



(51) International Patent Classification:

C08G 63/08 (2006.01) *C08G 101/00* (2006.01)
C08J 9/18 (2006.01) *C08G 63/90* (2006.01)
B01D 11/02 (2006.01)

(21) International Application Number:

PCT/SE2011/050394

(22) International Filing Date:

4 April 2011 (04.04.2011)

(25) Filing Language:

English

(26) Publication Language:

English

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

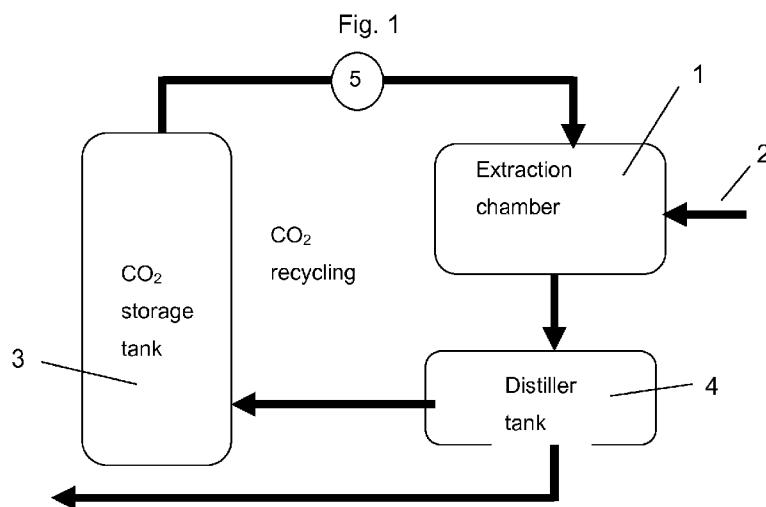
Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))

(54) Title: HIGHLY PURIFIED MATERIAL COMPRISING EXPANDED POLYLACTID ACID RESIN



(57) Abstract: A material comprising expanded polylactic acid (PLA) resin which comprises a total amount of extractives of 0-0,035 % by weight, calculated on the total weight of PLA, said extractives being substances that can be extracted from PLA with diethyl ether as extraction medium according to the method of determination of extractives in PLA as described in the description of this patent application.

Highly purified material comprising expanded polylactid acid resin

TECHNICAL FIELD

- 5 The present invention relates to a material comprising expanded polylactic acid (PLA) resin.

BACKGROUND OF THE INVENTION

- 10 There is an increasing demand for polylactic acid (PLA) resin foams for use in packaging applications, since such polymers are bio-derived and bio-degradable. These foams have good performance and are economic, and are often preferred over petroleum-derived foams such as polystyrene foam, due to increasing environmental awareness and consumer demands.

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- Carbon dioxide is a useful blowing agent for PLA foams, being an environmentally friendly blowing agent without any ozone depletion potential. Some processes that use carbon dioxide as a blowing agent involve foaming and moulding, and PLA resin beads impregnated with carbon dioxide may then be used. Such processes
20 generally involve impregnating the beads with gaseous or supercritical CO₂, pre-expanding the impregnated beads, resting and sometimes treating the pre-expanded beads, before re-impregnating them with more CO₂ or another blowing agent and further expanding and fusing them in a mould, see e.g. EP 1 378 538. Another known process involving impregnation of PLA resin beads with carbon
25 dioxide is disclosed in WO 2008/093284.

- In some packaging applications, in particular in food or medical grade packaging applications, it is important that the packaging foam material does not contain any undesired substances, to avoid any possible transfer of extractives from the
30 packaging foam to the package contents.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a foamed PLA material with very high purity useful for packaging application.

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The present invention thus relates to a material comprising expanded polylactic acid (PLA) resin that comprises a total amount of extractives of 0-0,035 % by weight, calculated on the total weight of PLA, said extractives being substances that can be extracted from PLA with diethyl ether as extraction medium according to the method
10 of determination of extractives in PLA as described in the description of this patent application. This material can be used for example in packaging applications, especially for packaging of foodstuff. Said extractives may comprise oligomers of lactic acid of which lactide is 0-0,020 % by weight, calculated on the total weight of PLA.

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The above material is obtainable by a process in which PLA beads are subject to a liquid CO₂ treatment, which involves impregnation and extraction with liquid CO₂.

The process may preferably comprise the following steps: subjecting PLA resin
20 beads to a liquid CO₂ treatment, which involves impregnation and extraction comprising at least one impregnation and extraction step, in which the PLA resin beads are brought into contact with 0,01-1000 kg pure liquid CO₂ /kg PLA, preferably 2-20 kg liquid CO₂ /kg PLA, in a reactor for a predetermined time period, at a temperature and pressure that prevents the beads from sticking together and
25 foaming; and a portion of the liquid CO₂ is drained from the PLA beads after completion of the impregnation and extraction step, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, while leaving at least 0,01 kg liquid CO₂/kg PLA, preferably 0,01-1 kg liquid CO₂/kg PLA in the reactor containing the PLA resin beads; followed by evacuation of CO₂
30 gas from the reactor so as to decrease the pressure to ambient pressure, whereby the remaining liquid CO₂ is evaporated, thereby decreasing the temperature so as to prevent foaming at ambient pressure; conditioning the impregnated and extracted PLA beads at a temperature and a pressure that prevents the beads from sticking together and foaming, to reduce the CO₂ content to 5-18 % by weight; increasing the

temperature to a pre-expansion temperature, so as to pre-expand the PLA beads; and increasing the temperature to a fusing temperature to allow moulding of the PLA beads.

