane.  
4

5 26) A tube, suitable for use in a fishing rod, the tube  
6 comprising a biocomposite material as claimed in any  
7 of claims 1 to 25.  
8

9 27) A method of producing cellulose fragments (2),  
10 comprising a network of cellulose microfibrils (3),  
11 from a plant material comprising the steps of:  
12 1) Producing a first pulp of the plant material;  
13 2) Mixing a first pulp with a bleach solution so that  
14 a quantity of pectins and hemicelluloses present  
15 within the plant material are dissolved within a  
16 resultant solution;  
17 3) Producing a second pulp by removing the bleach  
18 from the resultant solution; and  
19 4) Reducing the water content present within the  
20 second pulp.  
21

22 28) A method of producing cellulose fragments (2) as  
23 claimed in claim 27 wherein the method further  
24 comprises the step of filtering and washing the  
25 first pulp in water before mixing with the bleach  
26 solution;  
27

28 29) A method of producing cellulose fragments (2) as  
29 claimed in claim 27 or claim 28 wherein the step of  
30 producing the first pulp comprises the steps of:  
31 1) Heating the plant material so as to soften the  
32 plant material;



- 1           2) Filtering any resultant liquid from the softened  
2           plant material; and  
3           3) Blending the resultant residue with water.  
4

5   30) A method of producing cellulose fragments (2) as  
6       claimed in claim 27 wherein the step of producing  
7       the first pulp further comprises chopping of the  
8       plant material before heating.  
9

10   31) A method of producing cellulose fragments (2) as  
11       claimed in claim 29 or claim 30 the plant material  
12       is heated to temperature between 85°C and 120°C at  
13       atmospheric pressure.  
14

15   32) A method of producing cellulose fragments (2) as  
16       claimed in any of claims 29 to 31 wherein the  
17       blended resultant residue and water is allowed to  
18       stand for a period of at least one day.  
19

20   33) A method of producing cellulose fragments (2) as  
21       claimed in claim 32 wherein a micro-organism is  
22       added to the blended resultant residue so as to aid  
23       the breakdown of the plant material.  
24

25   34) A method of producing cellulose fragments (2) as  
26       claimed in claim 33 wherein the micro-organism  
27       comprises bacterium.  
28

29   35) A method of producing cellulose fragments (2) as  
30       claimed in claim 33 wherein the micro-organism  
31       comprises yeast.  
32

1 36) A method of producing cellulose fragments (2) as  
2 claimed in any of claims 27 to 35 wherein the  
3 mixture of the first pulp and the bleach solution is  
4 allowed to stand for a period of at least thirty  
5 minutes so as to form the resultant solution.

6  
7 37) A method of producing cellulose fragments (2) as  
8 claimed in any of claims 27 to 36 wherein the step  
9 of producing a second pulp comprises washing and  
10 filtering the resultant solution so as to remove the  
11 bleach and produce a second residue.

12  
13 38) A method of producing cellulose fragments (2) as  
14 claimed claim 37 wherein the step of producing the  
15 second pulp further comprises the step of  
16 homogenising the second residue.

17  
18 39) A method of producing cellulose fragments (2) as  
19 claimed in claim 38 wherein the second residue is  
20 homogenised by mixing the second residue within a  
21 high shear mixing process.

22  
23 40) A method of producing cellulose fragments (2) as  
24 claimed in claim 38 wherein the second residue is  
25 homogenised by pressurising the second residue at a  
26 pressure between 500 and 1000 bar.

27  
28 41) A method of producing cellulose fragments (2) as  
29 claimed in any of claims 27 to 36 wherein the step  
30 of producing a second pulp comprises homogenising  
31 the resultant solution and then washing and  
32 filtering the homogenised resultant solution so as  
33 to remove the bleach.

- 1  
2 42) A method of producing cellulose fragments (2) as  
3 claimed in any of claims 27 to 41 wherein the step  
4 of reducing the water content present within the  
5 second pulp comprises pressing the second pulp.  
6
- 7 43) A method of producing cellulose fragments (2) as  
8 claimed in claim 42 wherein the pressing of the  
9 second pulp results in the second pulp comprising at  
10 least 40% water by weight.  
11
- 12 44) A method of producing a biocomposite material (1)  
13 that is impermeable to water comprising the steps  
14 of:  
15 1) Producing a plurality of cellulose fragments  
16 (2), comprising a network of cellulose  
17 microfibrils (3);  
18 2) Incorporating a plurality hydrophilic binders  
19 (4) within the network of cellulose  
20 microfibrils (3); and  
21 3) Encapsulating the plurality of cellulose  
22 fragments (2) within a plurality of  
23 hydrophobic binders (5).  
24
- 25 45) A method of producing a biocomposite material (1) as  
26 claimed in Claim 44 wherein the step of producing  
27 the plurality cellulose fragments (2) comprises the  
28 method as claimed in any of claims 25 to 41.  
29
- 30 46) A method of producing a biocomposite material (1) as  
31 claimed in either of Claims 44 or 45 wherein the  
32 step of incorporating the plurality hydrophilic

