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(54) Title: BIODEGRADABLE COMPOSITE COMPRISING A BIODEGRADABLE POLYMER AND A GLASS FIBER

(57) Abstract: The invention is directed to biodegradable composite comprising a biodegradable polymer and 20-70 vol% glass fibers, wherein the biodegradable composite has a flexural strength between 100 and 600 MPa and to a process for the preparation of a biodegradable composite comprising a biodegradable polymer and a glass fiber, wherein a. the glass fibers are pre-treated with a solution of the biodegradable polymer in a solvent; b. the solvent is evaporated; c. the pre-treated glass fibers, optionally together with additional biodegradable polymer, is placed in a mold, where after the biodegradable polymer present on the glass fibers and/or added to the mold is melted by applying heat and pressure; d. the mold is cooled and the biodegradable composite is removed from the mold.



WO 2010/128039 A1

BIODEGRADABLE COMPOSITE  
COMPRISING A BIODEGRADABLE POLYMER AND A GLASS FIBER

The invention is directed to a biodegradable composite comprising a  
5 biodegradable polymer and 20-70 vol% glass fibers, a process for the preparation of a  
biodegradable composite and a medical implant comprising a biodegradable  
composite.

In orthopedic applications that require high strength, usually stainless  
steel or titanium alloys are used. Although these materials are inert, they are also used  
10 in situations in which the need for the implant is only temporary, like in fracture fixation.  
Often the implant has to be retrieved during a second surgery after healing because of  
inflammation of the host tissue. Besides that, stress shielding can occur due to the high  
stiffness of the metals, so that bone loses its original strength. Other disadvantages are  
that the metal implants are palpable and a cold sensation can occur.

15 In addition to the conventional metal devices, several polymer  
devices for temporary orthopedic applications were developed, that can be broken  
down by the human body. No second surgery to retrieve the implant is needed, but the  
strength of these devices is still insufficient.

This drawback can potentially be overcome by using composite  
20 technology. In composite materials, usually a relatively flexible matrix is combined with  
a stiff and strong reinforcement material to enhance the mechanical properties of the  
matrix. For these temporary high-strength applications, biodegradable glass or mineral  
material can be used to improve the stiffness and strength of a biodegradable polymer  
matrix. In the prior art several attempts to produce such a composite were reported.  
25 According to the prior art bioactive glass particles, hydroxyapatite powder, or short  
glass fibers were used to enhance the properties of a biodegradable polymer.  
However, the fracture strength of these composites is still low.

At the moment no appropriate biodegradable material is available for  
fracture fixation or other load-bearing orthopedic applications, because of the high  
30 strength that is required for this composite material.

There thus is a need for a composite material which is biodegradable  
and that can be used in medical applications that require high strength and a stiffness  
compared to the stiffness of bone. These medical applications include fracture fixation,  
tendon reattachment, spinal fixation, and spinal cages.

It has now surprisingly been discovered that a biodegradable composite material can be prepared from a biodegradable polymer and 20-70 vol% glassfibers, wherein the biodegradable composite has a flexural strength between 100 and 600 MPa. Preferably, the biodegradable composite has a flexural strength between  
5 150 and 500 MPa; more preferably between 250 and 500 MPa.

Preferably, the biodegradable composite also has a flexural modulus between 10 and 40 GPa, preferably between 15 and 35 GPa; more preferably between 20 and 35 GPa.

In the biodegradable composite material according to the invention  
10 20-70 vol% of glass fibers is used. Preferably, 30-60 vol%, more preferably 40-55 vol% glass fibers is used in the composite. The glass fibers that can be used are long (with an average length of more than 1.5 mm) or continuous fibers.

The glass fibers can be used in the biodegradable composite in a number of forms, such as strands, bundles, filaments, yarn, mats, woven fabrics and  
15 unwoven fabrics or roving. A continuous fiber can also be formed into a structure by using filament winding. Composites containing continuous fibers have a higher flexural strength than composites comprising long glass fibers. Composites containing continuous fibers are therefore preferred. The glass fibers can contain various sizings and finishes. A sizing is a surface treatment or coating applied to the glass fibers during  
20 the forming operation. A finishing is a surface treatment applied to the glass fibers after heat cleaning. This treatment usually consists of a water- or solvent-diluted coupling agent, which are designed to provide good interfacial adhesion of glass to the polymer.

