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(54) **Eljárás lignin-tartalmú prekursor szálak és szénszálak előállítására**

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(54) **METHOD FOR THE PRODUCTION OF LIGNIN-CONTAINING PRECURSOR FIBRES AND ALSO CARBON FIBRES**

VERFAHREN ZUR HERSTELLUNG VON LIGNINHALTIGEN VORLÄUFERFASERN UND KOHLENSTOFFFASERN

PROCÉDÉ DE PRODUCTION DE PRÉFIBRES CONTENANT DE LA LIGNINE AINSI QUE DE FIBRES DE CARBONE

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Description

[0001] The invention relates to a method for the production of a precursor for the production of carbon- and activated carbon fibres according to the wet- or air-gap spinning method, in which a solution of lignin and a fibre-forming polymer in a suitable solvent is extruded through the holes of a spinning nozzle into a coagulation bath, the formed thread is stretched and subsequently treated, dried at an elevated temperature and then wound up. The lignin-containing thread is an economical starting material for the production of carbon- and activated carbon fibres.

[0002] Carbon fibres are high-performance reinforcing fibres which are used essentially for composite materials in aircraft construction, high-performance vehicle construction (Formula I, high-performance sailing ships etc.), for sports equipment and increasingly for wind energy plants. Currently, extensive efforts are being made worldwide to introduce carbon fibres of average quality (at a reduced price level) into mass applications in automobile construction, the development of weight-reduced electric vehicles which is sought publicly in the meantime representing an essential driving force.

[0003] Carbon fibres are produced by heat treatment above 1,000°C of organic precursor fibres. The first carbon fibres were developed on the basis of cellulose precursors and used as filaments in lamps. Nowadays, polyacrylonitrile or copolymers of polyacrylonitrile are the dominating polymers for the production of precursors for carbon fibres. The palette of carbon fibres based on PAN is supplemented by high-modulus carbon fibre made from pitch. For PAN-based carbon fibres, the estimated annual capacity in 2010 was at approx. 77,000 t and, for pitch-based carbon fibres, at 1,830 t (technical textiles 3/2010), An overview of the production, the structure, the mechanical properties and also the application of PAN- and pitch-based carbon fibres is provided in: J. P. Donnet et al., Carbon fibers, third edition, Marcel Dekker, Inc. New York, Basle, Hong Kong.

[0004] Polyacrylonitrile and pitch are products of the petrochemical industry and hence are subject to the typical cost increase for this branch of industry. In the last few years, a development trend for developing precursors which are not linked to the oil price with respect to the raw materials resulted therefrom. This trend was forced by the demand for carbon fibres in the average quality segment and hence also in the average price segment for mass applications, as are seen in automobile construction.

[0005] Also biopolymers thereby came into focus. Reference was made already to cellulose (rayon) as raw material for the first carbon fibre. Also Lyocell fibres were examined as precursor (S. Peng et al., J. Appl. Polymer Sci. 90 (2003) 1941- 1947). It was shown that the Lyocell-based carbon fibres have somewhat greater strength than the rayon-based fibres produced under comparable conditions. 1 GPa for the strength and approx. 100 GPa

for the modulus of elasticity are however at a very low level for carbon fibres. In addition to the cellulose man-made fibre, also cellulose natural fibres were tested as precursor for carbon fibre. M. Zhang et al. (Die Angewandte makromolekulare Chemie (Applied macromolecular chemistry) 222 (1994) 147- 163) used sisal Fibre as precursor for carbon fibre production. With a strength of 0.82 GPa and a modulus of elasticity of 25 GPa, the carbon fibres produced therefrom are at a very low level.

[0006] Another biopolymer which increasingly is gaining importance in precursor development is lignin. Lignin is a polyaromatic polyol which is a component of wood and occurs in large quantities as a by-product of cellulose production. The carbon proportion is at approx. 60-65%. The chemical structure of lignin is determined by the type of wood used in the cellulose process and also the method of cellulose digestion which is applied. The main quantities of the resulting lignin are supplied for energy use. With lignin, an extremely economical raw material is available in very large quantities and is in practice not fibre-forming in the unmodified form. One objective was the development of melt-spun lignin-containing precursors. J.F. Kadla et al. (Carbon 40 (2002) 2913-2920) describe the production of lignin fibre by melt-spinning of a commercially available kraft lignin and also melt-spinning of a mixture of lignin with low proportions up to 5% of polyethylene oxide (PEO). Processing of pure lignin requires a thermal pre-treatment which increases the raw material costs and, in mixtures, only small proportions of PEO are possible since, with larger quantities of PEO, adhesion occurs in the stabilising process. The carbon fibres made from the melt-spun lignin-containing precursors had strengths of approx. 0.4 GPa and moduli in the range 40-50 GPa and hence still do not fulfil the mechanical characteristic values sought by automobile construction, strength approx. 1.7 GPa and modulus approx. 170 GPa.

[0007] Kubo et al. (Carbon 36 (1998) 1119- 1124) describe a process for the melt-spinning of lignin, in which, in a pretreatment step, the non-melting high-molecular components are removed from the lignin. In a further publication, K. Sudo et al. (J. Appl. Polymer Sci., 44 (1992) 127-134) describe the pretreatment of lignin with organic solvents with subsequent melt-spinning of the chloroform-soluble fraction. The carbon Fibres produced therefrom had merely a low strength level.