1 binders (4) within the network of cellulose  
2 microfibrils (3) comprises:

3 1) Re-hydrating the cellulose fragments (2) with  
4 a first emulsion comprising the hydrophilic  
5 binders (4) so as to produce a second  
6 emulsion; and

7 2) Removing excess water and excess hydrophilic  
8 binders (4) from the second emulsion.

9

10 47) A method of producing a biocomposite material (1) as  
11 claimed in any of Claims 44 to 46 wherein the step  
12 of encapsulating the plurality of cellulose  
13 fragments (2) comprises:

14 1) Producing a second emulsion comprising the  
15 plurality of hydrophobic binders (5);

16 2) Mixing the second emulsion and the paste  
17 containing the hydrophilic binder so as to  
18 produce a composite paste material;

19 3) Applying pressure to the paste material;

20 4) Removing water from the paste material; and

21 5) Curing the dried paste material.

22

23 48) A method of producing a biocomposite material (1) as  
24 claimed in Claim 47 wherein the production of the  
25 second emulsion involves mixing the hydrophobic  
26 binders (5) with a surfactant and water.

27

28 49) A method of producing a biocomposite material (1) as  
29 claimed in Claim 48 wherein the surfactant is non-  
30 ionic.

31

1 50) A method of producing a biocomposite material (1) as  
2 claimed in Claim 47 wherein the production of the  
3 second emulsion comprises the steps of:

4 1) Obtaining a sample of the second pulp;

5 2) Homogenising the sample so as to reduce the  
6 plurality of cellulose fragments (2) to  
7 individual cellulose fibrils and microfibrils  
8 (3); and

9 3) Mixing the hydrophobic binders (5) with the  
10 homogenised sample.  
11

12 51) A method of producing a biocomposite material (1) as  
13 claimed in any of Claims 47 to 50 wherein the ratio  
14 of the hydrophobic binders (5) to the water within  
15 the second emulsion is between 10:1 and 1:5.  
16

17 52) A method of producing a biocomposite material (1) as  
18 claimed in Claim 51 wherein the ratio of the  
19 hydrophobic binders (5) to the water within the  
20 second emulsion is between 10:1 and 5:1.  
21

22 53) A method of producing a biocomposite material (1) as  
23 claimed in any of Claims 47 to 52 wherein the step  
24 of removing water from the paste material comprises  
25 applying a vacuum to the paste.  
26

27 54) A method of producing a biocomposite material (1) as  
28 claimed Claim 53 wherein the step of removing water  
29 further comprises air drying the paste at a  
30 temperature below 120°C.  
31