Preferably, the biodegradable composite comprises glass fibers having a SiO<sub>2</sub> content of 15-60 wt%; preferably 20-50 wt%; more preferably 20-40 wt%.

25 Most preferably, the glass fibers are resorbable glass fibers. Resorbable means that the glass fibers are resorbed in the human or animal body mainly under the influence of water and/or enzymes. Resorbable glass fibers not always contain SiO<sub>2</sub>, but these glass fibers preferably contain more than 0.5 wt% of P<sub>2</sub>O<sub>5</sub>.

30 Specific examples of glass fibers that can be used are resorbable glass fibers of Vivoxid and Giltech.

The biodegradable composite also comprises a biodegradable polymer. A biodegradable polymer is a polymer that can decompose in the human or animal body during a certain period of time. Decomposition of the biodegradable  
35 polymer occurs mainly under the influence of water and/or enzymes.

Examples of biodegradable polymers are poly( $\alpha$ -esters), which include poly(lactic acid), poly(glycolic acid), poly(p-dioxanone) and poly(3-hydroxybutyrate); tyrosine-derived polymers, which include polycarbonates, polyarylates and copolymers of these with polyethyleneglycol (PEG); natural polymers, which include starch, chitosan, collagen, cellulose, including methyl cellulose and chitin; poly( $\epsilon$ -caprolactone), poly(propylene fumarate) and poly(trimethylene carbonate). It is also possible to use (block)copolymers made from the various monomers used to prepare the biodegradable polymers mentioned above.

Mixtures of the above-mentioned biodegradable polymers can also be used.

The poly( $\alpha$ -esters), more preferably poly(lactic acid), are preferred because the mechanical properties, i.e. the stiffness and strength, of these polymers are sufficient for use in a composite material.

The invention is also directed to a process for the preparation of a biodegradable composite, wherein

- a. the glass fibers are pre-treated with a solution of the biodegradable polymer in a solvent;
- b. the solvent is evaporated;
- c. the pre-treated glass fibers, optionally together with additional biodegradable polymer, is placed in a mold, where after the biodegradable polymer present on the fibers and/or added to the mold is melted by applying heat and pressure;
- d. the mold is cooled and the biodegradable composite is removed from the mold.

The solution of the biodegradable polymer can be easily made by the person skilled in the art. For instance, the solution can be made by dissolving granules of the biodegradable polymer in a suitable solvent. A dispersion of very small (i.e. sub-micron) polymer particles in a liquid can act as a solution, and thus can be used as well.

Examples of suitable solvents are water, alcohols, acetone, ethyl acetate, butanone, dimethyl sulfoxide, 1, 4-dioxane, tetrahydrofurane and chloroform.

The concentration of the biodegradable polymer in the solvent can be chosen within wide ranges and depends, for instance, on the amount of biodegradable polymer that one wants to apply on the fiber-containing glass fiber.

Evaporation of the solvent can be performed faster by the application of heat or an air stream.

The pre-treated glass fiber is placed in a mold, where after the biodegradable polymer present on the fiber is melted by applying heat and pressure. In this way a composite is made and a good contact between the glass fiber and the biodegradable polymer is obtained.

5                   It is possible to apply all biodegradable polymer onto the glass fiber by repeating the application of the solution of the biodegradable polymer on the glass fiber and evaporating the solvent several times. In this way one is able to apply more biodegradable polymer onto the glass fiber, but applying the solution and drying is time consuming. Thus, normally application of just one layer is performed to obtain a good  
10                   contact between the glass fiber and the biodegradable polymer.

The rest of the biodegradable polymer in the composite is applied to the mold together with the pre-treated glass fiber. The biodegradable polymer can be mixed with the pre-treated glass fiber, or applied to the mold before, after or between the pre-treated glass fibers.

15                   After filling the mold is closed and the biodegradable polymer is melted in the mold by applying heat and pressure.

The best adhesion between the glass fiber and the biodegradable polymer is obtained when the biodegradable polymer used for the pretreatment of the glass fiber is the same as the biodegradable polymer added to the mold. The better the  
20                   adhesion between the glass fiber and the biodegradable polymer is, the better are the stiffness and the strength of the composite.

The composite according to the invention may further contain one or more additives such as stabilizers, anti-oxidants, colorants, fillers, binders, fibers, meshes, substances providing radio-opacity, surface active or surface modifying  
25                   agents, foaming agents, processing aids, plasticizers, biostatic/biocidal agents, substances that provide or trigger bioactivity and any other known agents.