[0008] US 7,678,358 claims acetylation of lignin as precursor of lignin melt-spinning without however giving any information relating to the properties of the carbon fibres produced in this way. The state of the art shows that it is possible in principle to produce melt-spun lignin-containing precursors for carbon fibres. However it is also shown that the property level of carbon fibre based on PAN or pitch is not achieved. The question remains open as to whether the lignin modification required to make this suitable for melt-spinning does not again offset the cost advantage of the economical raw material, lignin.

[0009] The object underlying the invention is to develop

an economical method for the production of a lignin-containing precursor based on a solution-spinning method for the production of carbon- and activated carbon fibres.

[0010] Furthermore, it is the object of the present invention to indicate a corresponding lignin-containing precursor fibre. In addition, the present invention relates to further processing of the precursor fibres to form carbon fibres and also correspondingly produced activated carbon fibres.

[0011] This object is achieved with respect to the method for the production of a lignin-containing precursor fibre by the features of patent claim 1. Patent claim 14 relates to a correspondingly produced precursor fibre. In the case of the method according to the invention for the production of a lignin-containing precursor fibre for the production of carbon fibres and/or activated carbon fibres, a solution, comprising at least one sort of lignin and also at least one fibre-forming polymer selected from the group consisting of cellulose or cellulose derivatives in at least one solvent, selected from the group consisting of tertiary amine oxides and / or ionic Liquids, is introduced into a coagulation bath by extrusion of the solution through a spinning nozzle by the air-gap spinning method, the lignin-containing precursor fibre precipitating.

[0012] In the method according to the invention, the preferably low processing temperature of the solution, once produced, during extrusion thereof into the coagulation bath is particularly advantageous, the maximum upper limit of this temperature being prescribed by the nature of the coagulation bath (boiling point). Generally, the temperature of the coagulation bath is hence below 100°C. As a result, extremely gentle processing of the lignin fibres is provided, which surprisingly leads to the carbon fibres produced from these precursor fibres having significantly increased tensile strength.

[0013] There is understood, according to the invention, by the term "solution" that all the components of the solution, i.e. both the lignin and the fibre-forming polymer, are completely solvated by the solvent. However, this term likewise also includes the possibility that the lignin fibres and/or the fibre-forming polymer are present partly undissolved herein.

[0014] A preferred embodiment of the method provides that the solution used in step a) is produced by agitation or kneading of the at least one sort of lignin and also of the at least one fibre-forming polymer in the at least one solvent, preferably at temperatures of 60°C or more, particularly preferred of 80°C or more.

[0015] Furthermore, it is advantageous if the solution is filtered before introduction into the coagulation bath, any possibly contained insoluble components being able to be separated.

[0016] In a particularly preferred embodiment, the spinning hole diameter of the spinning nozzle is from 50 to 600 µm, preferably 100 to 500 µm.

[0017] The methods for shaping the solution and transferring it into the precipitation bath or coagulation bath are thereby effected in the air-gap spinning method, the

air gap in the case of an air-gap spinning method being preferably at least 10 mm, further preferred at least 20 mm and at most 500 mm.

[0018] Further advantageous aspects of the method according to the invention provide that the lignin-containing fibre according to step b)

a) is stretched, preferably is stretched to at least 1.1 times, further preferred to 1.1 to 12 times, particularly preferred to at least 1.5 times, particularly preferred to at least 2 times its length, in particular at a temperature of at least 60°C, preferably at least 80°C, further preferred at least 90°C, particularly preferred of at least 100°C, the stretching being implemented preferably in the precipitation bath, in air or in water vapour,

b) is washed, preferably washed with demineralised water,

c) is treated subsequently with textile aids for improving the thread strength and for avoiding electrostatic charges,

d) is dried, in particular by winding up or winding round of the fibre onto or around heated rollers and /or by through-flow drying at a temperature of at least 80°C, preferably at least 100°C and/ or

e) is wound up.

[0019] Furthermore, it is advantageously possible that the fibre is treated with a spinning oil before drying, after drying or before and after drying.

[0020] Preferred concentrations of the at least one sort of lignin are thereby from 1 to 99% by weight, preferably from 2 to 30% by weight, particularly preferred from 3 to 20% by weight, relative to the entire solution.

[0021] Advantageous concentrations of the at least fibre-forming polymer are thereby, relative to the entire solution, from 1 to 99% by weight, preferably from 5 to 40% by weight, particularly preferred from 7 to 30% by weight, likewise relative to the entire solution.

[0022] In a particularly preferred embodiment, the coagulation bath comprises water or a mixture of water and an organic liquid, such as aprotic polar solvents, in particular dimethylsulfoxid (DMSO), such as aliphatic amides which are liquid at room temperature, in particular dimethylformamide (DMF) or dimethylacetamide (DMAc); tertiary amine oxides, in particular N-methylmorpholine-N-oxide; ionic liquids, preferably ionic liquids selected from the group consisting of imidazolium compounds, pyridinium compounds or tetraalkylammonium compounds, particularly preferred 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium acetate and/ or mixtures hereof.

[0023] An advantageous pH value of the coagulation

bath is thereby between 1 and 7, preferably between 2 and 5.