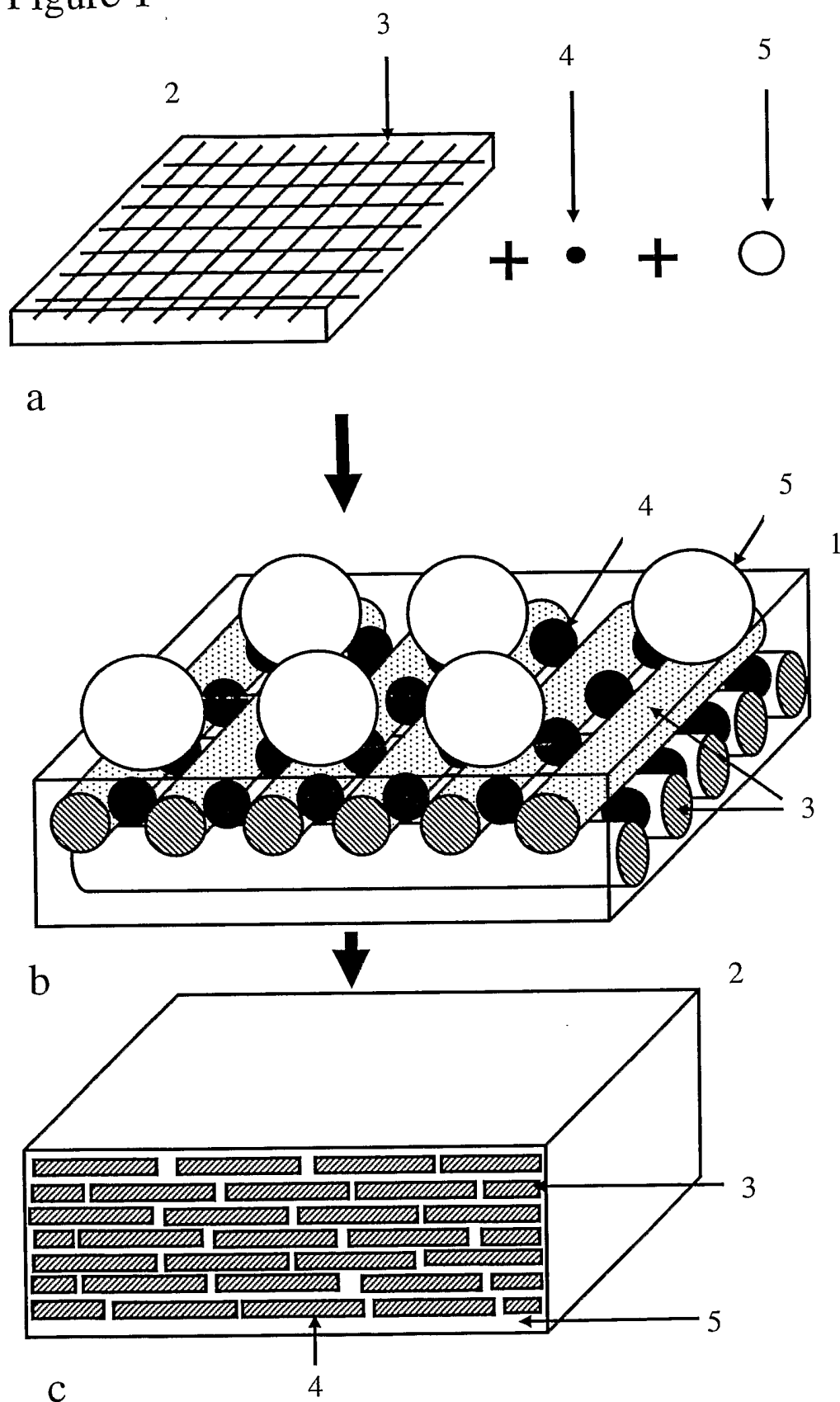
32 55) A method of producing a biocomposite material (1) as  
33 claimed in any of Claims 47 to 54 wherein the curing

1 of the dried paste material comprises a first curing  
2 of the dried paste material at a temperature within  
3 the range from ambient to 180°C.

4  
5 56) A method of producing a biocomposite material (1) as  
6 claimed in Claim 55 wherein the first curing of the  
7 dried paste material is carried out at a temperature  
8 within the range 80-160°C.

9  
10 57) A method of producing a biocomposite material (1) as  
11 claimed in either of Claims 55 or 56 wherein the  
12 step of curing of the dried paste material further  
13 comprises a second curing of the dried paste  
14 material at a temperature within the range 120-180°C.