Suitable examples of other fillers, which can be used in the composite in a small amount (for instance not more than 1 wt%), are e.g. bone-mineral based fillers, and binders which are described in U.S. Patent Number 6,808,585B2 in columns  
30                   8-10 and in U.S. Patent Number 7,044,972B2 in column 4, l. 30-43, which are herein incorporated by reference. Typical fillers are selected from the group of calcium-based fillers (such as calcium phosphate, hydroxyapatite, tricalcium phosphate, calcium sulfate, demineralized bone, autologous bone, coralline substances).

The invention is also directed to a medical implant comprising the  
35                   biodegradable composite.

Examples of medical implants are a screw, a pin, a plate, a suture, a mesh, a net, a film, a tube, a balloon, a bag, a rod, an anchor, a valve, a ring, a stent, a cage, a spacer, a graft, a porous or open structure, a scaffold and/or components thereof.

5                      The invention will hereafter be described in more detail by the following examples that by no means limit the scope of the invention.

### EXAMPLES

#### 10    Materials

##### Biodegradable polymers:

Poly(lactic acid) (PLA):            4032D from Natureworks LLC

Methyl cellulose (MC):            Methyl from Perfax

15

##### Solvent

Chloroform:                          solvent obtained from Sigma-Aldrich

##### Glass fibers

- 20            1.    Glass fiber textile: Satin weave SS0303 from Ten Cate Advanced Composites  
Chemical composition: 52-56 wt% SiO<sub>2</sub>, 16-25 wt% CaO, 12-16 wt% Al<sub>2</sub>O<sub>3</sub>,  
5-10 wt% B<sub>2</sub>O<sub>3</sub>, 0-2 wt% NaO and K<sub>2</sub>O, 0-5 wt% MgO, 0.05-0.4 wt% Fe<sub>2</sub>O<sub>3</sub>,  
0-0.8 wt% TiO<sub>2</sub>, 0-1.0 wt% fluorides
- 25            2.    Continuous glass fiber: EC9 136 from PPG  
Chemical composition: 52-56 wt% SiO<sub>2</sub>, 16-25 wt% CaO, 12-16 wt% Al<sub>2</sub>O<sub>3</sub>,  
5-10 wt% B<sub>2</sub>O<sub>3</sub>, 0-2 wt% NaO and K<sub>2</sub>O, 0-5 wt% MgO, 0.05-0.4 wt%  
Fe<sub>2</sub>O<sub>3</sub>, 0-0.8 wt% TiO<sub>2</sub>, 0-1.0 wt% fluorides

##### Flexural test

30                      The flexural modulus and flexural strength of the composites were determined according to ASTM test D790 on a Zwick/Roell 20 kN test bench. Test samples were prepared with a Unitom cutting machine while cooled with water to avoid defects on the edges that can cause premature failure. The flexural modulus was measured as the tangent at a loading of 20 N.

The maximal flexural strength ( $\sigma_{flex}$ ) is based on the maximal loading ( $F_{max}$ ):

$$\sigma_{flex} = \frac{3F_{max}L_{span}}{2wt^2}$$

5     with:

$$L = 40 \cdot t_{mean}$$

10    in which  $L_{span}$  is the span length,  $w$  is the width of the specimen,  $t$  is the thickness of the specimen, and  $t_{mean}$  is the average thickness of specimens of one composite.

#### Imaging

Three imaging techniques were utilized to gain insight in the quality of the composite: optical microscopy, scanning electron microscopy (SEM), and ultrasonic transmission scanning (C-scanning). Cross sections and interlaminar sections of test specimens were investigated with optical microscopy and SEM, while complete plates were investigated with C-scanning.

20    The sections of test specimens were sometimes embedded and polished to optimize the quality of the resulting images.

Optical microscopy was performed on a Leica DC 300F microscope with which magnifications varying from 2.5 to 100 could be obtained. In an optical microscope, visual light and a system of lenses are used to image small samples. In depth imaging of samples is not possible with this technique and limited magnification is feasible. Optical microscopy was used to get an indication of the quality of the composites.

Scanning electron microscopy was executed on a JEOL-JSM7500F.