[0024] The solvent for the spinning solution, i.e. the solution which comprises the lignin and also at least one fibre-forming polymer, is thereby selected preferably from the group consisting of tertiary amine oxides, in particular aqueous N-methylmorpholine-N-oxide (NMMNO, in particular NMMNO monohydrate); ionic liquids, preferably ionic liquids selected from the group consisting of imidazolium compounds, pyridinium compounds or tetraalkylammonium compounds, particularly preferred 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium acetate; and/or mixtures hereof

[0025] The fibre-forming polymers are selected from the group consisting of cellulose and/or cellulose derivatives, in particular cellulose carbamate, cellulose allophanate and hemicellulose and/or mixtures or blends hereof

[0026] Furthermore, it is advantageous in the case of the method according to the invention if the at least one sort of lignin results from wood and annual plant pulping methods and is selected in particular from the group consisting of alkali lignin, kraft lignin, lignosulphonate, thiolignin, organosolv lignin, ASAM lignin, lignins from digestion processes by means of ionic liquids or enzymes and/or combinations or mixtures hereof.

[0027] According to the invention, a precursor fibre for the production of carbon fibres is likewise indicated. The precursor fibre according to the invention is distinguished by

- a) a content of at least one sort of lignin of 1% to 99% by weight, preferably 20 to 60% by weight,
- b) a content of at least one sort of fibre-forming polymer, selected from the group consisting of cellulose and/or cellulose derivatives, of 1% to 99% by weight, preferably 40 to 80% by weight, and
- c) possibly a strength of at least 10 cN/tex, preferably at least 20 cN/tex, and/or
- d) possibly a modulus of elasticity of at least 1,000 cN/tex, preferably at least 1,300 cN/tex.

[0028] The precursor fibre according to the invention can be produced particularly advantageously according to a previously described method.

[0029] Concerning the definitions of lignin and the fibre forming polymers we refer to the method claims 12 and 13 and the description.

[0030] Furthermore, a method is indicated according to the present invention for the production of a carbon fibre, in which a precursor fibre according to one of the two preceding claims is stabilised at temperatures between 100 and 600°C and is carbonised above 800°C under inert conditions.

[0031] In a preferred embodiment, the carbon fibre is subjected to water vapour, after the carbonisation, at temperatures > 200°C, preferably > 300°C.

[0032] In addition, the present invention provides a carbon fibre which can be produced according to the previously described method for the production of the carbon fibre.

[0033] The present invention is explained in more detail with reference to the subsequent embodiments and examples without restricting the invention to the represented parameters.

[0034] The lignin is preferably mixed with the thread- or fibre-forming polymer and then dissolved in a suitable solvent by agitation or by a kneading process at an elevated temperature. The resulting solution is possibly filtered and then advantageously shaped to form filaments by wet- or air-gap spinning, which can be stretched under different conditions, washed, treated, dried and then wound up as a filament.

[0035] The different lignins, such as alkali lignin, lignosulphonate, thiolignin, organosolv lignin or types of lignin from alternative wood digestion processes, which are known to the person skilled in the art, as occur during cellulose production or also mixtures of these can be used. The lignins are washed intensively with water or possibly also with diluted acids up to an ash content of less than 1%.

[0036] As fibre-forming polymers, in particular cellulose or also cellulose derivatives, such as cellulose carbamate and cellulose allophanate, are used.

[0037] As solvent, for example aliphatic amides, such as DMF or DMAc, DMSO, tertiary amine oxides, preferably aqueous N-methylmorpholine-N-oxide, particular NMMO monohydrate or an ionic liquid, selected from the group consisting of imidazolium compounds, pyridinium compounds, tetraalkylammonium compounds and mixtures hereof, are used.

[0038] The spinning solution is preferably produced with agitation or by kneading at a temperature above 60°C, preferably above 80°C. The polymer concentration is adjusted for example to greater than 8%, preferably greater than 10%. The resulting viscous solution can be filtered using normal filtration devices and can be supplied as a homogeneous particle-free solution for intermediate storage before the spinning process.

[0039] The shaping of the spinning solution to form fibres or filaments is effected according to the wet-spinning or air-gap spinning method. In the case of the wet-spinning method, the spinning solution is pressed through the holes of a spinning nozzle, spinning nozzles with hole diameters of 50 to 500 µm being used. The extruded thread is solidified in the coagulation bath which consists of water or of a mixture of the polymer solvent and a nonsolvent. The nonsolvent can be preferably water or an aliphatic alcohol with a chain length up to C 8. When applying air-gap spinning, the viscous lignin-containing spinning solution is pressed through the holes of a spinning nozzle and the extruded threads are stretched in

the air gap. The preferred nozzle hole diameter is preferably greater than 100 μm and should not exceed 600 μm . The air-gap length is at least 10 mm. The air-stretched thread is then coagulated comparably to wet-spinning.

[0040] The thread is stretched in water and/or a mixture of water and the solvent at a temperature greater than 80°C, preferably greater than 90°C and in hot air and/or water vapour greater than 90°C, preferably greater than 100°C up to a multiple of its length but by at least 1.1 times. The stretching can be effected before or even after the washing process.

[0041] The stretched and washed thread is treated, before the drying or after the drying or before and after the drying, with a spinning oil with an antistatic effect. Drying is effected on heated rollers or also by through-flow drying at temperatures greater than 80°C, preferably greater than 100°C.

[0042] The thus produced fibre comprises at least 10% lignin, preferably > 20% lignin and one or more fibre-forming polymers, such as cellulose and/or cellulose derivatives, such as cellulose carbamate and/or cellulose allophanate. The fibres produced according to the invention have a tensile strength of at least 10 cN/tex and a modulus greater than 500 cN/tex and can be converted, according to known methods for stabilising and carbonisation, into carbon fibres and also, by a subsequent water vapour treatment, into activated carbon fibres with a high specific surface.

