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(54) **Honeycomb structure based on lignocellulosic materials and process for producing the same**

(57) The invention relates to a lignocellulosic structure, to a process for producing a lignocellulosic structure, and to use of a boric acid derivatives in a lignocellulosic structure.

The lignocellulosic structure of the invention comprises a layer with a thickness of 0.01 μm to 10 μm comprising SiO_2 on at least part of its surface, the structure being in the form of a honeycomb structure, and the structure being obtainable by contacting the lignocellulosic structure with a SiO_2 precursor, wherein the structure further comprising a boric acid derivative.

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Description

[0001] The invention relates to honeycomb structures based on lignocellulosic materials and processes for producing these structures.

[0002] Honeycomb paper is applied as an intermediate ("sandwich") layer having a low specific mass in various types of constructions.

[0003] Honeycomb structures based on recycled paper (ligno-fibers") provide certain advantages, such as a light weight and a relatively high compression strength, at low costs. Another advantage of paper based honeycomb structures is their high flexibility. This makes it possible to fold the honeycomb structures and reduce the diameter of the honeycomb structures, as a result of which the required amount of space for storage, transport and handling can be relatively low.

[0004] On the other hand, honeycomb structures based on paper often have a limited biological stability (*viz*, they are susceptible of attack by microorganisms, such as moulds), a limited water stability (*viz.* their mechanical strength may drop considerably when wet or when in humid atmosphere) and have a limited fire resistance. In order to compensate these effects, substances are combined with the paper material, *e.g.* by impregnating the paper. When the paper is impregnated with these (fire resistant) resins, this generally results in a product having an increased stiffness, as a result of which the honeycomb structures often can not be compacted by folding and so they take up a lot of space. Also, some frequently used resins, such as phenol based resins, that need to be heated at high temperatures release formaldehyde, which is .a hazardous compound and this must be avoided, especially for indoor applications. After curing, the honeycomb structures maintain their stiffness, which presents another drawback. Because of this bulkiness, large transport volumes are required.

[0005] The paper should have a glueability that is sufficient to produce the honeycomb structures therefrom. For instance water glass, an aqueous solution of sodium silicate, is commonly employed as a glue in this type of applications. As long as the paper remains its flexibility during the processing, in principle an endless honeycomb structure can be made, which would be very desirable from a process economic point of view.

[0006] It is furthermore very desirable if the paper itself has a certain elasticity (especially if compression pressure is applied), because this facilitates the production of composites with a core layer of honeycomb. If the core layer is more elastic, the compression strength can be better maintained in the composite after assembling the composites (gluing and pressing the skins onto the core layer),

[0007] Furthermore, the amount of compounds that are brought into contact with the paper material should be as low as possible but still homogeneously distributed in a thin layer on surfaces of the paper (and fibers), *viz*, sufficient to bring about the desired effect, while avoiding any detrimental effect,

[0008] It would be highly desirable to provide a lignocellulose based honeycomb structure that meets all the needs. The present invention aims at providing this.

[0009] It was found that this object can be met by applying silica in thin layers to the lignocellulosic fibers (paper surface). Thus, in a first aspect, the present invention is directed to a lignocellulosic structure comprising a thin layer comprising SiO_2 on at least part of its surface.

[0010] The thin SiO_2 based,layer can be applied in various ways.

[0011] A highly preferred method comprises contacting the lignocellulosic structure with a suitable precursor *e.g.* by submerging the lignocellulosic structure in a bath of SiO_2 precursor or by spraying the SiO_2 precursor on the structure or application of the silica using plasma technology,

[0012] A suitable plasma technology is the surface dielectric barrier discharge (SDBD) which works under atmospheric pressure and is therefore suitable for continuous production processes

[0013] Silica sol-gel is a suitable precursor. The silica sol-gel component is typically based on silicon alkoxide, $Si(OR)_4$, wherein R is an alkyl, preferably methyl or ethyl. These compounds can be subjected to hydrolysis and gelation, whereby silane groups (Si-OH) and and siloxane groups (Si-O-Si) are broken and formed, respectively. Commercially widely available sol-gel components are TEOS (tetraethylorthosilicate) and TMOS (tetramethylorthosilicate). The silica content of the SiO_2 precursor typically ranges from 1-10% silica and the solvent (such as ethanol, isopropanol or other alcohols, acetone or other ketones) content typically ranges from 10-70%. Using these types of solvents, in particular ethanol as a solvent has a very limited risk, because these solvents have limited toxicity. These solvents tend to evaporate easily. It is highly preferred to collect the vapours comprising the evaporated solvents and thus recover the solvent therefrom so that it may be recycled.