SEM images sample surfaces by scanning with a high-energy beam of electrons and measuring the electrons that are scattered by the surface as well as the electrons produced by it. SEM is able to image samples in depth and to magnify from 25 up to  $10^6$  times. With this imaging technique, the quality of the composite, including wetting of fibers, voids, microcracks, and adhesion was investigated, as well as the failure mechanism occurring in the flexural test.

Ultrasonic transmission scanning was performed on a Midas system.

35    With this technique, the acoustic impedance of a material is measured by transmitting

ultrasonic energy to the sample and measuring the reflected energy. In a program (ALIS), the intensity of the reflected energy is converted from decibels to a tone of grey, in which darker grey represents a higher intensity.

The acoustic impedance is increased by voids, cracks, porosity, fiber-matrix interfaces, fiber distribution, fiber volume fraction, foreign inclusions, and so on. Consequently, dark grey indicated that more irregularities were present in that area. Intact parts of the composite plates were scanned in order to make a rough estimation of the quality of the composite.

## 10 Sample preparation

### Comparative experiment A

The steps that were carried out in the preparation of a composite of PLA sheets and glass fiber textile are listed below.

- 15     1. The PLA granules were dried in an oven at 80 °C during five hours.
2. 30 g PLA granules were compressed to sheets according to the protocol given below. This was repeated nine times to obtain nine sheets. The resulting sheets had a thickness of 1-2 mm.
3. Eight sheets (30x30 cm) of glass fiber textile were made.
- 20     4. The eight glass fiber textiles and nine PLA sheets were subsequently stacked, and consolidated in a Joos press (LAP100) by heating up the stack while compression was applied. The protocol used in this process was a standard consolidation protocol of the Joos press.

## 25 Pressing protocol of PLA sheets

Heat up press to 200 °C.

Stack stainless steel plates, Teflon sheets (to separate the PLA from the press), and PLA granules.

Heat up PLA without applying pressure during 10 minutes

30     Apply 10 kN during 5 minutes

Apply 20 kN during 5 minutes

Apply 30 kN during 5 minutes

Apply 40 kN during 5 minutes

Apply 50 kN during 5 minutes

35     Apply 60 kN during 5 minutes



Remove Teflon sheets with PLA sheet in between from the press  
Cool the PLA sheet in ambient air during approximately 5 minutes  
Separate PLA sheet from Teflon sheets

## 5 Comparative experiment B

The steps that were carried out in the preparation of a composite of glass fiber textile and PLA powder are listed below.

1. The mass of the PLA and the number of glass fiber textiles was calculated based on the required dimensions and fiber volume fraction. The goal was to make a plate of 300x150x2.5 mm with a fiber volume fraction of 0.5. To obtain this, nine sheets of glass fiber textile were needed, combined with 80 g of PLA.
2. The PLA granules were ground three times in a concentric grinder under nitrogen to granules with a diameter of approximately 1-2 mm.
3. Eight sheets (30x15 cm) of glass fiber textile were made.
4. 8 g of PLA powder was distributed manually over the bottom of the mold. After this a glass fiber textile sheet was added on top of this layer. Then the next 8 g of PLA was distributed on top of the glass fiber textile. This was repeated until nine layers of PLA and eight layers of glass fiber textile were stacked subsequently. Finally, the mold was closed.

The system was consolidated in a Fontijne press (TP 1000). The consolidation steps are shown below.

### Consolidation protocol of the composite of glass fiber textiles and PLA powder.

- 25 Heat up press to 200 °C.  
Place the mold in the press and use Teflon sheets to separate the mold from the press  
Apply a force of 5 kN during 13 minutes  
Apply a force of 8 kN during 9 minutes  
Cool down the press to 41 °C, while the applied force is maintained at 8 kN
- 30 Take the mold out of the press and open it

### Example I

The steps that were carried out in the preparation of a composite of pre-wetted glass fiber textiles are listed below.

1. The mass of PLA and the number of glass fiber textiles was calculated based on the required dimensions. The goal was to make a plate of 300x150x2.5 mm. Therefore, eleven sheets of glass fiber textiles were combined with 73 g PLA.
- 5 2. Eleven sheets (30x15 cm) of glass fiber textile were made.
3. A solution of PLA and chloroform was prepared by adding 80 g PLA granules in parts to 800 mL chloroform. The solution was stirred overnight.
4. Multiple layers of the solution were applied to eleven glass fiber textiles (30x15  
10 cm). The first layer was applied by dipping the sheets in the solution, while the following layers were applied to the sheets with a brush. Before a next layer was added, the sheets were dried for at least one hour in a hood on a Teflon sheet.
5. The textiles were cut into rectangular impregnated textiles of 14x29 cm.
- 15 6. The eleven sheets were stacked on top of each other in the mold and the mold was closed. The composite was consolidated in a Fontijne press. The steps of the consolidation process are shown below. During the process, the temperatures in the mold were monitored.