Example 1

[0043] 60 g of a cellulose (DPCuox = 490) which comprises up to 12% hemicellulose are mixed with 29 g air-dried organocell lignin in 500 g 1-butyl-3-methylimidazolium chloride and dissolved in a horizontal kneader at a temperature of 90°C within 3 h. The resulting black, homogeneous solution is free of fibre residues and has a zero shear viscosity, measured at 80°C, of 578 Pas.

[0044] The solution was pressed through a 40-hole spinning nozzle (hole diameter 200 μm) with the help of an extruder stretched with a drawing ratio of 14 in the air gap and the filaments were precipitated in the acetic acid coagulation bath (pH = 2.5). Washing of the filaments was effected with distilled water, drying was effected in air. The filaments had a strength of 25 cN/tex, an elongation of 7.6% and also a modulus of elasticity of 1,320 cN/tex. The lignin content was 20.3%.

Example 2

[0045] 75 g of an air-dried chemical cellulose (DPCuox = 560) are mixed with 48 g air-dried kraft lignin in 500 g 1-ethyl-3-methylimidazolium acetate and dissolved in a horizontal kneader at a temperature of 90°C within 3 h. The resulting black, homogeneous solution is free of fibre residues and has a zero shear viscosity, measured at 100°C, of 374 Pas. The solution was pressed through a

40-hole spinning nozzle (hole diameter 200 μm) with the help of an extruder, stretched with a drawing ratio of 18 in the air-gap and the filaments were precipitated in the aqueous coagulation bath. Washing of the filaments was effected with distilled water, drying was effected in air. The filaments had a strength of 28 cN/tex, an elongation of 9.6% and also a modulus of elasticity of 1,560 cN/tex. The lignin content was 36.4%.

10 Example 3

[0046] 30 g cellulose carbamate (DPCuox = 258, DS = 0.4) are mixed with 10 g air-dried organosolv lignin and 70 g 1-butyl-3-methylimidazolium acetate and dissolved in a horizontal kneader at a temperature of 110°C, within 2 h. The resulting black, homogeneous solution is free of fibre residues and has a zero shear viscosity, measured at 100°C, of 1,215 Pas. The solution was pressed through a 12-hole spinning nozzle (hole diameter 150 μm) with the help of an extruder, stretched with a drawing ratio of 30 in the air gap and the lignin-containing cellulose carbamate fibre was precipitated in the aqueous coagulation bath with 15% 1-butyl-3-methylimidazolium acetate. Washing of the filaments was effected with distilled water, drying was effected in air. The filaments had a strength of 45 cN/tex, an elongation of 6.4% and also a modulus of elasticity of 2,346 cN/tex. The lignin content was 18.3%.

30 Example 4

[0047] 447 g of an air-dried chemical cellulose (DPCuox = 560) are mixed with 276 g air-dried kraft lignin and also 2.1 g propylgallate in 5.2 kg 52% N-methylmorpholine-N-oxide hydrate and dissolved in a horizontal kneader at a temperature of 90°C with distillative water separation within 3 h. The resulting black, homogeneous solution is free of fibre residues and has a zero shear viscosity, measured at 90°C, of 642 Pas. The solution was pressed through a 40-hole spinning nozzle (hole diameter 200 μm) with the help of an extruder, stretched with a drawing ratio of 20 in the air gap and the filaments were precipitated in the aqueous coagulation bath. Washing of the filaments was effected with distilled water, drying was effected in air. The filaments had a strength of 42 cN/tex, an elongation of 5.4% and also a modulus of elasticity of 2,164 cN/tex. The lignin content was 52.4%.

50 Claims

1. Method for the production of a lignin-containing precursor fibre for the production of carbon fibres and/or activated carbon fibres, in which

55 a) a solution, comprising at least one sort of lignin and also at least one fibre-forming polymer selected from the group consisting of cellulose