- 5 The liquid CO₂ treatment involving impregnation and extraction may alternatively comprise impregnation and extraction in a continuous process, wherein PLA resin beads are held in a reactor, in which the PLA resin beads are brought into contact with liquid CO₂ for a predetermined time period, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, and pure liquid CO₂ is continuously fed at one end of the reactor, and is drained from another end of the reactor; and wherein a portion of the liquid CO₂ is drained from the PLA beads upon completion of the impregnation and extraction, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, while leaving at least 0,01 kg liquid CO₂/kg PLA, preferably 0,01-1 kg liquid CO₂/kg PLA in the reactor containing the PLA resin beads; followed by evacuation of CO₂ gas from the reactor so as to decrease the pressure to ambient pressure, whereby the remaining liquid CO₂ is evaporated, thereby decreasing the temperature so as to prevent foaming at ambient pressure.
- 20 By means of draining the liquid CO₂ from the reactor, instead of evaporating the CO₂, extractable substances can conveniently be removed from the PLA material, since such substances will be present in the liquid CO₂. In the method, the impregnation and extraction step may preferably comprise 2 or more successive steps, wherein the PLA resin beads are brought into contact with pure liquid CO₂ in each successive step for a predetermined time period at a temperature and pressure that prevents the beads from sticking together and foaming, and wherein at least a portion of the liquid CO₂ is drained from the PLA beads at the end of each step, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form.
- 30 The PLA beads are impregnated and extracted with liquid CO₂ advantageously at a pressure of above 1 MPa, preferably 4,5-8 MPa. The PLA beads are impregnated and extracted with liquid CO₂ at a temperature suitably above -50 °C, but below the

glass transition temperature of PLA at the pressure used, preferably -10 to +15 °C, for 10 to 240 minutes, preferably 30 to 90 minutes.

5 The PLA beads are impregnated and extracted with liquid CO₂ that may contain additives such as coloring agents, anti-static agents, flame retardants, adhesives.

The PLA resin beads may comprise 50-100% by weight of PLA, preferably 80-100% by weight. The PLA is preferably amorphous PLA. If desired the material of the invention may further comprise one or more of fillers, reinforcing agents, coloring
10 agents.

DRAWINGS

Figure 1 shows a schematic view of a system, useful for performing impregnation
15 and purification of PLA resin beads.

Figure 2 shows a schematic view of a system, similar to the one of Figure 1, and which includes a pump.

DETAILED DESCRIPTION

20 The material of the present invention is an expanded polylactic acid (PLA) resin having a total content of extractives of 0-0,035 % by weight, calculated on the total weight of PLA, said extractives being substances that can be extracted from PLA with diethyl ether as extraction medium according to the method of determination of
25 extractives in PLA as described in the description of this patent application. The extractives comprise oligomers of lactic acid, of which lactide is 0-0,020 % by weight, calculated on the total weight of PLA.

The material may be obtained by a process utilizing CO₂ as blowing agent, and in
30 which PLA beads are subject to an a liquid CO₂ treatment, which involves impregnation and extraction with liquid CO₂, which preferably includes at least one impregnation and extraction step, and draining of the CO₂ in liquid form. The process may further include conditioning and pre-expanding the PLA beads, before

increasing the temperature to a fusing temperature to allow moulding of the PLA beads.

5 In the present context the term "extractables" refers to substances that are extracted from PLA during impregnation with carbon dioxide.

The term "extractives" refers to substances that can be extracted from PLA with diethyl ether as extraction medium according to the method of determination of extractives in PLA as described in the description of this patent application.

10

Additives or coating materials can be added to the PLA resin beads during impregnation and extraction. Accordingly, by means of the present invention various functionalities can effectively be added to the material, since impregnation, extraction and addition of additives can be performed in one process, without any

15 need for additional process steps.

Polylactic acid or PLA is a polymer or copolymer comprising lactic acid monomer units. For the purposes of the present invention references to polylactic acid includes crystalline and amorphous polymers and mixtures thereof. The PLA resin

20 beads may comprise about 50-100 % by weight of PLA. The PLA may comprise amorphous PLA or a blend of amorphous PLA and crystalline PLA. Preferred blends comprise at least about 50 % by weight of amorphous PLA and about 0-50 % by weight of crystalline PLA. The lactic acid in the resin beads may comprise one or more lactic acid isomers including L-lactic acid, D-lactic acid or DL-lactic acid. The

25 lactic acid is preferably L-lactic acid. The PLA may be produced industrially by polymerisation of lactic acid obtained by the bacterial fermentation of biomass such as beet, sugarcane, cornstarch or milk products.

Commercially available PLA resin beads can be impregnated without any pre-

30 treatment using liquid CO₂. Amorphous, crystalline, and amorphous-crystalline blends may be used but results with highly crystalline grades are sometimes of lesser quality at the preferred pressure and temperature ranges. Reference to resin "beads" is intended to mean the crude resin material (often in the form of pellets) obtained from manufacturers and the terms beads, granules and pellets may be

used interchangeably. The beads may also be in the form of fibres. Beads may be resized by extrusion and pelletizing of the commercially available material using known techniques.

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The present invention is based on the use of liquid CO₂ for the impregnation of PLA. In liquid CO₂ impregnation the PLA beads have little tendency to stick to each other, especially when using sub-cooled liquid CO₂, i.e. liquid CO₂ at higher pressure than equilibrium pressure at a given temperature.

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Liquid CO₂ impregnation requires moderate temperature and pressure. The impregnated beads do not stick together and after releasing the pressure from the impregnation reactor they can be handled as a bulk commodity.

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In the method of impregnating and purifying polylactic acid (PLA) according to the present invention PLA resin beads are subjected to a liquid CO₂ treatment, which involves impregnation and extraction. The liquid CO₂ treatment comprises at least one impregnation and extraction step, in which the PLA resin beads are brought into contact with 0,01-1000 kg pure liquid CO₂/kg PLA in a reactor for a predetermined time period, at a temperature and pressure that prevents the beads from sticking together and foaming. During the impregnation and extraction step, CO₂ is impregnated into the PLA resin beads, and at the same time extractable substances are dissolved into the liquid CO₂. After completion of the impregnation and extraction step a portion of the liquid CO₂ is drained from the PLA beads, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, while leaving at least 0,01 kg liquid CO₂/kg PLA, preferably 0,01-1 kg liquid CO₂/kg PLA in the reactor containing the PLA resin beads. Thereafter, evacuation of CO₂ gas from the reactor is performed so as to decrease the pressure to ambient pressure, whereby the remaining liquid CO₂ is evaporated, thereby decreasing the temperature so as to prevent foaming at ambient pressure.

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It has been found that liquid CO₂ is effective in extracting undesired substances from the PLA. By ensuring that the CO₂ is drained from the reactor in liquid form, the

substances extracted from the PLA beads are effectively removed. By leaving a small portion of the liquid CO₂ in the reactor after draining it can thus be ensured that the temperature of the beads is kept low to prevent foaming when the pressure is decreased to ambient pressure at the end of the process.