20 Consolidation protocol of prewetted glass fiber textiles.

Heat up press to 200 °C.

Place the mold in the press and use Teflon sheets to separate the mold from the press

Apply a force of 20 kN during 15 minutes

Apply a force of 30 kN during 4 minutes

- 25 Apply a force of 50 kN during two minutes

Cool down the press to 36 °C, while the applied force is maintained at 50 kN

Take the mold out of the press and open it.

Example II

- 30 The steps that were carried out in the preparation of a composite of pre-wetted glass fiber textiles and PLA powder are listed below.

1. The mass of the PLA and the number of glass fiber textiles was calculated based on the required dimensions and fiber volume fraction. The goal was to make a plate with the same dimensions and fiber volume fraction as the plate

obtained from glass fiber textiles combined with PLA powder. Therefore, eight sheets of glass fiber textile were needed and 80 g of PLA was added to this.

2. Eight sheets (30x15 cm) of glass fiber textile were made.
3. The PLA granules were ground three times in a concentric grinder under  
5 nitrogen to granules with a diameter of approximately 1 mm.
4. A solution of 11 g in 110 mL chloroform was prepared. The solution was applied to one side of the glass fiber textiles with a brush.
5. A solution of 11 g in 110 mL chloroform was prepared. The solution was applied to the other side of the glass fiber textiles with a brush.
- 10 6. 6 g of PLA powder was distributed manually over the bottom of the mold. After this, a glass fiber textile sheet was added on top of this layer. This was repeated until nine layers of PLA and eight layers of glass fiber textile were stacked subsequently. Finally, the mold was closed.
7. The composite was consolidated in a Joos press, of which the protocol is  
15 shown below.

Consolidation protocol of the composite of pre-wetted glass fiber textiles and PLA powder.

Heat up press to 200 °C.

- 20 Place the mold in the press and use Teflon sheets to separate the mold from the press and apply 5 kN until the temperature within the mold is 195 °C.  
Apply 20 kN during 5 minutes  
Apply 30 kN during 5 minutes  
Cool down the press to 20 °C, while the applied force is maintained at 30 kN
- 25 Take the mold out of the press and open it

Example III

The steps that were carried out to make a composite of filament wound continuous glass fiber and PLA is listed below.

- 30 1. The fiber volume fraction, the mass of PLA, the shift between fibers, and the number of layers were defined, considering the trade-off between shift, fiber volume fraction, and thickness of the final composite. The goal was to produce two plates of 150x150x1.4 mm with a fiber volume fraction of 0.4. Therefore, a total of 23 layers was needed with a distance of 1.5 mm between the fibers  
35 and 2 times 33.9 g PLA.

2. Three layers of glass fiber with a tex-value of 136 g/km were filament wound around a winding mold with a shift of 1.5 mm.
  3. A solution of 11.0 g of PLA in 170 mL chloroform was prepared.
  4. A layer of this solution was applied to one side of the wound structure and  
5 dried for one hour.
  5. A layer of this solution was applied to the other side of the wound structure and dried for one hour.
  6. The two obtained plates were cut out.
  7. The rest of the solution was applied to both sheets on both sides with a brush.
  - 10 8. The following layers were produced according to the procedure described above under numbers 2-7. These fiber layers were treated with a solution of 14.2 g PLA dissolved in approximately 200 mL chloroform, which was applied to the fibers.
  9. The obtained layers were placed in the mold in two stacks. The direction of  
15 one layer was different from the previous or next layer to obtain a 0°-90°-0°-:-  
0 ° ply sequence.
  10. The mold was closed and the composite was consolidated according to the protocol shown below.
- 20 Consolidation protocol of the composite of filament wound glass fibers and PLA.  
Heat up press to 200 °C.  
Place the mold in the press and use Teflon sheets to separate the mold from the press  
Close the press and apply 5 kN until the temperature in the mold is 195 °C.  
Apply 20 kN during 5 minutes  
25 Apply 30 kN during 5 minutes  
Cool down the press to 20 °C, while the applied force is maintained at 30 kN

Table A

Overview of the flexural properties and the quality of all prepared and tested composites.

