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(54) BIODEGRADABLE CELLULOSE BASED COMPOSITE MATERIAL AND PROCESS FOR THE PRODUCTION THEREOF

(57) The present invention relates to a biodegradable composite material comprising:
a) pure cellulose pulp;
b) gelatin; and
c) a crosslinking agent.

The present invention further relates to the use of the biodegradable composite material above in the production of eyewear articles.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a completely biodegradable cellulose based composite material and to a process for manufacturing it.

BACKGROUND OF THE INVENTION

[0002] In recent years the environmental impact of any industrial process has become a key aspect in the decision making not only of those involved in the production of goods, but most importantly of those buying goods.

[0003] Many manufacturers in a wide array of fields have felt the need to minimize the use of toxic and/or polluting agents and machineries in their production processes. At the same time a huge effort has been put in providing new eco-friendly materials, in particular biodegradable materials, which could be used as substitute for more polluting, usually plastic-based, ones.

[0004] However, the biggest problem to face when trying to replace plastic and/or metal based materials with more eco-friendly ones, is that to maintain the mechanical and aesthetic performances, while at the same time obtaining a material that can be easily decomposed.

[0005] It is in this context that the most recent research on cellulose-based composite materials has been focused.

[0006] Cellulose is a polysaccharide consisting of a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked D-glucose units. It is an important structural component of the primary cell wall of green plants, as well as of wood, and it is mainly used to produce paperboard and paper.

[0007] Cellulose fibers have been used for years to reinforce polymeric materials and in textiles, and more recent developments have been made towards cellulose foams useful as insulation in the building industry. Nanostructured cellulose has also found application as reinforcing fillers.

[0008] All these composite materials, however, couple the environmentally friendly cellulose with more robust, non-biodegradable materials.

[0009] Therefore there is still the need for materials of 100% natural origin, completely recyclable and biodegradable, that can be used in a wide range of applications.

SUMMARY OF THE INVENTION

[0010] The Applicant has faced the problem of providing a completely biodegradable material, obtainable by an environmentally friendly process, characterized by excellent physical and mechanical properties as well as an aesthetically pleasing finish.

[0011] More in particular, the Applicant faced the problem of providing a recyclable material at the same time characterized by high durability and excellent workability, able to withstand the stresses due to the various processing steps, as well as characterized by vivid colours and pleasant texture, hence highly versatile and useful in a plethora of different applications.

[0012] Also, the Applicant faced the problem of providing such a material through a process with a low environmental impact, using materials of natural origin, minimizing the use of toxic and polluting agents, as well as the amount of waste.

[0013] Thus, in a first aspect, the present invention relates to a biodegradable composite material comprising:

a) pure cellulose pulp;
b) gelatin; and
c) a crosslinking agent.

[0014] Preferably, in the biodegradable composite material according to the present invention the pure cellulose pulp is in form of a sheet of paper.

[0015] Preferably, the paper is a sheet of absorbent and optionally coloured paper.

[0016] Preferably, the biodegradable composite material according to the present invention comprises pure cellulose pulp, or paper from pure cellulose pulp, in an amount of at least 70%.

[0017] Preferably, in the biodegradable composite material according to the present invention the gelatin is in an amount of from 5 to 20%.

[0018] Preferably, in the biodegradable composite material according to the present invention the crosslinking agent is in an amount below 75 ppm.

[0019] Preferably, in the biodegradable composite material according to the present invention the residual humidity is of less than 10%.

[0020] In a second aspect, the present invention relates to a process to obtain the biodegradable composite material disclosed above, the process comprising the steps of:

i) providing one or more sheet of paper made of pure cellulose pulp;
ii) laminating the one or more sheet of paper together with gelatin and optionally one or more additives;
iii) hanging the laminated sheet obtained in step ii) until hardening of the gelatin;
iv) crosslinking the laminated sheet in a crosslinking bath;
v) drying the crosslinked laminated sheet; and
vi) pressing the sheet.