- or cellulose derivatives in at least one solvent, selected from the group consisting of tertiary amine oxides and/or ionic liquids,
- b) is transferred into a coagulation bath by extrusion of the solution through a spinning nozzle by the air-gap spinning method, the lignin-containing precursor fibre precipitating.
2. Method according to claim 1, **characterised in that** the solution used in step a) is produced by agitation or kneading of the at least one sort of lignin and also of the at least one fibre-forming polymer in the at least one solvent, preferably at temperatures of 60°C or more, particularly preferred of 80°C or more.
 3. Method according to one of the preceding claims, **characterised in that** the solution is filtered before introduction into the coagulation bath.
 4. Method according to one of the preceding claims, **characterised in that** the spinning hole diameter of the spinning nozzle is from 50 to 600 μm , preferably 100 to 500 μm .
 5. Method according to the preceding claim, **characterised in that** the shaping is performed by the air-gap spinning method, wherein the air gap being preferably at least 10 mm, preferably at least 20 mm and at most 500 mm.
 6. Method according to one of the preceding claims, **characterised in that** the lignin-containing fibre according to b)
 - a) is stretched, preferably is stretched to at least 1.1 times, further preferred to 1.1 to 12 times, particularly preferred to at least 1.5 times, particularly preferred to at least 2 times its length, in particular at a temperature of at least 60°C, preferably at least 80°C, further preferred at least 90°C, particularly preferred of at least 100°C, the stretching being implemented preferably in the precipitation bath, in air or in water vapour,
 - b) is washed, preferably washed with demineralised water,
 - c) is treated subsequently with textile aids for improving the thread strength and for avoiding electrostatic charges,
 - d) is dried, in particular by winding up or winding round of the fibre onto or around heated rollers and/or by through-flow drying at a temperature of at least 80°C, preferably at least 100°C and/or
 - e) is wound up.
 7. Method according to the preceding claim, **characterised in that** the fibre is treated with a spinning oil before drying, after drying or before and after drying.
 8. Method according to one of the preceding claims, **characterised in that**, respectively relative to the entire solution, the concentration
 - a) of the at least one sort of lignin is from 1 to 99% by weight, preferably from 2 to 30% by weight, particularly preferred from 3 to 20% by weight, and/or
 - b) of the at least one fibre-forming polymer is from 1 to 99% by weight, preferably from 5 to 40% by weight, particularly preferred from 7 to 30% by weight.
 9. Method according to one of the preceding claims, **characterised in that** the coagulation bath comprises water or a mixture of water and an organic liquid, such as aprotic polar solvents, in particular DMSO; such as aliphatic amides which are liquid at room temperature, in particular dimethylformamide (DMF) or dimethylacetamide (DMAc); tertiary amine oxides, in particular N-methylmorpholine-N-oxide; ionic liquids, preferably ionic liquids selected from the group consisting of imidazolium compounds, pyridinium compounds or tetraalkylammonium compounds, particularly preferred 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium acetate.
 10. Method according to the preceding claim, **characterised in that** the pH value of the coagulation bath is between 1 and 7, preferably between 2 and 5.
 11. Method according to one of the preceding claims, **characterised in that** the tertiary amine oxide, is aqueous N-methylmorpholine-N-oxide (NMMO), particular NMMNO monohydrate and the ionic liquids, are selected from the group consisting of imidazolium compounds, pyridinium compounds or tetraalkylammonium compounds, particularly preferred 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium acetate; and/or mixtures hereof.
 12. Method according to one of the preceding claims, **characterised in that** the cellulose and/or cellulose derivatives, are selected of the group consisting of cellulose carbamate, cellulose allophanate, and hemicellulose; and/or mixtures or blends hereof.
 13. Method according to one of the preceding claims, **characterised in that** the at least one sort of lignin results from wood and annual plant pulping methods and is selected in particular from the group consisting of alkali lignin, kraft lignin, lignosulphonate, thiolignin, organosolv lignin, ASAM lignin, lignins from digestion processes by means of ionic liquids or enzymes and/or combinations or mixtures hereof.

14. Precursor fibre for the production of carbon fibres, characterised by

- a) a content of at least one sort of lignin of 1 % to 99% weight,
- b) a content of at least one sort of fibre-forming polymer, selected from the group consisting of cellulose and/or cellulose derivatives, of 1 to 99% by weight, and
- c) a strength of at least 20 cN/tex, and /or
- d) a modulus of elasticity of at least 1,000 cN/tex, preferably at least 1,300 cN/tex.

Patentansprüche

1. Verfahren zur Herstellung einer ligninhaltigen Vorläuferfaser zur Herstellung von Carbonfasern und/oder Aktivkohlefasern, wobei

- a) eine Lösung, die mindestens eine Art von Lignin und zudem mindestens ein faserbildendes Polymer umfasst, das ausgewählt ist aus der Gruppe bestehend aus Cellulose oder Cellulosederivaten in mindestens einem Lösungsmittel, das ausgewählt ist aus der Gruppe bestehend aus tertiären Aminoxiden und/oder ionischen Flüssigkeiten,
- b) durch Extrusion der Lösung durch eine rotierende Düse mittels des Luftspaltspinnverfahrens in ein Koagulationsbad übertragen wird, wobei die ligninhaltige Vorläuferfaser ausgefällt wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die in Schritt a) verwendete Lösung durch Bewegen oder Kneten der mindestens einen Art von Lignin und auch des mindestens einen faserbildenden Polymers in dem mindestens einen Lösungsmittel bevorzugt bei Temperaturen von 60 °C oder mehr, insbesondere bevorzugt von 80 °C oder mehr, hergestellt wird.

3. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Lösung vor dem Einbringen in das Koagulationsbad gefiltert wird.

4. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass der Spinnlochdurchmesser der rotierenden Düse von 50 bis 600 µm bevorzugt 100 bis 500 µm beträgt.

5. Verfahren nach vorstehendem Anspruch, dadurch gekennzeichnet, dass das Formen durch das Luftspaltspinnverfahren ausgeführt wird, wobei der Luftspalt bevorzugt mindestens 10 mm, bevorzugt mindestens 20 mm und am meisten 500 mm beträgt.