[0014] According to the present invention materials can be provided that provide excellent fire-retardant properties, while at the same time conserving all other requirements and where the transport volume of structures produced is minimized.

[0015] The thin SiO_2 based layer preferably has a thickness of 0.01 μm to 10 μm, preferably about 0.2 to 5 μm, more preferably about 0.5 to 2.5 μm.

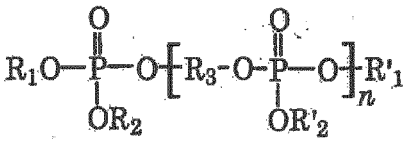
[0016] The paper surface may be treated with further substances, such as fire retardants, These further components may be applied together with the SiO_2 film, but it is also possible to apply them in a separate process step *e.g.* a

subsequent dipping or spraying step or a plasma treatment. Phosphorus based fire retardants are very suitable for this purpose, The combination of phosphorus based fire retardants and silica sol-gel provides materials that have excellent flre-retardant properties, while at the same time conserving all other above-mentioned requirements and where the transport volume of structures produced is minimized.

[0017] The (phosphorus based) fire retardant used in the present invention is preferably a phosphate ester and more preferably an oligomeric phosphate ester. The .fire retardant composition of the present invention can be used to impregnate paper in order to create honeycomb structures. The structures thus obtained show excellent properties with respect to water resistance, fire retardant properties, compressibility and durability, At the same time, the product can still be combined with water glass in the conventional method of lamination. The composition of the invention typically comprises 1 to 90 wt,% oligomeric phosphate ester, preferably from 5 to 50 wt.%, based on weight of the total composition.

[0018] The contacting of the lignocellulosic material with the SiO_2 precursor can be carried out in a continuous fashion by using a conventional paper treatment process, *e.g.* by submerging a continuous belt of lignocellulosic material (paper) through a bath containing the sol-gel composition and optionally the fire retardant composition, application of coating processes as used in the paper industry or plasma treatment under atmospheric pressure. The impregnated paper maintains its flexibility in the length direction, by which it can be stored and transported without requiring much space, due to its compactness. The structures that are thus produced have dimensions that are "enmess", *viz.* up to *e.g.* 50 m or more. Also no emission of harmful compounds occurs during the production process, If a silica sol-gel comprising ethanol is used, the solvent can be collected as vapor and recycled.

[0019] The .phosphate esters that find use in the present invention are commercially known fire-retardants. Suitable (oligomeric or monomeric) phosphate esters may be represented by the following formula I:



(I)

wherein each of R_1, R'_1, R_2, R'_2 and R_3 is independently hydrogen or hydrocarbon side chain, in particular straight, branched or cyclic C_1-C_{10} alkyl or alkenyl (preferably C_2-C_8 alkyl or alkenyl), optionally substituted, *e.g.* with halogen, epoxide hydroxyl, amino; and *n* is an integer from 0 to typically about 10. In case *n* is zero, the the compounds of formula I are monomeric phosphate esters. Examples of suitable oligomeric phosphate ester compound s and their production are given *e.g.* in US-A-3 767 732 and US-A-4 382 042.