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The impregnation and extraction step preferably comprises 2 or more successive steps, wherein the PLA resin beads are brought into contact with pure liquid CO₂ in each successive step for a predetermined time period at a temperature and pressure that prevents the beads from sticking together and foaming. In the first of these impregnation and extraction steps, a part of the total impregnation is obtained. The following steps continue the impregnation and the PLA resin beads are extracted with liquid CO₂, each time further lowering the content of extractable substances in the PLA resin beads. At the end of each successive step at least a portion of the liquid CO₂ is drained from the PLA beads, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form. By draining away the liquid CO₂ after each successive step, substances extracted into the liquid CO₂ are removed from the PLA beads, and pure liquid CO₂ is then added so that the next successive impregnation and extraction step can be carried out. Thus, the content of extractable undesired substances is successively reduced until a desired purity has been reached. If desired, the first impregnation and extraction step be continued until the impregnation is completed, and extraction steps are then performed subsequently. The total treatment time will then be longer than necessary from a removal of extractives point of view, but may be desired for other reasons, such as addition of additives to the PLA.

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The liquid CO₂ treatment, involving impregnation and extraction treatment may be carried out in a batch process or in a continuous process.

In a batch process the PLA resin beads are held in a reactor to which an amount of liquid CO₂ is added, and after a certain time period the liquid CO₂ is drained from the reactor, while substantially maintaining the pressure. A new amount of pure liquid CO₂ is then added to the reactor at the same pressure. After completion of the last impregnation and extraction step, a portion of the liquid CO₂ is drained from the PLA beads, and a smaller amount of liquid CO₂ is left in the reactor. As said above, the

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remaining liquid CO₂ is evaporated when CO₂ gas is evacuated from the reactor and the temperature is thereby decreased so as to prevent sticking together and foaming at ambient pressure. The PLA beads may be placed in a rotating drum during the impregnation and extraction step. When gas is evacuated from the drum, the cold liquid CO₂ is distributed evenly in the PLA material, which gives a thorough and even cooling of the PLA beads.

When carrying out the liquid CO₂ treatment in a continuous process the PLA resin beads are held in a reactor, in which the PLA resin beads are brought into contact with liquid CO₂ for a predetermined time period, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form. Pure liquid CO₂ is continuously fed at one end of the reactor, and the liquid CO₂ is continuously drained from another end of the reactor, so that the liquid CO₂ flows through the reactor. The reactor is dimensioned so that the time of contact between the PLA resin beads and the liquid CO₂ is sufficient to achieve the desired impregnation and extraction. Upon completion of the impregnation and extraction a portion of the liquid CO₂ is drained from the PLA beads, and a smaller amount of liquid CO₂ is left in the reactor, and is evaporated during evacuation of CO₂ gas from the reactor whereby the temperature is decreased. Also in a continuous process, the PLA beads may be placed in a rotating drum during the impregnation and extraction step. When gas is evacuated from the drum, the cold liquid CO₂ is distributed evenly in the PLA material, which gives a thorough and even cooling of the PLA beads.

The pressure and temperature during the impregnation and extraction are chosen so as to prevent the PLA resin beads from sticking together and foaming, and to provide the CO₂ in liquid phase. The impregnation and extraction may be performed at a pressure above 1 MPa, to ensure that the CO₂ can be present in liquid phase in a workable temperature range, and to avoid formation of solid CO₂. More preferably the pressure during impregnation and extraction is 4,5-8 MPa, so as to provide conditions under which CO₂ can be in liquid phase at temperatures around 0 °C, and which leads to reasonable treatment time. The temperature of the impregnation and the extraction is advantageously performed at above -50 °C to ensure liquid phase CO₂ during the treatment, but below the glass transition temperature of PLA at the CO₂ pressure used to avoid the PLA beads from sticking together. The

temperature of the impregnation and the extraction is more preferably -10 to +15 °C, in order to achieve reasonable treatment time and ensures that CO₂ is liquid at the pressure chosen in the range of 4,5-8 MPa. The total amount of liquid CO₂ used in the liquid CO₂ treatment is advantageously in the range of 2-20 kg CO₂/kg PLA.

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The liquid CO₂ drained from the impregnation and extraction may be transferred to a recovery equipment, in which the CO₂ is recovered by separation of extractives from the CO₂ by distillation. The recovered CO₂ may then be recycled to an impregnation and extraction step of PLA resin beads. Accordingly, the CO₂ can be recirculated in a closed circuit, which is advantageous from both an environmental and an economical point of view.

In the impregnation and extraction step the PLA resin beads are placed the reactor (a pressure vessel) under impregnation pressure and temperature, and liquid CO₂ is then added to the reactor until the PLA resin beads are at least partially submerged, or if a rotating drum is used, until the amount of liquid CO₂ is sufficient to wet the PLA beads. The PLA resin beads are left in contact with the liquid CO₂ for a predetermined time, preferably 10 to 240 minutes, to achieve sufficient CO₂ content and at the same time avoid unnecessary treatment time in order to save costs.

20

Achieving equilibrium takes approximately 30-90 minutes when using *PLA Ingeo 4060DTM* (NatureWorks LLC, USA), a commonly available commercial amorphous grade but may take longer or shorter depending on the size of the beads and the grade and composition of the beads. After substantially achieving equilibrium at the preferred temperature and pressure ranges, the beads comprise about 18-35 % CO₂ by weight. When using PLA Ingeo 4060DTM and CO₂ at 6 MPa and 10 °C equilibrium results in the beads having around 30 % by weight CO₂.

After the impregnation and extraction of the liquid CO₂ treatment, the impregnated and extracted PLA resin beads are stored in a freezer until CO₂ is desorbed and dispersed evenly throughout the impregnated bead, and leads to even foaming and good cell structure.