Example/ Experiment	Volume Fraction of fibers	Flexural Modulus of Composite (GPa)	Flexural Strength of the Composite (MPa)	Failure mode	Adhesion
A	0.62	29.6	334.4	Delamination	2
B	0.53	20.4	362.5	Delamination and fiber fracture	2
I	0.59	33.0	453.1	Fiber fracture	2
II	0.44	18.5	408.9	Fiber fracture	2
III	0.42	26.4	487.7	Fiber fracture	2

- 5                      The adhesion was categorized in four groups: 0 = no matrix in between fibers or on loose fibers; 1 = matrix present in between fibers, but not on loose fibers; 2 = matrix present in between fibers, and some matrix sticking to loose fibers; 3 = matrix present in between fibers and a lot of matrix is sticking to loose fibers.

- 10                     The goal of the examples was to prepare a biodegradable composite with a flexural stiffness, as shown by the flexural modulus, and flexural strength comparable to that of bone. The flexural stiffness of bone is 20-40 GPa; the flexural strength of bone is about 200 MPa.

                         The flexural strength of the composite should preferably be higher than the flexural strength of bone to limit the risk of failure of the implant.

- 15                     It is clear from the examples that a biodegradable composite, wherein the glass fiber was pre-treated with a solution of PLA, has a much higher flexural strength when compared to a composite prepared from a glass fiber which is not pre-treated.

CLAIMS

1. Biodegradable composite comprising a biodegradable polymer and 20-70 vol% glass fibers, wherein the biodegradable composite has a flexural strength between 100 and 600 MPa.
2. Biodegradable composite according to claim 1, wherein the biodegradable composite has a flexural modulus between 10 and 40 GPa.
3. Biodegradable composite according to claim 1 or 2, wherein the glass fibers are continuous glass fibers.
4. Biodegradable composite according to any one of claims 1-3, wherein the glass fibers have a SiO<sub>2</sub> content of 15-60 wt%.
5. Biodegradable composite according to any one of claims 1-4, wherein the glass fibers are resorbable glass fibers.
6. Biodegradable composite according to any one of claims 1-5, wherein the biodegradable polymer comprises a poly( $\alpha$ -ester) or copolymers thereof.
7. Biodegradable composite according to any one of claims 1-6, wherein the biodegradable polymer is poly(lactic acid).
8. Process for the preparation of a biodegradable composite according to anyone of claims 1-7, wherein
  - a. the glass fibers are pre-treated with a solution of the biodegradable polymer in a solvent;
  - b. the solvent is evaporated;
  - c. the pre-treated glass fibers, optionally together with additional biodegradable polymer, is placed in a mold, where after the biodegradable polymer present on the fibers and/or added to the mold is melted by applying heat and pressure;
  - d. the mold is cooled and the biodegradable composite is removed from the mold.
9. Process according to claim 8, wherein the biodegradable polymer used for the pretreatment of the glass fibers is the same as the biodegradable polymer added to the mold.
10. Medical implant comprising a biodegradable composite according to claim 1-6, wherein the medical implant is chosen from a screw, a pin, a plate, a suture, a mesh, a net, a film, a tube, a balloon, a bag, a rod, an anchor, a valve, a ring,

a stent, a cage, a spacer, a graft, a porous or open structure, a scaffold and/or components thereof.

## INTERNATIONAL SEARCH REPORT

International application No

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## A. CLASSIFICATION OF SUBJECT MATTER

INV. B29C70/02 A61F2/30 A61L27/44 A61L27/58  
ADD.

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)

B29C A61F A61L

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 344 496 B1 (NIEDERAUER GABRIELE [US] ET AL) 5 February 2002 (2002-02-05) column 1, line 11 - line 54 column 3, line 10 - line 18 column 4, line 1 - line 26 claims 1-10	1-7, 10
X	EP 1 872 806 A1 (VIVOXID OY [FI]) 2 January 2008 (2008-01-02) paragraph [0001] paragraph [0004] paragraph [0021] - paragraph [0022] paragraph [0024] paragraph [0042] - paragraph [0044] paragraph [0046] - paragraph [0053] ----- -/--	1-7, 10



Further documents are listed in the continuation of Box C.



See patent family annex.

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International application No

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