[0020] Preferred compounds are those of formula I having R_1 and/or R'_1= (substituted) phenyl, hydrogen, methyl, ethyl, propyl, butyl or pentyl; R_2 and/or R'_2 = (substituted) phenyl, methyl, ethyl, propyl, butyl or pentyl; and R_3= (substituted) phenyl, bisphenol A or biphenyl A suitable monomeric compound is triphenyl phosphate, which corresponds to a compound of Formula I having R_1=R_1'=R_2=Phenyl and *n*=0. A suitable oligomeric phosphate ester is resorcinol bis (diphenyl phosphate) (RDP), commercially available as Fyrolflex™ RDP (Akzo Nobel), which corresponds to a compound of formula I having R_1=R_1'=R_2=R_2=R_3=phenyl and *n*=1.

[0021] Single compositions of the present invention can be prepared by admixing the ingredients in any order. Preferably, the (oligomeric) phosphate esters are mixed into the sol-get composition.

[0022] In a preferred embodiment a boric acid derivative is present in the compositions of the present invention, in particular those described in DE-A-198 33 479. It was found that the,addition of these boric acid compounds has a positive effect on the durability of the lignocellulosic products that are impregnated with the compositions of the present invention. Suitable boric acid derivatives for this purpose are boric acid, trialkylborate (*e.g.* tributyl borate; tri-isopropyl borate; or tri-tert-butyl borate). The boric acid derivatives may be present in amounts of typically 0 to 10 wt.%, preferably 0.5 to 5 wit.%, based on weight of the total composition. The boric acid provides further protection against biological degradation (that may be caused by degrading organisms like fungi and insects) and has positive effects on the fire resistance.

[0023] It was found that the leaching of the boric acid that commonly occurs can be reduced by using the SiO_2 in accordance with the present invention.

[0024] Honeycomb structures can be prepared by known process, *e.g.* the paper honeycomb production processes described in Pflug et al. (5th Global Wood and Natural Fibre Composites Symposium, Kassel (DE), 27-28 April 2004) typically out of low cost recycled paper (*e.g.* Testliner). Figure 3 shows schematically the different process steps in a suitable production process for making expanded honeycombs. In a first step adhesive lines are printed on the paper, which may come from one or several paper rolls (1). Then a stack of several sheets is made and bonded together (2). Those sheets can be cut to strips prior or after stacking to a slice (3). In the third step many slices are stacked and bonded together to produce an unexpanded endless paper honeycomb core (4). Finally, the sheets are pulled apart (5)

expanding the stack onto a hexagonal honeycomb core (6). The residual stresses in paper honeycombs can be relaxed after expansion by a controlled application of heat.

[0025] Typically the structures that are produced in this way comprise walls formed of paper strips having a width of several cm, *e.g.* about 1-6 cm. A typical honeycomb structure is has a diameter of the cells of *e.g.* 5 - 50 mm and a thickness of the total honeycomb layer of *e.g.* 5 - 60 mm. The paper weight is usually between 80 g/m^2 and 250 g/m^2.

[0026] Figure 4 shows a scanning electron micrograph (SEM), of a sample that is prepared in accordance with the present invention. A thin silica film on a cell wall of a paper fiber can be seen.

[0027] The invention is further illustrated by the following illustrative embodiments.

1. Lignocellulosic structure comprising a thin layer comprising SiO_2 on at least of its surface.
2. Lignocellulosic structure according to embodiment 1, wherein said thin layer has a thickness of 0.01 μm to 10 μm.
3. Lignocellulosic structure according to any of the previous embodiments, wherein the SiO_2 layer obtained by contacting the lignocellulosic structure with a silica sol-gel component, which is preferably a silicon alkoxide, $Si(OR)_4$, wherein R is an alkyl, more preferably methyl or ethyl.
4. Lignocellulosic structure according to any of the previous embodiments, further comprising a fire retardant, which is preferably a phosphorus based fire retardant, more preferably an oligomeric phosphate ester.
5. Lignocellulosic structure according to any of the previous embodiments, which is produced by contacting the lignocellulosic structure with a SiO_2 precursor, optionally using plasma technology.
6. Lignocellulosic structure according to any of the previous embodiments, which is in the for of a honeycomb structure.
7. Lignocellulosic structure according to embodiment 6, wherein the cells have an average diameter of 5-50 mm and wherein the thickness of the honeycomb layer is 5-60 mm.