30

- Pre-expansion is conducted at different temperatures and for different times according to the individual foaming characteristics of impregnated beads which in turn depends on blend and CO₂ content and the differences in minimum foaming temperatures that are the consequence of these factors. Preferably the pre-expansion is conducted at temperatures ranging from 50 °C to 90 °C at ambient pressure and more preferably commercially available amorphous PLA beads having been impregnated to about 30 % by weight CO₂, refrigerated until the CO₂ percentage reduces to 5-18 %, and pre-expanded at 50-75 °C.
- 10 The pre-expanded beads are promptly transferred into a mould and steam (or other heating providing a temperature higher than the pre-expansion temperature) is applied to further expand the beads and fuse them together in the mould. A vacuum may also be applied before cooling and removal from the mould. The mould is preferably adapted to produce a moulded product including moulded blocks and
- 15 shaped moulded products, especially blocks adapted to form packing material and shaped moulded products in the form of packaging material or convenience items such as packaging and storage products. Preferred convenience items include containers such as clamshell containers, pots, boxes, bowls, cups, plates and trays.
- 20 A person skilled in the art will be aware that the absorption percentages, temperatures and pressures can be manipulated relative to each other at the different stages of the method of the invention to achieve substantially the same result with the major limiting factors being the preference for keeping the CO₂ weight percentage within or close to the optimum range of percentages, avoiding the
- 25 excessive formation of solid CO₂ in the pressure vessel, and retaining control of the foaming steps.

METHOD OF DETERMINATION OF EXTRACTIVES IN PLA

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The material of the present invention is an expanded polylactic acid (PLA) resin which comprises a total amount of extractives of 0-0,035 % by weight. The total amount of extractives is calculated based on the total weight of PLA, said

extractives being substances that can be extracted from PLA with diethyl ether as extraction medium.

5 The total amount of extractives is determined by means of the following method, which accordingly is a method used to describe the quantitative determination of extractable compounds in PLA (polylactic acid). 2,6-diethylnaphthalene (DiEN) is used as internal standard (ISTD). No correction is made to compensate for the individual extractives detector responses in relation to the internal standard. In the determination method standard solutions are prepared, said solutions being an
10 internal standard stock solution (ISTD0) and an internal standard working solution (ISTD1).

Preparation of internal standard solution - stock solution, ISTD 0

15 The stock solution is prepared by dissolving 0.04 to 0.05 g of DiEN in 50 mL of acetone (99.9%). The concentration of DiEN will be approximately 0.9 g/L. The true concentration is calculated.

Preparation of internal standard solution - working solution, ISTD 1

20 Dilute 5 mL of stock solution to 25 mL with acetone (99.9%). The concentration of DiEN will be approximately 180 mg/L. The true concentration is calculated.

Sample preparation and extraction of extractives

25 PLA beads are ground in a centrifugal mill (Retsch ZM1) under cooling with liquid nitrogen. The sample is ground to a size of 0.5 mm. An amount of approximately 1 g ground sample is put into a round bottom flask for reflux and 100 mL of diethyl ether is added (the true amount of PLA sample is noted). A few anti-bumping granules are put into the round bottom flask. Before starting the reflux, the sample is standing for 5 minutes. The reflux is performed for 1 hour and the diethyl ether is thereafter collected and reduced to 10 mL and 10 μ L of ISTD 1 is added.

30

Analysis of extractives. The extractives were analysed by Thermo Finnigan Trace gas chromatograph-mass spectrometer (GC-MS)

Instrument parameters and settings

Column: Zebron zb-5MSi, 30 m, id 0.25 mm, thickness 0.25 µm.

Column temperature: 80°C for 1 min and then 10°C/min until 350°C is reached and finally, 350°C for 8 min

- 5 Carrier gas: 0.7 mL/min of helium at a constant flow

Inlet temperature: 250°C

Splitless injection for 1 minute, where the whole sample is let into to the column.

Transfer temperature (temperature between GC and MS): 320°C

Temperature in ion source: 200°C

- 10 MS mode: Total ion current (TIC)

Calculations

The concentration of extractives (Ci) in sample extract is calculated as follows

- 15 $C_i \text{ (mg/L)} = C_{is} * (A_i/A_{is})$

C_{is} = concentration of ISTD in sample extract (mg/L)

A_i = peak area of extractives

A_{is} = peak area of ISTD

- 20

Amount of extractives in PLA (C_p) is calculated

$$C_p \text{ (mg/kg)} = C_i * V / m$$

- 25 V = volume of sample extract (L)

m = dry content of PLA (kg)

Gas analysis performed for Example 2 below

- 30 The followed procedure was applied for gas analysis (example 2). 5-hexen-1-ol was used as internal standard, and a working solution was prepared by dissolving approximately 1 gram of 5-hexen-1-ol in 250 mL methanol. The true concentration was calculated. From the working solution 2 µL was injected into the gas-tight bag used in example 2. The bag was conditioned in room temperature for 1 hour before

analysis. Solid phase microextraction (SPME) supplied with Carboxen 0,75 µm absorption phase was inserted into the gas-tight bag. After the SPME phase has been exposed to the sampled gas for 30 minutes it was transferred to the GC-MS for analysis.

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Instrument parameters and settings:

Column: Zebron zb-624, 30 m, id 0.25 mm, film thickness 1.40 µm

Column temperature: 40°C for 4 min and then 10°C/min until 250°C followed by 250°C for 6 min

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Carrier gas: 1 mL/min of helium at a constant flow

Inlet temperature: 240°C

Splittless injection for 1 minute

Transfer temperature (temperature between GC and MS): 240°C

Temperature in ion source: 200°C

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MS mode: Total ion current (TIC)

EXAMPLES

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The invention will now be illustrated in non-limiting ways by reference to the following examples of impregnation of PLA resin beads. In the examples below PLA beads were used without additional treatment, i.e. as commercially available.

Example 1 - analysis of reference sample

25

PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was extracted with diethyl ether according to the above described procedure for determining extractives in PLA, and analysed with GC-MS regarding extractable low molecular compounds. Among detected extractives, lactide was dominating followed by other lactic acid oligomers. The result is shown in Table 1.

30

Example 2 - liquid CO₂ drained off

The aim of Example 2 was to determine extractable substances extracted from the PLA, which may not have been detected by the extraction with diethylether.

PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was placed in an autoclave which was filled with liquid carbon dioxide and pressurised to 60 bars at 0-2 °C. The ratio by weight between PLA and carbon dioxide was 1/10. After four hours, liquid CO₂ was drained off and CO₂ was collected in a gas-tight bag (1L, Tedlar, SKC). The gas-tight bag was carefully cleaned and checked for background before sample collection. The CO₂ liquid level was allowed to decrease until the ratio by weight between PLA and CO₂ was 1/2. The remaining liquid CO₂ was evaporated during the evacuation of CO₂, thereby decreasing the temperature below T_g for PLA impregnated with CO₂.

10

The impregnated beads were stored at -19 °C over night and thereafter pre-expanded in hot water. A mould was filled with pre-expanded beads and moulded by applying steam mixed with air.