[0021] Preferably, the step ii) is carried out at a temperature of from 35°C to 55°C for a period of 20 to 600 seconds.
[0022] Preferably, the step iii) is carried out at a temperature of from 2°C to 18°C until complete hardening of the gelatin.
[0023] Preferably, the step iv) is carried out in a bath containing an aqueous solution of a crosslinking agent for a period of 20 to 600 seconds.
[0024] Preferably, the step v) is carried out at a temperature of from 25°C to 40°C for a period of from 2 to 18 days.
[0025] Preferably, the step vi) is carried out at a temperature of from 50°C to 85°C for a period of from 2 to 30 minutes.
[0026] In a third aspect, the present invention relates to the use of the biodegradable composite material disclosed above in the production of eyewear articles.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0027] According to the present invention, the terms "pure cellulose pulp" means a material consisting essentially of cellulose, i.e. at least 70% cellulose, preferably 80%, even more preferably 90%, 95%, 96%, 97%, 98%, 99%, or even 100% cellulose.

Detailed description

[0028] A first aspect of the present invention is a biodegradable composite material comprising:

a) pure cellulose pulp;
b) gelatin; and
c) a crosslinking agent.

[0029] Preferably, the biodegradable composite material according to the present invention comprises or essentially consists of:

a) pure cellulose pulp;
b) gelatin;
c) a crosslinking agent; and
d) water or residual humidity.

[0030] In a preferred embodiment, the pure cellulose pulp is in form of a sheet of paper.
[0031] Preferably, the paper is a sheet of absorbent and optionally coloured paper, even more preferably a sheet of decor paper.
[0032] Advantageously, the paper is coloured with a natural pigment, preferably a pigment approved for animal and human consumption, preferably selected from the group comprising. The use of coloured paper allows obtaining a coloured composite material with excellent durability, i.e. the color does not fade away even after repeated and/or prolonged exposure to light and other environmental agents. By using several sheets of differently coloured paper it is possible to obtain the most disparate chromatic effects desired in the finished product.
[0033] Advantageously, the paper has a grammage of from 120 to 195 grams, preferably of about 145-160 grams, and a Gurley of from 5,0 s/100 ml to 30,0 s/100 ml.
[0034] The gelatin is a gelatin of natural origin, such as technical grade gelatin, preferably in grains with a granulometry of between 4 and 16 mesh.
[0035] Preferably the crosslinking agent is selected form the group comprising formaldehyde, glutaric dialdehyde, methanol, glioxal, ethylene glycol, and mixtures thereof.
[0036] The biodegradable material according to the present invention comprises pure cellulose pulp, or paper from

pure cellulose pulp, in an amount of at least 70%, preferably of from 70 to 90%, more preferably of from 75 to 85%, even more preferably of from 80 to 83%.

[0037] The biodegradable material according to the present invention comprises gelatin in an amount of from 5 to 20%, more preferably of from 7 to 15%, even more preferably of from 9 to 12%.

[0038] The biodegradable material according to the present invention comprises a crosslinking agent in an amount within the limits allowed for materials in contact with human skin, i.e. below 75 ppm.

[0039] Preferably, the biodegradable material according to the present invention has an amount of residual humidity of less than 10%, preferably between 8 and 9%.

[0040] In embodiments of the present invention, the biodegradable material further comprises additives such as colorants, dyes, polishing agents, gloss agents, hardening agents, fillers, binders, etc.

[0041] Preferably, the biodegradable material according to the present invention has a thickness of from 0.5 mm to 10 mm, preferably or from 1 to 8, even more preferably of from 3 to 8 mm.

[0042] The biodegradable composite material according to the present invention is extremely compact and is dimensionally stable, characterized by excellent mechanical properties. It is very versatile and can undergo multiple processes as regards both cutting, shaping, and finishing, such as: blade cutting, die cutting, laser, cold or hot shaping, grinding, tumbling, etc..