[0028] The invention will now be illustrated by the following examples.

Example 1

[0029] Paper (140 g/m^2) was treated with silica in ethanol (concentration 18 %) using a coating treatment. The coated paper was dried at 105 ºC over a period of 12 hours.

[0030] After being exposed to a humid atmosphere (relative humidity of 96%) at 20 °C for 5 days, the paper was subjected to a repeated stress/strain measurement. Three repeated measurements were carried out on each sample wherein the stress was increased to the maximum that could be achieved and then released again. The results for an untreated sample are given in Figure 1.

[0031] The results of the paper that was treated as described above are given in Figure 2.

[0032] From these results it clearly follows that the paper that is treated in accordance with the present invention maintains it strength after the first and second measurement. Furthermore, the flexibility of the honeycomb structure in the length direction was maintained. Also the paper had an excellent glueability so that it could be easily glued with water glass.

Claims

1. Lignocellulosic structure comprising a layer with a thickness of 0.01 μm to 10 μm comprising SiO_2 on at least part of its surface, which structure its in the form of a honeycomb structure, and which structure is obtainable by contacting the lignocellulosic structure with a SiO_2 precursor, wherein the structure further comprises a boric acid derivative.

2. Lignocellulosic structure according to claim 1, wherein said boric acid derivative is selected from the group consisting of boric acid and trialkylborate, such as tributyl borate, tri-isopropyl borate and tri-tert-butyl borate

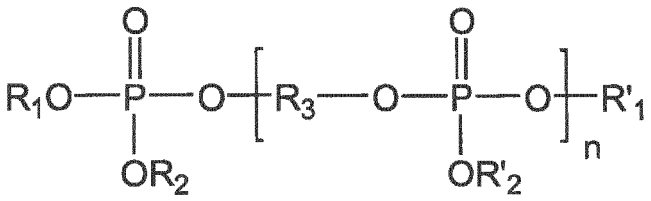
3. Lignocellulosic structure according to claim 1 or 2, wherein said layer has a thickness of 0.2 μm to 5 μm, preferably 0.5 to 2.5 μm.

4. Lignocellulosic structure according to any one of claims 1-3, wherein the cells have an average diameter of 5-50 mm and wherein the thickness of the honeycomb layer is 5-6 mm.

5. Process for producing a lignocellulosic structure comprising a layer with a thickness of 0.01 μm to 10 μm comprising SiO_2 on at least part of its surface, which structure is in the form of a honeycomb structure, said process comprising impregnating the lignocellulosic structure with a composition that comprises a SiO_2 precursor and a boric acid derivative.

6. Process according to claim 5, wherein said composition further comprises a fire retardant or wherein a fire retardant is applied in a separate process step, which fire retardant is preferably a phosphorus based fire retardant, more preferably an oligomeric phosphate ester.

7. Process according to claim 6, wherein said phosphate ester is represented by the following formula



wherein each of R_1, R'_1, R_2, R'_2 and R_3 is independently hydrogen or straight, branched or cyclic C_1-C_{10} alkyl or alkenyl, optionally substituted; and n is an integer from 0 to 10.

8. Process according to any one of claims 5-7, wherein said composition comprises 1 to 90 wt.% of oligomeric phosphate ester, preferably 5 to 50 wt.%, based on weight of the total composition.

9. Process according to any one of claims 5-8, wherein said SiO_2 precursor is a silica sol-gel, which is referably a silicon alkoxide, $Si(OR)_4$, wherein is an alkyl, more preferably methyl or ethyl.

10. Process according to any one of claims 5-9, wherein said boric acid derivative is selected from the group consisting of boric acid and trialkylborate, such as tributyl borate, tri-isopropyl borate and tri-tert-butyl borate.

11. Process according to any one of claims 5-10, wherein said boric acid derivative is present in an amount of 0.5-5 wt. % base on of the total composition.

12. Use of a boric acid derivative in a lignocellulosic structure for enhancing the durability, wherein said lignocellulosic structure comprising a layer with a thickness of 0.01 μm to 10 μm comprising SiO_2 on at least part of its surface, which structure is in the for of a honeycomb structure.