15 Extractable substances in the gas phase were analysed according to the gas analysis procedure as described above. Lactide was dominating followed by other lactic acid oligomers.

Example 3 - liquid phase CO₂ removed by evaporation

20 The aim of Example 3 was to determine substances extracted from the PLA, which may not have been detected by the extraction with diethyl ether, by a method different to the one used in Example 2.

25 PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was placed in an autoclave which was filled with liquid carbon dioxide (PLA/CO₂; 1/10 by weight) and pressurised to 50 bars at 0 °C. After 80 minutes, the liquid phase CO₂ was removed by evaporation and the pressure released. Substances released from PLA during impregnation were collected from the reactor chamber by extraction of the reactor with acetone, and analysed with GC-MS.

30 Among detected extractable substances, lactide was dominating followed by other lactic acid oligomers.

Example 4 – liquid CO₂ drained off (1 impregnation and extraction step)

PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was placed in an autoclave and treated with liquid carbon dioxide (PLA/CO₂, 1/100 by weight) at 53 bars at 0°C for 90 minutes. The liquid phase was drained off until the ratio by weight between PLA and CO₂ was 1/20 and the remaining liquid CO₂ was evaporated during evacuation of CO₂ gas in order to lower the temperature below T_g for CO₂ impregnated PLA.

The remaining low molecular substances in the purified PLA was determined by extraction with diethyl ether according to the above described method and analysed with GC-MS. Detected substances were lactide and other lactic acid oligomers. The result is shown in Table 1.

The impregnated beads were also stored, pre-expanded, foamed and moulded according to the method described in example 2.

Example 5 - liquid CO₂ drained off (2 impregnation and extraction steps)

PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was placed in an autoclave and treated with liquid carbon dioxide (PLA/CO₂, 1/100 by weight) at 53 bars at 0 °C for 90 minutes. The liquid phase was drained off until the ratio by weight between PLA and CO₂ was 1/20. A second treatment in which pure liquid CO₂ was added at 53 bars was done at 53 bars, -5-0 °C for 90 minutes. The liquid phase was drained off until the ratio by weight between PLA and CO₂ was 1/20 and the remaining liquid CO₂ was evaporated during evacuation of CO₂ gas in order to lower the temperature below T_g for CO₂ impregnated PLA. .

The remaining low molecular substances in the purified PLA were determined by extraction with diethyl ether according to the described method and analysed with GC-MS. Detected substances was lactide and other lactic acid oligomers. The result is shown in Table 1.

Example 6 - liquid CO₂ drained off (3 impregnation and extraction steps)

PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was placed in an autoclave. PLA was treated with liquid carbon dioxide (PLA/CO₂, 1/100 by

weight) at 53 bars, 0 °C for 90 minutes. The liquid phase was drained off until the ratio by weight between PLA and CO₂ was 1/20. The procedure was repeated with pure liquid CO₂ two more times. The liquid phase was drained off until the ratio by weight between PLA and CO₂ was 1/20 and the remaining liquid CO₂ was
 5 evaporated during evacuation of CO₂ gas in order to lower the temperature below T_g for CO₂ impregnated PLA. The result is shown in Table 1.

The remaining low molecular substances in the purified PLA were determined by extraction with diethyl ether according to the described method and analysed with
 10 GC-MS. Detected substances were lactide and other lactic acid oligomers.

Example 7 - liquid CO₂ drained off (4 impregnation and extraction steps)

PLA Ingeo 4060DTM (NatureWorks LLC, USA) as commercially available was placed in an autoclave. PLA was treated with liquid carbon dioxide (PLA/CO₂, 1/100 by weight) at 53 bars, 0 °C for 90 minutes. The liquid phase was drained off until the
 15 ratio by weight between PLA and CO₂ was 1/20. The procedure was repeated with pure liquid CO₂ three times. The liquid phase was drained off until the ratio by weight between PLA and CO₂ was 1/20 and the remaining liquid CO₂ was evaporated during evacuation of CO₂ gas in order to lower the temperature below
 20 T_g for CO₂ impregnated PLA. The result is shown in Table 1.

The remaining low molecular substances in the purified PLA were determined by extraction with diethyl ether according to the described method and analysed with
 25 GC-MS. Detected substances were lactide and other lactic acid oligomers.

The remaining extractives in PLA beads after impregnation and extraction in Examples 1 and 4-7 are shown in Table 1.

Table 1

Example	Number of impregnation and extraction steps	Total amount of extractives* % by weight	Lactide % by weight	Others* % by weight
1	0	0,043	0,026	0,017
4	1	0,031	0,017	0,014
5	2	0,027	0,014	0,013

6	3	0,013	0,005	0,008
7	4	0,013	0,006	0,007

* dominating substances were lactic acid oligomers.

The results shown in Table 1 indicate that draining off the liquid CO₂ in liquid phase after the impregnating and extraction step, is very effective to remove extractable substances, and that repeated impregnating and extraction steps further enhances this effect.

The results in Table 1 shows that three impregnation and extraction steps may be sufficient to decrease the amount of extractives to a reasonable level, which is considerably lower than the initial levels in the PLA material.

Example 8 -dying

PLA Nature Works Ingeo 4060D, re-extruded to beads with the appropriate size of 1,5 x1,5 mm, was placed in an autoclave together with a cotton bag containing, the colouring agent 1,4-diamino anthraquinone (Sigma-Aldrich) 0,4% by weight PLA . Liquid CO₂ was added at 47 bars and 0-1 °C until the ratio by weight between PLA and CO₂ was 1/10 . After 90 minutes treatment liquid CO₂ was drained off until the ratio by weight between PLA and CO₂ was 1/2, and the remaining liquid CO₂ was evaporated during evacuation of CO₂ gas in order to lower the temperature below T_g for CO₂ impregnated PLA. Purple PLA pellets were collected from the reactor. After storage at -19 °C, the impregnated beads were foamed and moulded according to the method described in example 2. The foam was light purple.

EXEMPLIFYING EMBODIMENTS

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Figure 1 shows a schematic view of a system for performing a process including the method of impregnating and purifying PLA resin.