6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die ligninhaltige Faser gemäß b)

- a) gestreckt wird, bevorzugt auf mindestens das 1,1-fache, weiter bevorzugt auf das 1,1- bis 12-fache, insbesondere bevorzugt auf mindestens das 1,5-fache, insbesondere bevorzugt auf mindestens das 2-fache seiner Länge insbesondere bei einer Temperatur von mindestens 60 °C, bevorzugt von mindestens 80 °C, weiter bevorzugt von mindestens 90 °C, insbesondere bevorzugt von mindestens 100 °C gestreckt wird, wobei das Strecken bevorzugt im Fällbad, in Luft oder in Wasserdampf implementiert wird,
- b) gewaschen wird, bevorzugt mit Deionat gewaschen wird,
- c) anschließend mit Textilhilfsmitteln behandelt wird, um die Fadenfestigkeit zu verbessern und elektrostatische Aufladungen zu vermeiden,
- d) getrocknet wird, insbesondere mittels Aufwickeln oder Herumwickeln der Faser auf oder um erwärmte Rollen und/oder mittels Durchströmtrocknen bei einer Temperatur von mindestens 80 °C, bevorzugt mindestens 100 °C, und/oder
- e) aufgewickelt wird.

7. Verfahren nach vorstehendem Anspruch, dadurch gekennzeichnet, dass die Faser vor dem Trocknen, nach dem Trocknen oder vor und nach dem Trocknen mit einem Spinnöl behandelt wird.

8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass entsprechend relativ zur gesamten Lösung die Konzentration

- a) der mindestens einen Art von Lignin von 1 bis 99 Gew.-%, bevorzugt von 2 bis 30 Gew.-%, insbesondere bevorzugt von 3 bis 20 Gew.-% und/oder
- b) von dem mindestens einen faserbildenden Polymer von 1 bis 99 Gew.-%, bevorzugt von 5 bis 40 Gew.-%, insbesondere bevorzugt von 7 bis 30 Gew.-% beträgt.

9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass das Koagulationsbad Wasser oder eine Mischung aus Wasser und einer organischen Flüssigkeit, wie beispielsweise aprotische polare Lösungsmittel, und insbesondere DMSO umfasst; wie beispielsweise aliphatische Amide, die bei Raumtemperatur flüssig sind, insbesondere Dimethylformamid (DMF) oder Dimethylacetamid (DMAc); tertiäre Aminoxide, insbesondere N-Methylmorpholin-N-oxid; ionische Flüssigkeiten, bevorzugt ionische Flüssigkeiten, die ausgewählt sind aus der Gruppe bestehend aus Imidazoliumverbindungen, Pyridiniumverbindungen oder Tetraalky-

l ammoniumverbindungen, insbesondere bevorzugt 1-Butyl-3-methylimidazoliumchlorid, 1-Butyl-3-methylimidazoliumacetat, 1-Ethyl-3-methylimidazoliumacetat.

10. Verfahren nach vorstehendem Anspruch, **dadurch gekennzeichnet, dass** sich der pH-Wert des Koagulationsbads zwischen 1 und 7, bevorzugt zwischen 2 und 5 liegt.
11. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** das tertiäre Aminoxid wässriges N-Methylmorpholin-N-oxid (NMMO) ist und insbesondere NMMO-Monohydrat und die ionischen Flüssigkeiten ausgewählt sind aus der Gruppe bestehend aus Imidazoliumverbindungen, Pyridiniumverbindungen oder Tetraalkylammoniumverbindungen, insbesondere bevorzugt 1-Butyl-3-methylimidazoliumchlorid, 1-Butyl-3-methylimidazolium, 1-Ethyl-3-methylimidazoliumacetat und/oder Mischungen davon.
12. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die Cellulose und/oder Cellulosederivate ausgewählt sind aus der Gruppe bestehend aus Carbamat, Cellulose, Celluloseallophanat und Hemicellulose und/oder Gemischen oder Mischungen davon.
13. Verfahren nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, dass** die mindestens eine Art von Lignin aus Holz- und Einjahrespflanzenaufschlussverfahren resultiert und insbesondere ausgewählt ist aus der Gruppe bestehend aus Alkalilignin, Kraft-Lignin, Ligninsulfonat, Thiolignin, Organosolvignin, ASAM-Lignin, Ligninen von Aufschlussprozessen mittels ionischer Flüssigkeiten oder Enzymen und/oder Kombinationen oder Mischungen davon.
14. Vorläuferfaser zur Herstellung von Carbonfasern, **dadurch gekennzeichnet, dass**
- a) ein Gehalt von mindestens einer Art von Lignin von 1 bis 99 Gew.-%,
 - b) ein Gehalt von mindestens einer Art von faserbildendem Polymer, das ausgewählt ist aus der Gruppe bestehend aus Cellulose und/oder Cellulosederivaten, von 1 bis 99 Gew.-% und
 - c) eine Stärke von mindestens 20 cN/tex und/oder
 - d) ein Elastizitätsmodul von mindestens 1.000 cN/tex, bevorzugt mindestens 1.300 cN/tex beträgt.