13. Use of a boric acid derivative in a lignocellulosic structure for protecting against biological degradation, wherein said lignocellulosic structure comprising a layer with a thickness of 0.01 μm to 10 μm comprising SiO_2 on at least part of its surface, which structure is in the form of a honeycomb structure.

14. Use of a boric acid derivative in a lignocellulosic structure for improving fire resistance, wherein said lignocellulosic structure comprising a layer with a thickness of 0.01 μm to 10 μm comprising SiO_2 on at least part of its surface, which structure is in the form of a honeycomb structure.

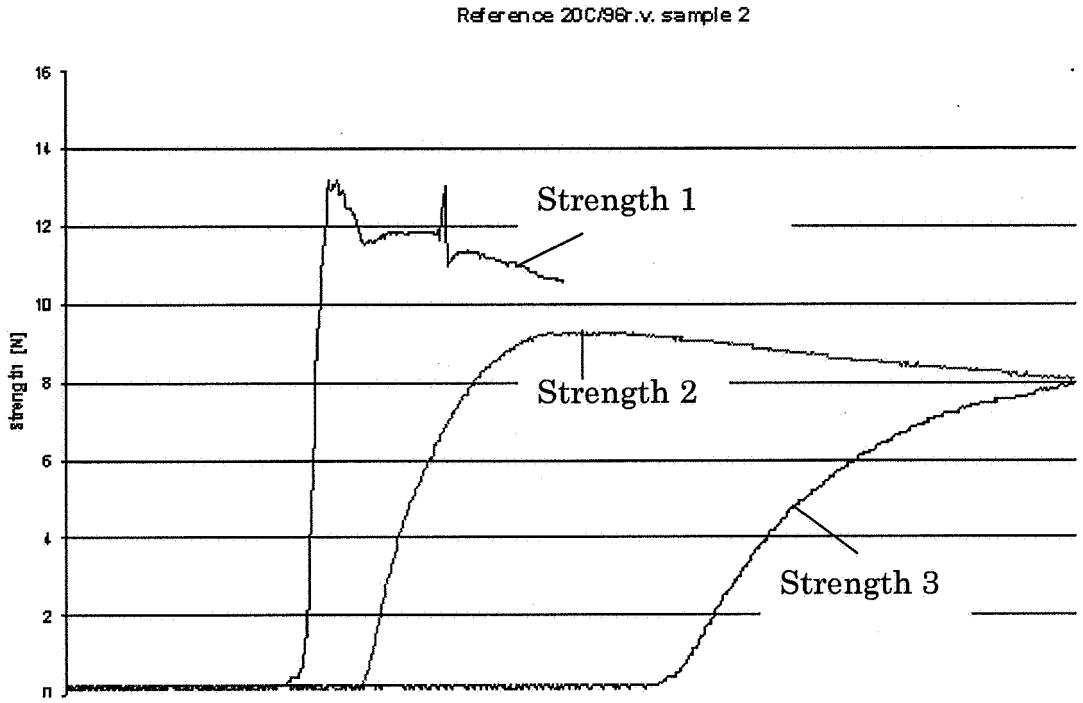

Reference 20C/98r.v. sample 2
strength [N]
16
14
12
10
8
6
4
2
0
Strength 1
Strength 2
Strength 3