In the start-up phase of the process an extraction chamber 1 is loaded with PLA resin beads through an inlet 2. The extraction chamber may be a reactor in the form of an autoclave or any other vessel that may be pressurised. Air present in the extraction chamber 1 is evacuated by means of a vacuum pump. During start-up of the process, CO₂ gas is supplied to the extraction chamber 1 from a CO₂ storage

tank 3, so as to pressurize the extraction chamber 1 to approximately 6 MPa with CO₂ gas. Sensors in the system monitor the level of CO₂ in the storage tank 3, and additional CO₂ is added to the extraction chamber 1 from a storage tank 3 from an external source (not shown in figure 1) if necessary.

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In the impregnation and extraction phase, the pressures in the extraction chamber 1 and the storage tank 3 are balanced to a pressure P₀. Liquid CO₂ is added from the storage tank 3 to the extraction chamber 1 at the pressure P₀, and the temperature T₀, by means of a compressor, which sucks gas from extraction chamber 1 and pushes out liquid CO₂ from the bottom of the storage tank 3 by adding it to the top. If desired additives for coating or impregnating into the PLA material can be added to the liquid CO₂. The temperature in the extraction chamber 1 is decreased by evaporation of liquid CO₂ to a pressure P₁ and temperature T₁. CO₂ gas is taken from the storage tank 3 by the compressor and is supplied at the top of the extraction chamber 1 to a pressure P₂ at a temperature T₁, thereby achieving a subcooling of the liquid CO₂, thus preventing the PLA resin beads from sticking together. The temperature T₁ should be below the glass transition temperature T_g of PLA for the actual CO₂ pressure. Evaporation and addition of CO₂ gas so as to achieve subcooling of the liquid CO₂ is repeated as often as necessary to maintain the desired conditions in the extraction chamber 1. After a predetermined treatment time period, the pressures between the extraction chamber 1 and the distiller tank 4 are balanced, and liquid CO₂ is drained off from the extraction chamber to the distiller tank 4. The impregnation and extraction phase may be repeated several times, as desired.

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When the impregnation and extraction treatment in the liquid CO₂ treatment of the PLA resin beads is completed a last draining of the liquid CO₂ is carried out, in which the liquid CO₂ is partially drained off from the extraction chamber to the distiller tank 4. The remaining liquid CO₂ is evaporated and is transferred via a compressor via a heat exchanger/cooler to the storage tank 3. Thereby, the impregnated PLA resin beads are cooled and undesired expansion is prevented, while the pressure in the extraction chamber is lowered to atmospheric pressure. Rotation of the PLA beads during this step is preferred in order to get a uniform

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cooling of PLA. The impregnated PLA resin beads can then be taken out from the extraction chamber and be transferred to further processing.

5 Liquid CO₂ received in the distiller tank 4 comprises extractable substances originating from the PLA resin beads. The CO₂ is separated from these extractable substances by distillation, and the pure CO₂ thereby obtained is recycled to the storage tank 1. The extractable substances remain at the bottom of the distiller tank 4, and can be removed as a concentrate.

10 The above system relates to a batch process. However, the process may as well be performed continuously, and the system is then adapted thereto.

Figure 2 shows a schematic view of a system for performing a process including the method of impregnating and purifying PLA resin. In the start-up phase of the process an extraction chamber 1 is loaded with PLA resin beads through an inlet 2.
15 The extraction chamber may be a reactor in the form of an autoclave or any other vessel that may be pressurized. Air present in the extraction chamber 1 is evacuated by means of a vacuum pump. During start-up of the process, CO₂ gas is supplied to the extraction chamber 1 from a CO₂ storage tank 3, so as to pressurize
20 the extraction chamber 1 to approximately 6 MPa with CO₂ gas. Sensors in the system monitor the level of CO₂ in the storage tank 3, and additional CO₂ is added to the extraction chamber 1 from an external source if necessary.

In the impregnation and extraction phase, the pressures between the extraction
25 chamber 1 and the storage tank 3 are balanced to a pressure P₀. Liquid CO₂ is added from the storage tank 3 to the extraction chamber 1 using a liquid CO₂ pump 5. The setpoint temperature is maintained using a cooling unit. The pump is used to maintain the setpoint pressure in the extraction chamber during the extraction/impregnation. The PLA particles are rotated in a drum in the extraction
30 chamber 1. The CO₂ in the extraction chamber 1 is drained to the distiller tank 4 after a predetermined time. New CO₂ is added from the storage tank 3 to the extraction chamber 1 while CO₂ in the distiller tank 4 is distilled and transported to storage tank 3 while extraction/impregnation of PLA occurs in the extraction chamber 1 in the same way as in the first bath. The number of CO₂ baths can vary

depending on purity level of the PLA. In any of the baths an additive can be added to the extraction chamber 1 to modify the properties of the PLA.

- When the liquid CO₂ treatment, which involves impregnation and extraction of the
- 5 PLA resin beads, is completed a last draining of the liquid CO₂ is carried out, in which the liquid CO₂ is partially drained off from the extraction chamber to the distiller tank 4. The remaining liquid CO₂ is evaporated and is transferred via a compressor via a heat exchanger/cooler to the storage tank 3. Thereby, the impregnated PLA resin beads are cooled and an undesired expansion is prevented,
- 10 while the pressure in the extraction chamber is lowered to atmospheric pressure. Rotation of the PLA beads during this step is preferred in order to get a uniform cooling of PLA. The impregnated PLA resin beads can then be taken out from the extraction chamber and be transferred to further processing.

CLAIMS

1. A material comprising expanded polylactic acid (PLA) resin **characterized in** that
5 it comprises a total amount of extractives of 0-0,035 % by weight, calculated on the total weight of PLA, said extractives being substances that can be extracted from PLA with diethyl ether as extraction medium according to the method of determination of extractives in PLA as described in the description of this patent application.
- 10 2. The material of claim 1, wherein said extractives comprise oligomers of lactic acid of which lactide is 0-0,020 % by weight, calculated on the total weight of PLA.
3. The material of claim 1 or 2, wherein the material is obtainable by a process in
15 which PLA beads are subjected to a liquid CO₂ treatment, which involves impregnation and extraction with liquid CO₂.
4. The material of claim 3, wherein the process comprises the following steps:
- subjecting PLA resin beads to a liquid CO₂ treatment, which involves
20 impregnation and extraction comprising
 - at least one impregnation and extraction step, in which the PLA resin beads are brought into contact with 0,01-1000 kg pure liquid CO₂ /kg PLA, preferably 2-20 kg liquid CO₂ /kg PLA, in a reactor for a predetermined time period, at a temperature and pressure that
25 prevents the beads from sticking together and foaming, and that
 - a portion of the liquid CO₂ is drained from the PLA beads after completion of the impregnation and extraction step, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, while leaving at least 0,01 kg liquid
30 CO₂/kg PLA, preferably 0,01-1 kg liquid CO₂/kg PLA in the reactor containing the PLA resin beads, followed by
 - evacuation of CO₂ gas from the reactor so as to decrease the pressure to ambient pressure, whereby the remaining liquid CO₂ is

evaporated, thereby decreasing the temperature so as to prevent foaming at ambient pressure;