Revendications

1. Procédé de production d'une fibre de précurseur contenant de la lignine pour la production de fibres de carbone et/ou de fibres de carbone activé/ dans lequel
- a) une solution, comprenant au moins une sorte de lignine et aussi au moins un polymère fibrogène choisi dans le groupe constitué de la cellulose ou de dérivés de cellulose dans au moins un solvant, choisi dans le groupe constitué d'amines oxydes tertiaires et/ou de liquides ioniques,
 - b) est transférée dans un bain de coagulation par extrusion de la solution à travers une filière au moyen d'un procédé de filage à travers une fente, entraînant la précipitation de la fibre de précurseur contenant la lignine.
2. Procédé selon la revendication 1, **caractérisé en ce que** la solution utilisée dans l'étape a) est produite en agitant ou en malaxant au moins une sorte de lignine et aussi au moins un polymère fibrogène dans au moins un solvant, de préférence à des températures de 60 °C ou plus, idéalement à 80 °C ou plus.
3. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la solution est filtrée avant l'introduction dans le bain de coagulation.
4. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le diamètre du trou de filage de la filière est de 50 à 600 µm, de préférence de 100 à 500 µm.
5. Procédé selon la revendication précédente, **caractérisé en ce que** le façonnage est réalisé par le procédé de filage à travers une fente, où la fente est de préférence d'au moins 10 mm, de préférence d'au moins 20 mm et maximum de 500 mm.
6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la fibre contenant de la lignine selon b)
- a) est étirée, de préférence au moins 1,1 fois, plus préférentiellement de 1,1 à 12 fois, idéalement au moins 1,5 fois, idéalement au moins 2 fois dans sa longueur, en particulier à une température d'au moins 60 °C, de préférence à au moins 80 °C, plus préférentiellement à au moins 90 °C, idéalement à au moins 100 °C, l'étirement étant exécuté de préférence dans le bain de précipitation, dans de l'air ou dans de la vapeur d'eau,
 - b) est lavée, de préférence avec de l'eau démi-

- néralisée,
- c) est par la suite traitée avec des adjuvants textiles pour améliorer la résistance du fil et pour éviter les charges électrostatiques,
- d) est séchée, en particulier par renvidage ou enroulement de la fibre sur ou autour de rouleaux chauffés, et/ou par un séchage par écoulement traversant à une température d'au moins 80 °C, de préférence d'au moins 100 °C et/ou
- e) est renvidée.
7. Procédé selon la revendication précédente, **caractérisé en ce que** la fibre est traitée avec une huile d'ensimage avant le séchage, après le séchage ou avant et après le séchage.
8. Procédé selon une quelconque des revendications précédentes, **caractérisé en ce que**, par rapport respectivement à la totalité de la solution, la concentration
- a) d'au moins une sorte de lignine est de 1 à 99 % en poids, de préférence de 2 à 30 % en poids, idéalement de 3 à 20 % en poids, et/ou
- b) de l'au moins un polymère fibrogène est de 1 à 99 % en poids, de préférence de 5 à 40 % en poids, idéalement de 7 à 30 % en poids.
9. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le bain de coagulation comprend de l'eau ou un mélange d'eau et d'un liquide organique, tels que des solvants polaires aprotiques, en particulier le DMSO ; tels que les amides aliphatiques qui sont liquides à la température ambiante, en particulier le diméthylformamide (DMF) ou le diméthylacétamide (DMAc) ; les amines oxydes tertiaires, en particulier la N-méthylmorpholine-N-oxyde ; les liquides ioniques, de préférence les liquides ioniques choisis dans le groupe constitué de composés de l'imidazolium, de composés de pyridinium ou de composés du tétraalkylammonium, idéalement le chlorure de 1-butyle-3-méthylimidazolium, l'acétate de 1-butyle-3-méthylimidazolium, l'acétate de 1-éthyl-3-méthylimidazolium.
10. Procédé selon la revendication précédente, **caractérisé en ce que** la valeur du pH du bain de coagulation est comprise entre 1 et 7, de préférence entre 2 et 5.
11. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'amine oxyde tertiaire est du N-méthylmorpholine-N-oxyde (NMMO) aqueux, en particulier un monohydrate de NMMO et les liquides ioniques sont choisis dans le groupe constitué de composés d'imidazolium, de composés de pyridinium ou de composés de tétraalkylammonium, idéalement le chlorure de 1-butyle-3-méthylimidazolium, l'acétate de 1-butyle-3-méthylimidazolium, l'acétate de 1-éthyl-3-méthylimidazolium ; et/ou un mélange de ceux-ci.
12. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** la cellulose et/ou les dérivés de cellulose sont choisis dans le groupe constitué du carbamate de cellulose, de l'allopphanate de cellulose et de l'hémicellulose ; et /ou de mélanges ou combinaisons de ceux-ci.
13. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**au moins une sorte de lignine est obtenue de procédés de réduction en pâte de bois et de plantes annuelles et qu'elle est en particulier choisie dans le groupe constitué d'alcalilignine, de lignine Kraft, de lignosulfonate, de thiolignine, de lignine organosolv, de lignine ASAM, de lignines de procédés de digestion au moyen de liquides ioniques, ou d'enzymes, et/ou de combinaisons ou de mélanges de ceux-ci.
14. Fibre de précurseur pour la production de fibres de carbone, **caractérisée par**
- a) une teneur en au moins une sorte de lignine de 1% à 99 % en poids,
- b) une teneur en au moins une sorte de polymère fibrogène, choisi dans le groupe constitué de la cellulose et/ou des dérivés de cellulose, de 1 à 99 % en poids, et
- c) une résistance d'au moins 20 cN/tex, et/ou
- d) un module d'élasticité d'au moins 1000 cN/tex, de préférence d'au moins 1300 cN/tex.