[0043] A second aspect of the present invention relates to a process to obtain the biodegradable composite material disclosed above, the process comprising the steps of:

i) providing one or more sheet of paper made of pure cellulose pulp;
ii) laminating the one or more sheet of paper together with gelatin and optionally one or more additives;
iii) hanging the laminated sheet obtained in step ii) until hardening of the gelatin;
iv) crosslinking the laminated sheet in a crosslinking bath;
v) drying the crosslinked laminated sheet; and
vi) pressing the sheet.

[0044] Advantageously, the process according to the present invention may comprise additional steps, that can be carried out before or after any of the steps i)-vi) above, such as a cutting step, a sanding step, a polishing step, a dying step, and any other processing known to those expert in the field.

[0045] The process according to the present invention can be carried out using machines and conditions known to those expert in the field.

[0046] In the lamination step ii) of the process according to the present invention, a sheet of paper is placed in a tank together with the gelatin, water and optionally additives.

[0047] Preferably, the water is at a pH of from 5.5 to 7.

[0048] Preferably, the gelatin is in a concentration of from 5 to 20%, more preferably of from 7.5 to 15%, even more preferably of about 11%.

[0049] The lamination step is preferably carried out at a temperature of from 35°C to 55°C, preferably 40-45°C, for a period of 20 to 600 seconds.

[0050] Subsequently, in the step iii) of the process, the laminated sheet of paper is hung at a temperature of from 2°C to 18°C until complete hardening of the gelatin, preferably for a period of 2 to 30 minutes.

[0051] The crosslinking step iv) of the process according to the present invention, is carried out in a bath with an aqueous solution of a crosslinking agent in which the laminated sheet obtained in step iii) is placed for a period of 20 to 600 seconds.

[0052] Then, in the drying step v) of the process, the material is placed in a dryer at a temperature of from 25°C to 40°C, preferably of 28°-34°C, to reduce the residual humidity to about 6-12%, preferably 8-9%, generally for a period of from 2 to 18 days.

[0053] Finally, in step vi), the material obtained is placed in an ironing press at a temperature of from 50°C to 85°C, generally for a period of from 2 to 30 minutes.

[0054] Preferably, the pressing step is carried out until the material becomes completely flat.

[0055] Advantageously, the biodegradable composite material according to the present invention can be used in a wide range of fields for the production of different kinds of articles, such as eyewear, footwear, watches, buckles, buttons, heels, covers for phones and tablets, fashion accessories, toys, furnishings and furnishing accessories, jewellery, costume jewellery, packaging, technical sports equipment, click frames, industrial frames, knives, auto motive, and musical instruments.

[0056] Thus in a third aspect, the present invention relates to the use of the biodegradable composite material disclosed above in the production of eyewear articles.

[0057] Advantageously, eyewear articles can be obtained from the biodegradable composite material of the present invention with the processes commonly known in the field.

[0058] For example, a sheet of the material obtained as disclosed in detail above can be wet with water in order to render it more easily processed, then subjected to a hot press step at a temperature of 60°-180°C, shaped as desired and let to cool before cutting it according to the technical drawing of the eyewear to obtain. The article can then be subjected to any other step known to those skilled in the art, such as polishing, dying, sanding, tumbling, etc..

[0059] In a fourth aspect, the present invention relates to the use of the biodegradable composite material disclosed above in the production of footwear articles, in particular shoe insoles.

[0060] Advantageously, shoe insoles may be made up of a tri-layer composition as follows: a about 1.0 mm thick layer of the composite material according to the present invention in the rear / upper part of the insole (towards the foot) generally called trunk, a layer of commonly used flexible cellulosic material for the entire length of the insoles (up to the tip) in the middle, and a about 2.0 mm thick layer of the composite material according to the present invention upwards in the lower part of the trunk.

[0061] The following examples are meant to further illustrate the present invention, without limiting it.

EXPERIMENTAL SECTION

Biodegradation test

[0062] Samples of the composite material according to the present invention were buried in the soil for different time periods and exposed to the test soil according to standard ISO 11721-2:2003.

[0063] The samples were cut into the form of standard dumbbell-shaped test specimens for the determination of the tensile properties of composite materials, according to ASTM D638M-84.