- conditioning the impregnated and extracted PLA beads at a temperature and a pressure that prevents the beads from sticking together and foaming, to reduce the CO₂ content to 5-18 % by weight;
- increasing the temperature to a pre-expansion temperature, so as to pre-expand the PLA beads; and
- increasing the temperature to a fusing temperature to allow moulding of the PLA beads.

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5. The material of claim 4, wherein the impregnation and extraction step comprises 2 or more successive steps, wherein

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- the PLA resin beads are brought into contact with pure liquid CO₂ in each successive step for a predetermined time period at a temperature and pressure that prevents the beads from sticking together and foaming, and wherein
- at least a portion of the liquid CO₂ is drained from the PLA beads at the end of each step, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form.

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6. The material of claim 3, wherein the liquid CO₂ treatment, which involves impregnation and extraction, comprises

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- impregnation and extraction in a continuous process, wherein PLA resin beads are held in a reactor, in which the PLA resin beads are brought into contact with liquid CO₂ for a predetermined time period, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, and
- pure liquid CO₂ is continuously fed at one end of the reactor, and is drained from another end of the reactor, and wherein

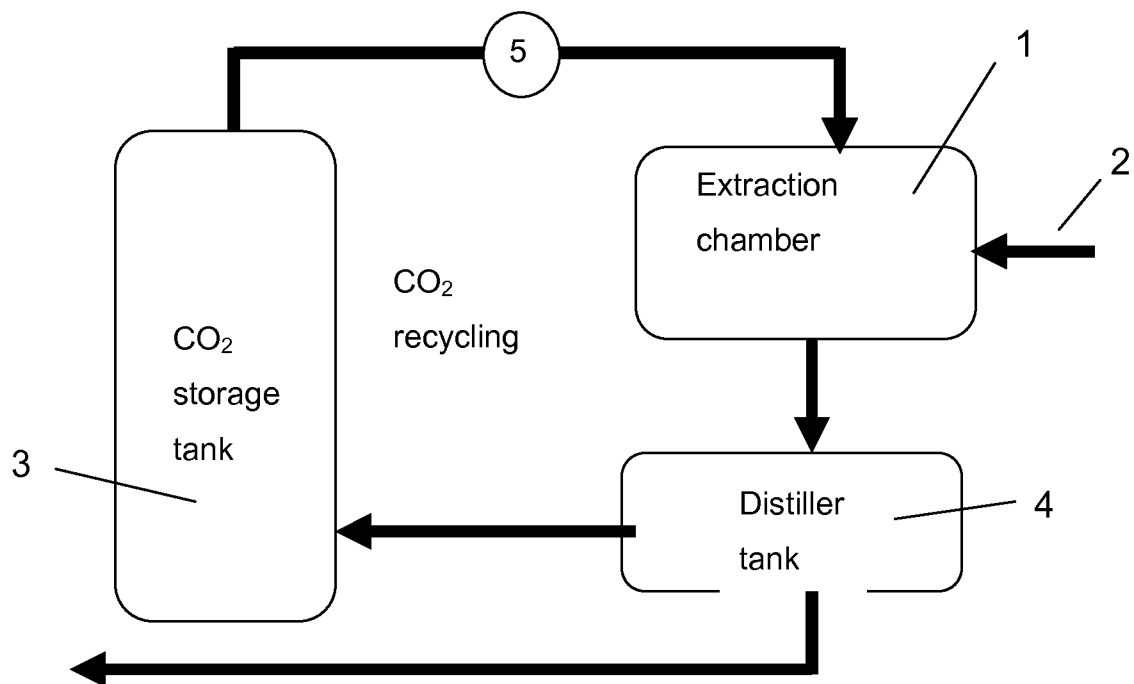
30

- a portion of the liquid CO₂ is drained from the PLA beads upon completion of the impregnation and extraction, at a temperature that prevents the beads from sticking together and foaming, and at which the CO₂ is in liquid form, while leaving at least 0,01 kg liquid CO₂/kg PLA, preferably 0,01-1 kg liquid CO₂/kg PLA in the reactor containing the PLA resin beads, followed by

- evacuation of CO₂ gas from the reactor so as to decrease the pressure to ambient pressure, whereby the remaining liquid CO₂ is evaporated, thereby decreasing the temperature so as to prevent foaming at ambient pressure.