Figure 1



2

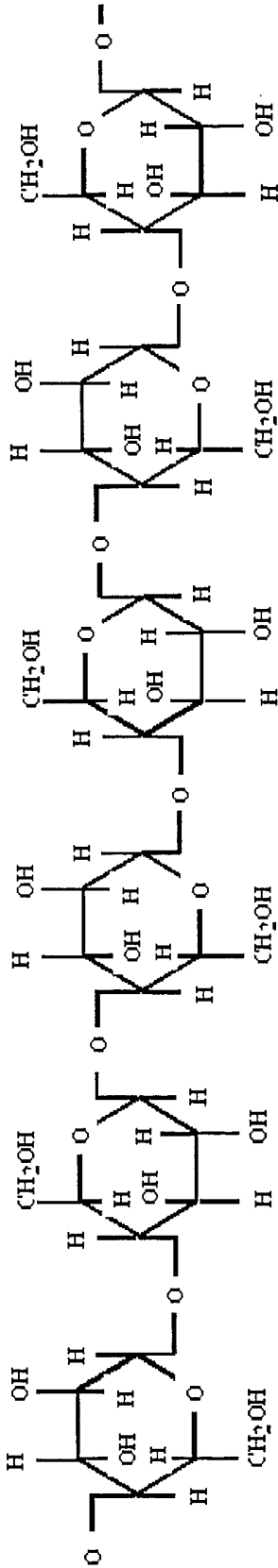


Figure 2



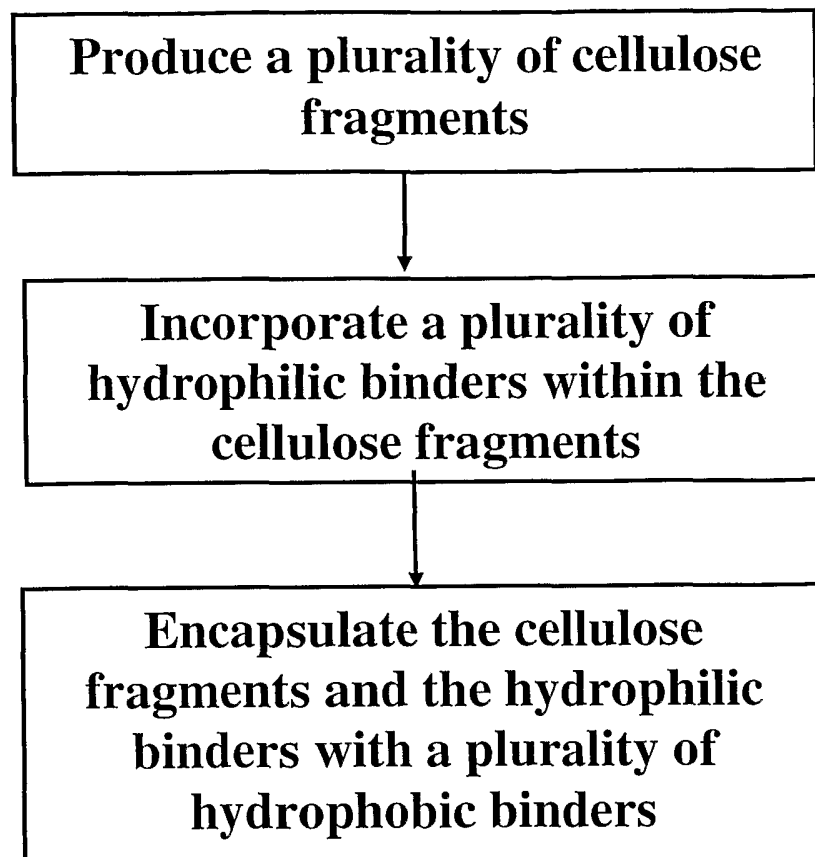
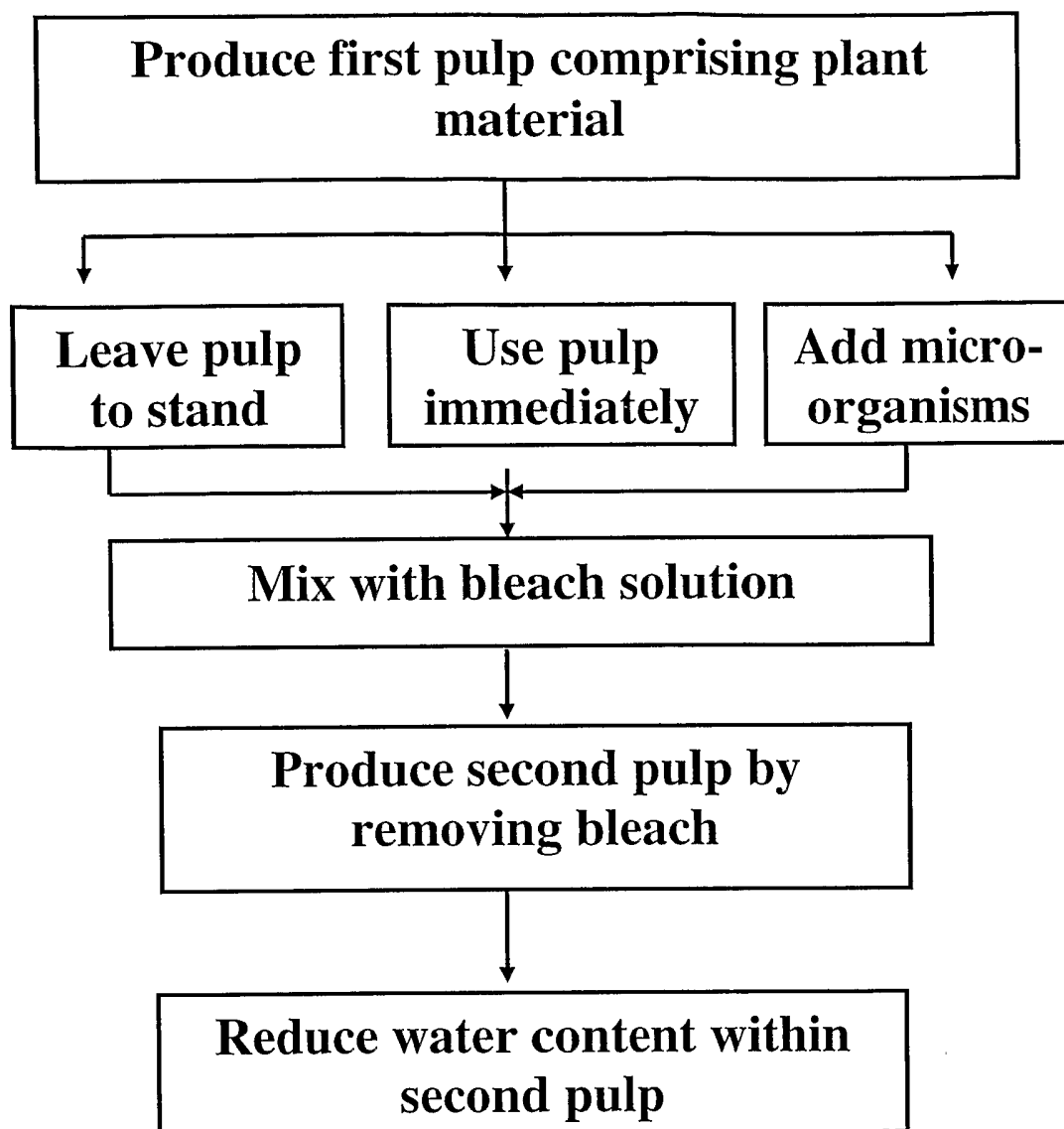