Fig. 1

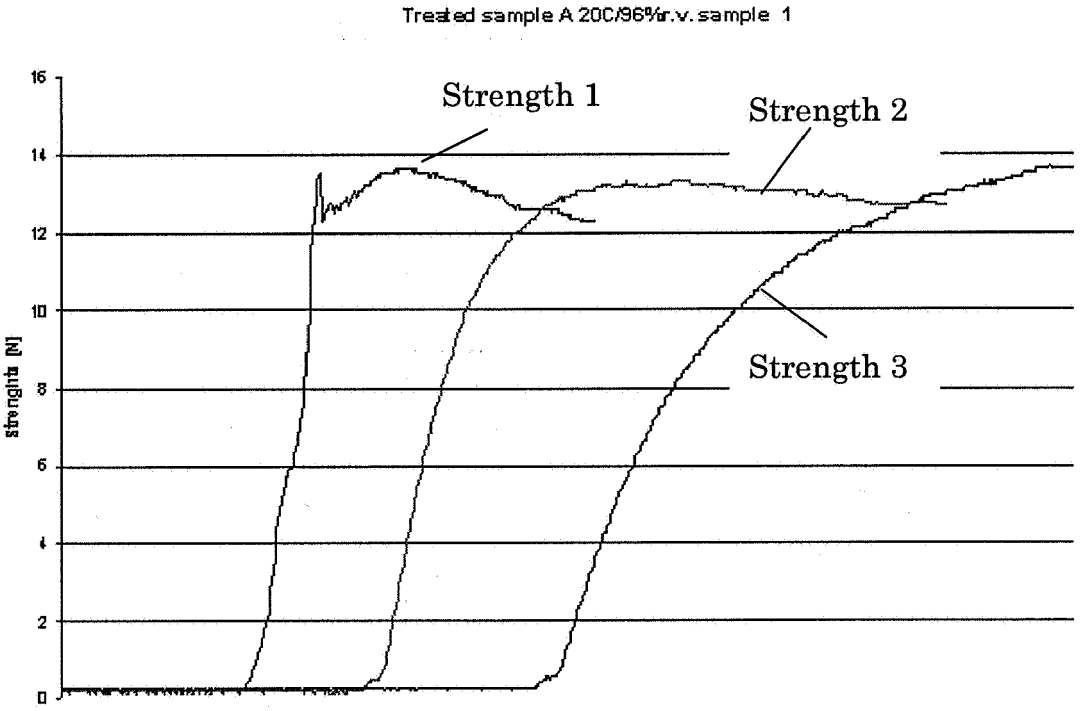

Treated sample A 20C/96%r.v. sample 1
strength [N]
16
14
12
10
8
6
4
2
0
Strength 1
Strength 2
Strength 3