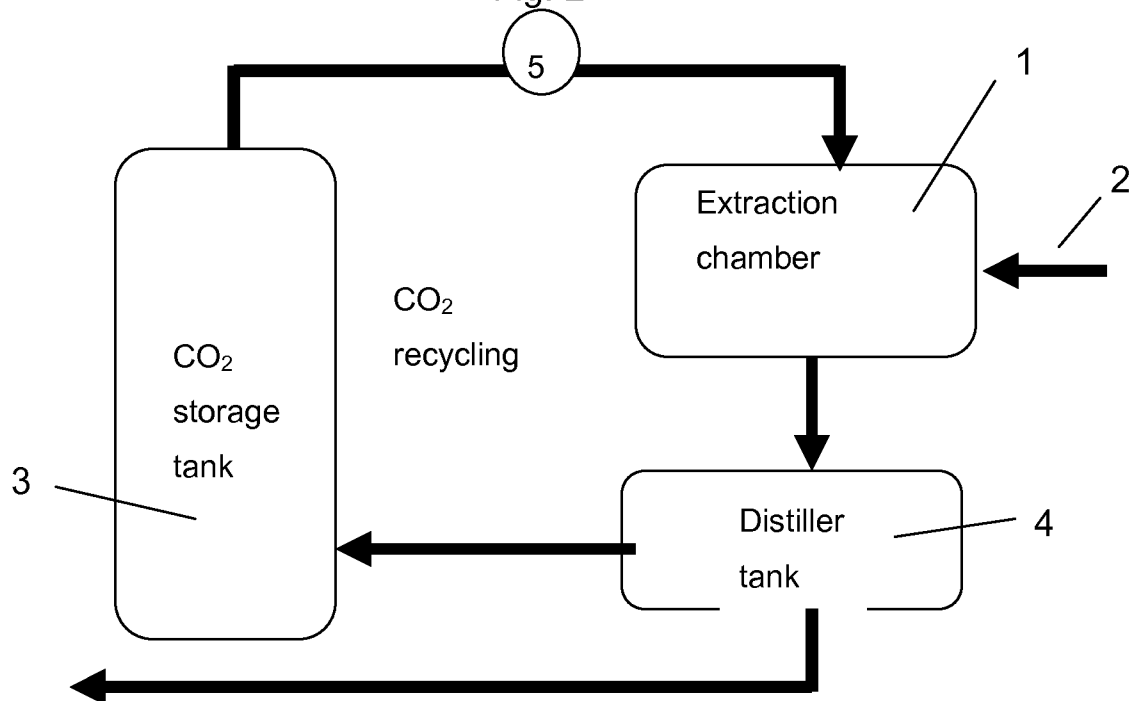
- 5 7. The material of any one of claims 4-6, wherein the beads are impregnated and extracted with liquid CO₂ at a pressure of above 1 MPa, preferably 4,5-8 MPa.
8. The material of any one of claims 4-7, wherein the beads are impregnated and extracted with liquid CO₂ at a temperature above -50 °C but below the glass
- 10 transition temperature of PLA at the pressure used, preferably -10 to +15 °C, for 10 to 240 minutes, preferably 30 to 90 minutes.
9. The material of any one of claims 4-8, wherein the beads are impregnated and extracted with a liquid CO₂ containing additives chosen from coloring agents, anti-
- 15 static agents, flame retardants, adhesives and fragrances.
10. The material of any one of claims 1-9, wherein the PLA resin beads comprise 50-100% by weight of PLA, preferably 80-100 % by weight.
- 20 11. The material of any one of claims 1-10, wherein the PLA is amorphous PLA.
12. The material of any one of claims 1-11, further comprising one or more of fillers, reinforcing agents and coloring agents.

Fig. 1



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Fig. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2011/050394

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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)

IPC: B01D, C08G, C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, BIOSIS, COMPENDEX, EMBASE, MEDLINE, PUBCHEM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008093284 A1 (BIOPOLYMER NETWORK LTD ET AL), 7 August 2008 (2008-08-07); claims 3-4; [0002]-[0003], [0005]-[0006], [0023], [0025], [0029], [0043], [0052]-[0053], [0093]	1-12
Y	--	1
Y	US 20080269449 A1 (CHATTOPADHYAY PRATIBHASH ET AL), 30 October 2008 (2008-10-30); claims 1-3; [0038]-[0040], Table 2	1
A	US 5049328 A (MEYER BERNARD H ET AL), 17 September 1991 (1991-09-17); claim 1; Table 1	1-12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

06-12-2011

Date of mailing of the international search report

07-12-2011

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2011/050394

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-12
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

See Extra Sheet
.../...

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Continuation of: Box No. II

Present claims 1-12 relate to a compound defined (inter alia) by reference to the following parameter:

P1: a total amount of extractives by weight, defined as substances that can be extracted from PLA with diethyl ether according to a method defined in the description.

Since this method is not a standardised or well recognised method within the technical field, the use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the following:

PLA resins with a low amount of residual monomers or other low molecular weight impurities.

Thence it follows that a reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability only is established for the matter that has been searched.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2011/050394

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008045516 A1 (QLT USA INC ET AL), 17 April 2008 (2008-04-17); claims 1-9; Table 1 --	1-12
A	WO 2010053242 A1 (SAMYANG CORP ET AL), 14 May 2010 (2010-05-14); claim 1; [91]-[94], Table 1 --	1-12
A	KOEGLER, W.S. et al. "Carbon Dioxide Extraction of Residual Chloroform from Biodegradable Polymers" In: Journal of Biomedical Materials Research, 2002, Aug., Vol. 63, No. 5, p. 567-576, ISSN: 0021-9304 --	1-12
A	HERBERGER, J. et al. " Carbon dioxide extraction of residual solvents in poly(lactide-co-glycolide) microparticles" In: Journal of Controlled Release, 2003, Jun., Vol. 90, No. 2, p. 181-195, ISSN: 0168-3659 --	1-12
A	PACK, J.W. et al. "Ring-Opening Polymerization of L-Lactide and Preparation of Its Microsphere in Supercritical Fluids" In: Macromolecular Bioscience, 2004, Mar., Vol. 4, No. 3, p. 340-345, ISSN: 1616-5187 -- -----	1-12

Continuation of: second sheet

International Patent Classification (IPC)

C08G 63/90 (2006.01)

C08G 63/08 (2006.01)

C08J 9/18 (2006.01)

B01D 11/02 (2006.01)

C08G 101/00 (2006.01)

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Cited literature, if any, will be enclosed in paper form.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SE2011/050394

WO	2008093284 A1	07/08/2008	AU	2008211581 A1	07/08/2008
			CA	2675473 A1	07/08/2008
			CN	101675101 A	17/03/2010
			EP	2115053 A4	16/03/2011
			JP	2010516884 A	20/05/2010
			NZ	552936 A	25/09/2009
			US	20100029793 A1	04/02/2010
US	20080269449 A1	30/10/2008	US	7745566 B2	29/06/2010
US	5049328 A	17/09/1991	AU	8013391 A	02/01/1992
			AU	635183 B2	11/03/1993
			CA	2046003 C	24/05/1994
			EP	0467551 A3	17/06/1992
			JP	4226549 A	17/08/1992
WO	2008045516 A1	17/04/2008	CA	2666341 A1	17/04/2008
			EP	2079767 A1	22/07/2009
			JP	2010506965 A	04/03/2010
WO	2010053242 A1	14/05/2010	AU	2009311895 A1	14/05/2010
			CA	2742361 A1	14/05/2010
			CN	102209743 A	05/10/2011
			EP	2364332 A1	14/09/2011
			KR	20100051531 A	17/05/2010
			US	20110207834 A1	25/08/2011