REFERENCES CITED IN THE DESCRIPTION

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Eljárás lignin-tartalmú prekursor szálak és szénszálak előállítására

SZABADALMI IGÉNYPONTOK

1. Eljárás szénszálak és/vagy aktivált szénszálak előállítására szolgáló lignin-tartalmú prekursor szálak előállítására, ahol
 - a) egy oldatot, mely legalább egy fajta lignint és legalább egy, a cellulózból vagy cellulózszármazékokból álló csoportból kiválasztott szálképző polimert tartalmaz, legalább egy oldószerben, mely a tercier amin-oxidok és/vagy ionos folyadékok csoportból van kiválasztva,
 - b) fonó fűvőkán keresztül légréses fonási módszerrel extrudálással koaguláltató fürdőbe továbbítunk, a lignin-tartalmú prekursor szálak kicsapására.
2. Az 1. igénypont szerinti eljárás, azzal jellemezve, hogy az a) lépésben alkalmazott oldatot a legalább egy fajta ligninnek és legalább egy szálképző polimernek a legalább egy oldószerben előnyösen 60°C-on vagy magasabb hőmérsékleten, különösen előnyösen 80°C-on vagy magasabb hőmérsékleten végzett mozgatásával vagy gyűrésével állítjuk elő.
3. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy az oldatot a koaguláltató fürdőbe való bevezetése előtt szűrjük.
4. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a fonó fűvőka fonó lyuk átmérője 50-600 µm, előnyösen 100-500 µm.
5. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a formázást légréses fonási módszerrel végezzük, ahol a légrés előnyösen legalább 10 mm, előnyösen legalább 20 mm és legfeljebb 500 mm.
6. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a b) szerinti lignin-tartalmú szálakat
 - a) nyújtjuk, előnyösen hosszúságának legalább 1,1-szeresére, továbbá előnyösen 1,1-12-szeresére, különösen előnyösen legalább 1,5-szeresére, különösen előnyösen legalább 2-szeresére, különösen legalább 60°C, előnyösen legalább 80°C, továbbá előnyösen legalább 90°C, különösen előnyösen legalább 100°C hőmérsékleten, a nyújtást előnyösen a kicsapó fürdőben, levegőben vagy vízgőzben hajtjuk végre,
 - b) mossuk, előnyösen ionmentesített vízzel mossuk,

- c) ezt követően textil segédanyaggal kezeljük a szál szilárdságának javítására és az elektrosztatikus töltések elkerülésére,
- d) szárítjuk, különösen a szálak fűtött hengere való feltekerésével vagy körültekercselésével és/vagy legalább 80°C-on, előnyösen legalább 100°C-on végzett átáramoltatásos szárítással és/vagy
- e) feltekeréseljük.
7. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a szálakat fonóolajjal kezeljük szárítás előtt, szárítás után vagy szárítás előtt és után.
8. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a teljes oldatra vonatkoztatott koncentráció
- a) legalább egy fajta lignin 1-99 tömeg%, előnyösen 2-30 tömeg%, különösen előnyösen 3-20 tömeg%, és/vagy
- b) legalább egy szálképző polimer 1-99 tömeg%, előnyösen 5-40 tömeg%, különösen előnyösen 7-30 tömeg%.
9. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a koaguláltató fürdő vizet vagy víz és egy szerves oldószer elegyét tartalmazza, például aprotikus poláris oldószerek, különösen DMSO; például alifás amidok, melyek szobahőmérsékleten folyadékok, különösen dimetilformamid (DMF) vagy dimetilacetamid (DMAc); tercier amin-oxidok, különösen N-metilmorfolin-N-oxid; ionos folyadékok, előnyösen az imidazolium-vegyületek, piridinium-vegyületek vagy tetraalkilammónium-vegyületek csoportból kiválasztott ionos folyadékok, különösen előnyösen 1-butil-3-metilimidazolium-klorid, 1-butil-3-metilimidazolium-acetát, 1-etil-3-metilimidazolium-acetát.
10. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a koaguláltató fürdő pH értéke 1 és 7 közötti, előnyösen 2 és 5 közötti.
11. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a tercier amin-oxid vizes N-metilmorfolin-N-oxid (NMMO), különösen NMMNO monohidrát és az ionos folyadékok az imidazolium-vegyületek, piridinium-vegyületek, vagy tetraalkilammónium-vegyületek csoportból vannak kiválasztva, különösen előnyösen 1-butil-3-metilimidazolium-klorid, 1-butil-3-metilimidazolium-acetát, 1-etil-3-metilimidazolium-acetát; és/vagy ezek elegyei.
12. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a cellulóz és/vagy cellulóz-származékok a cellulóz-karbamát, cellulóz-allofanát, és hemicellulóz csoportból vannak kiválasztva; és/vagy ezek elegyei vagy keverékei.

13. Az előző igénypontok bármelyike szerinti eljárás, azzal jellemezve, hogy a legalább egy fajta lignin fából származik és egyéves növényből pépesítő eljárással, és különösen az alkáli-lignin, kraft lignin, lignoszulfonát, tiolignin, organoszolv-lignin, ASAM lignin, ionos folyadékokkal vagy enzimekkel való emésztési eljárásokból származó lignin és/vagy ezek elegyei vagy kombinációi közül van kiválasztva.

14. Prekurzor szál szénszál előállításához, azzal jellemezve, hogy

- a) I tömeg%-99 tömeg% legalább egy fajta lignin tartalma van,
- b) I tömeg%-99 tömeg%, legalább egy fajta szálképző polimer tartalma van, a cellulóz és/vagy cellulóz-származékok csoportból kiválasztva, és
- c) szilárdsága legalább 20 cN/tex, és/vagy
- d) rugalmassági modulusa legalább 1 000 cN/tex, előnyösen legalább 1 300 cN/tex.