Fig. 2

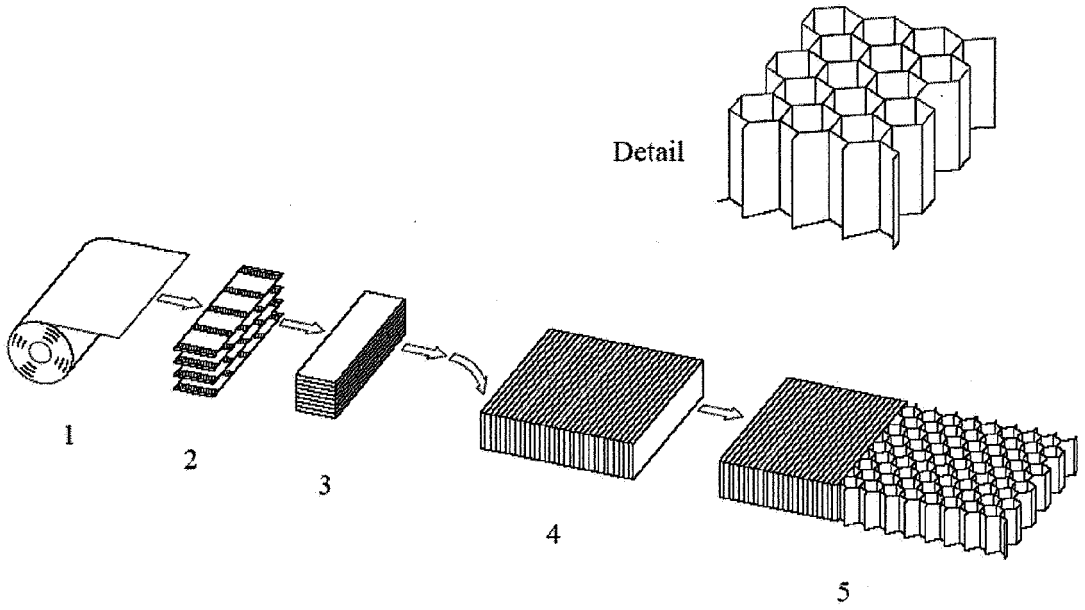

Detail
1
2
3
4
5

Fig. 3

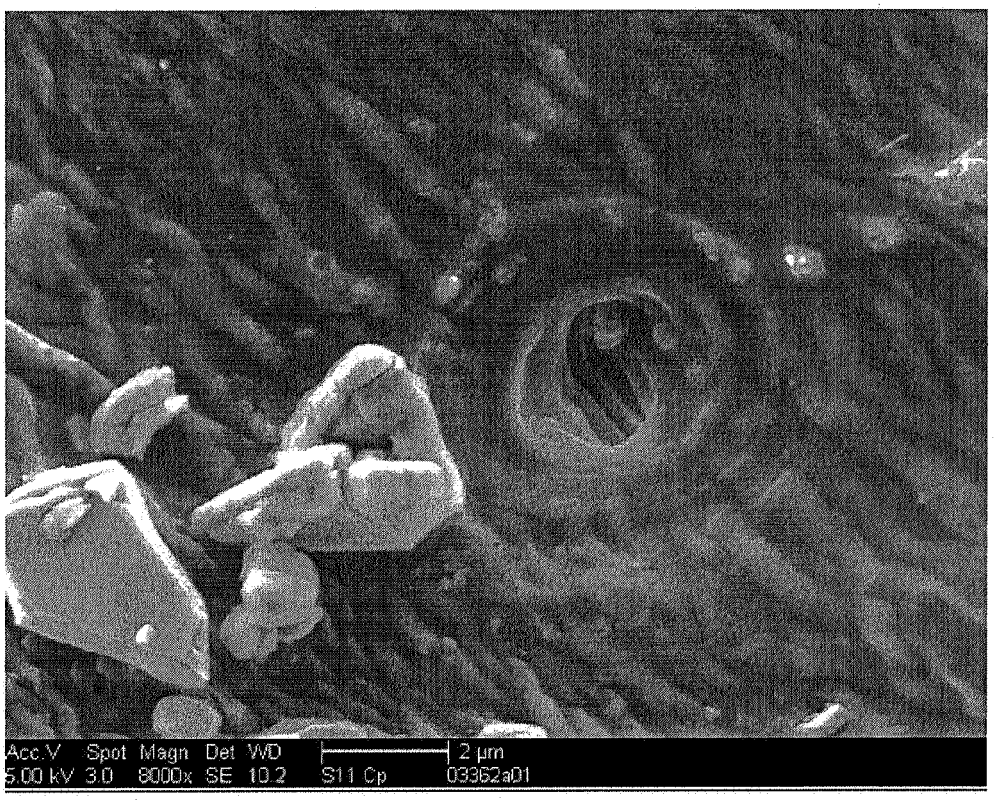

Acc.V Spot Magn Det WD 2 µm
5.00 kV 3.0 8000x SE 10.2 S11 Cp 03362a01

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 12 16 4779

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 1 130 161 A1 (PROFLUTE AB [SE]) 5 September 2001 (2001-09-05) * page 3, line 39 - page 5, line 48; figures 3,4 * -----	1-14	INV. D21H19/40 ADD. D21H27/40
A	US 6 066 379 A (MA TUNG CHAN [US] ET AL) 23 May 2000 (2000-05-23) * claims 1,7; table II * -----	1-14	
A	US 5 254 195 A (TSENG PEN C [TW] ET AL) 19 October 1993 (1993-10-19) * the whole document * -----	1-14	

TECHNICAL FIELDS SEARCHED (IPC)

D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	5 June 2012	Ponsaud, Philippe

CATEGORY OF CITED DOCUMENTS

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05-06-2012

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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- DE 19833479 A **[0022]**

Non-patent literature cited in the description

- **PFLUG et al.** *5th Global Wood and Natural Fibre Composites Symposium,* 27 April 2004 **[0024]**