[0064] The samples were put in soil into beakers of 20L capacity, the soil used was stabilized and matured compost obtained by organic fractions with a particle size of 300-800 μm. The content of volatile compounds was of 7% (according to wet mass). The water content of the test soil was 55-65% of the maximum moisture retention capacity and the pH of the test soil was in the range of 5.0 to 7.5, with an average temperature of 21.5°C.

[0065] The degradation has been analysed by visual inspection of the samples, as well as instrumental analysis, in particular thermogravimetric analysis (TGA).

[0066] Samples of 1 mm thickness were significantly degraded already after 4 weeks, while samples of 3 mm thickness were significantly degraded after 8 weeks. In all cases, complete degradation was reached at 12 weeks.

Mechanical properties

[0067] Results of mechanical tests carried out on samples of the composite material according to the present invention are summarised in Table 1 below.

Table 1

Sample thickness (mm)	**0.6**	**1.0**	**1.6**	**3.0**
Density (gr/cm^3)	1.17	1.17	1.29	1.28
Longitudinal tensile strength (Kg/mm^2)	7.6	9.3	9.8	9.5
Transversal tensile strength (Kg/mm^2)	5.4	6.6	7.1	6.7
Longitudinal extension (%)	8	9	14	11
Transversal extension (%)	11	14	19	19

Claims

1. A biodegradable composite material comprising:

   a) pure cellulose pulp;
   b) gelatin; and
   c) a crosslinking agent.

2. The biodegradable composite material according to claim 1, wherein the pure cellulose pulp is in form of a sheet of paper.

3. The biodegradable composite material according to claim 2, wherein the paper is a sheet of absorbent and optionally coloured paper.

4. The biodegradable composite material according to any one of the preceding claims comprising pure cellulose pulp, or paper from pure cellulose pulp, in an amount of at least 70%.

5. The biodegradable composite material according to any one of the preceding claims, wherein said gelatin is in an amount of from 5 to 20%.

6. The biodegradable composite material according to any one of the preceding claims, wherein said crosslinking agent is in an amount below 75 ppm.

7. The biodegradable composite material according to any one of the preceding claims, wherein the residual humidity is of less than 10%.

8. A process to obtain a biodegradable composite material, the process comprising the steps of:

i) providing one or more sheet of paper made of pure cellulose pulp;
ii) laminating the one or more sheet of paper together with gelatin and optionally one or more additives;
iii) hanging the laminated sheet obtained in step ii) until hardening of the gelatin;
iv) crosslinking the laminated sheet in a crosslinking bath;
v) drying the crosslinked laminated sheet; and
vi) pressing the sheet.

9. The process according to claim 8, wherein the step ii) is carried out at a temperature of from 35°C to 55°C for a period of 20 to 600 seconds.

10. The process according to claims 8-9, wherein the step iii) is carried out at a temperature of from 2°C to 18°C until complete hardening of the gelatin.

11. The process according to claims 8-10, wherein the step iv) is carried out in a bath containing an aqueous solution of a crosslinking agent for a period of 20 to 600 seconds.

12. The process according to claims 8-11, wherein the step v) is carried out at a temperature of from 25°C to 40°C for a period of from 2 to 18 days.

13. The process according to claims 8-12, wherein the step vi) is carried out at a temperature of from 50°C to 85°C for a period of from 2 to 30 minutes.

14. Use of the biodegradable composite material as defined in claims 1-7 in the production of eyewear articles.

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EUROPEAN SEARCH REPORT

Application Number
EP 20 18 9287

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	* page 1, line 68 - line 82 * * page 1, line 106 - page 2, line 130 * * figures 1, 2, 4, 5 * * page 3, line 15 - line 71 * -----	14	D21H19/50 D21H21/16 D21H17/06
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Y	* page 1, paragraph 1 - paragraph 3 * * page 2, paragraph 4 - page 3, paragraph 2 * -----	8	
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Y	* page 1, line 1 - line 37 * * claims 1-3; example 1 * -----	8	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	12 January 2021	Billet, Aina

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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