Figure 3

**Figure 4**

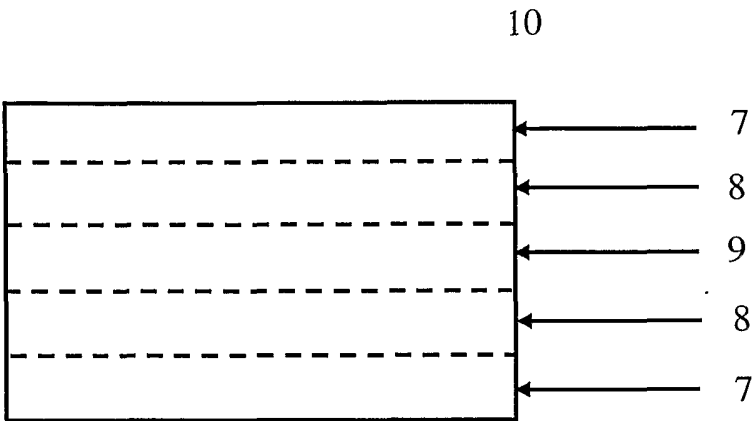


Figure 5

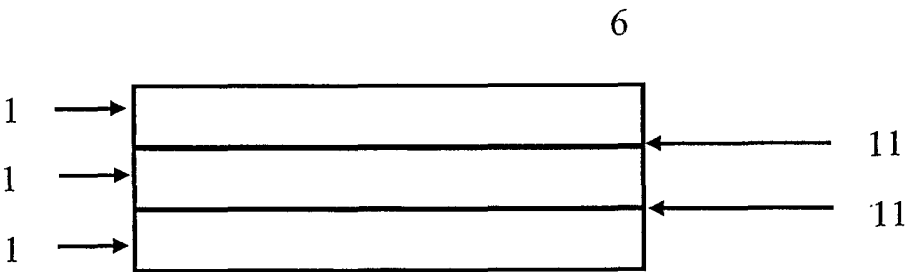


Figure 6

# INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2005/004322

**A. CLASSIFICATION OF SUBJECT MATTER**

C08B37/00 D21H11/18

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)

C08B D21H

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, PAJ, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 469 126 A (KANSAI TECHNOLOGY LICENSING ORGANIZATION CO., LTD) 20 October 2004 (2004-10-20) paragraphs '0022! - '0029! claims; examples	1-57
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

10 February 2006

Date of mailing of the international search report

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Information on patent family members

International application No

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