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(54) Title: BAMBOO FIBER-REINFORCED COMPOSITE MATERIAL, USE THEREOF AND METHOD FOR PRODUCING A BAMBOO FIBER-REINFORCED COMPOSITE MATERIAL

(57) Abstract: A bamboo fiber-reinforced composite material comprising a polymer resin matrix incorporating sections or boards of bamboo culms having separated individual fibers or fiber bundles, the polymer resin matrix at least partially filling the interspaces between the individual fibers or fiber bundles is disclosed, wherein the sections or boards have been treated with a solution comprising at least one metal-containing Lewis acid and/or at least one compound of an early transition metal. The use of a bamboo fiber-reinforced composite material in construction materials, in particular in reinforcements for concrete components, doors and/or door frames, doors and/or window frames, or in water drain tanks or water drain gutters; indoor and outdoor floor coverings; automobile accessories and/or automobile constituents; and sports equipment, and to a method for producing a bamboo fiber-reinforced composite material, especially a bamboo fiber-reinforced composite material are also disclosed.

Bamboo fiber-reinforced composite material, use thereof and method for producing a bamboo fiber-reinforced composite material

The present invention relates to the technical field of fiber-reinforced composite materials, in particular of bamboo fiber-reinforced composite materials. More particularly, the present invention relates to bamboo fiber-reinforced composite materials comprising a polymer resin matrix incorporating sections or boards of bamboo culms having separated individual fibers or fiber bundles, the polymer resin matrix at least partially filling the interspaces between the individual fibers or fiber bundles. The present invention further relates to the use of a bamboo fiber-reinforced composite material of the invention and to a method for producing a bamboo fiber-reinforced composite material.

Fiber-reinforced composite materials, in particular natural fiber-reinforced composite materials, are already being used today in various technical fields of use, and the significance thereof is likely to increase in the future. Firstly, they often have excellent mechanical properties; secondly, the use thereof is becoming ever more efficient from an environmental and economic point of view as well, against the background of changing environmental awareness and constantly rising raw material and energy costs. Of particular significance in this connection are the natural fiber-filled composite materials which are often referred to as natural fiber-reinforced plastics (NFRPs) and contain fibers of natural or biological origin in a polymer matrix. Wood plastic composites (WPCs) are a known and economically significant subgroup of the natural fiber-reinforced plastics. Composites of this kind contain wood fibers and/or wood flour in a polymer matrix and are often viewed as a separate group of composite materials because of their particular significance and variety of possible uses. Natural fiber-filled composite materials and natural fiber-reinforced plastics are being used, for example, in the automotive industry for production of interior trim and/or as insulation materials. In addition, natural fiber-filled composite materials also find use in the production of construction materials, furniture and floor coverings.

Natural fiber-filled composite materials of this kind are of economic interest because it is possible via the incorporation of the fibers to control the mechanical properties of the composite material or composite and, moreover, to replace a portion of the polymer material with less costly fibers, especially natural fibers. In the composite materials, the

fibers firstly serve as filler, and the incorporated fibers secondly increase in particular the tensile strength of the composite materials compared to the mere polymer materials. The use of bamboo fibers is particularly preferred here because of their high tensile strength and the rapid regrowth of the bamboo plant.

A bamboo fiber-reinforced composite material for construction materials, a method for the production thereof and the use thereof as construction materials are known from WO 2014/137294 A1. With the method known from WO 2014/137294 A1, it is possible to obtain bamboo fiber-reinforced composite materials having a high tensile strength.

This is the starting point for the present invention, an object of which is to further improve a bamboo fiber-reinforced composite material according to the prior art. More particularly, the bamboo fiber-reinforced composite material of the invention is to have a further increase in tensile strength compared to known composite materials and be easily obtainable. It is a further object of the present invention to provide a method for producing such a bamboo fiber-reinforced composite material and for the use of such a bamboo fiber-reinforced composite material.

These and further objects are achieved by a bamboo fiber-reinforced composite material having the features of claim 1, by a use having the features of claim 7 and by a production method having the features of claim 8. Preferred embodiments of the bamboo fiber-reinforced composite material of the invention, of the use of the invention or of the production method of the invention are described in the respective dependent claims.

According to the present invention, it has been recognized that, surprisingly, the tensile strength of a bamboo fiber-reinforced composite material can be increased significantly when, prior to the incorporation of sections or boards having separated individual fibers or fiber bundles that have been separated from bamboo culms into a polymer resin matrix, the sections or boards are contacted with a solution comprising a metal-containing Lewis acid and/or a compound of an early transition metal. It is probable that the metal-containing Lewis acid and/or the compound of the early transition metal bring about an intermolecular interaction between the three-dimensional network of the fibers and the polymer resin matrix once the fibers that have been treated in accordance with the invention have been incorporated into a polymer resin matrix in such a way that the polymer resin matrix at least partially fills the interspaces between the individual fibers or fiber bundles. In this way, it is

possible to obtain bamboo fiber-reinforced composite materials having elevated tensile strength, with values of more than 400 MPa being achieved.

Accordingly, the present invention, in one aspect, lies in the provision of a bamboo fiber-reinforced composite material comprising a polymer resin matrix incorporating sections or boards of bamboo culms having separated individual fibers or fiber bundles, the polymer resin matrix at least partially filling the interspaces between the individual fibers or fiber bundles, wherein the sections or boards have been treated with a solution comprising at least one metal-containing Lewis acid and/or at least one compound of an early transition metal. The present invention further provides, in a further aspect, for the use of a bamboo fiber-reinforced composite material of the invention in construction materials, especially in reinforcements for concrete components, doors and/or door frames; doors and/or window frames, or in water drain tanks or water drain gutters; indoor and outdoor floor coverings; automobile accessories and/or automobile constituents; and sports equipment. With regard to the detailed configuration of construction materials containing a bamboo fiber-reinforced composite material of the invention, WO 2014/137294 A1 shall expressly be incorporated herein by reference, with mere replacement of the bamboo fiber-reinforced composite material with that described herein in comparison to the construction materials described therein. Lastly, the present invention also provides, in a third aspect, a method for producing a bamboo fiber-reinforced composite material, especially a bamboo fiber-reinforced composite material of the invention, comprising the following stages:

(a) providing bamboo culms;
(b) separating sections or boards from the bamboo culms in such a way that the longitudinal axis of the sections or boards essentially corresponds to the fiber direction of the bamboo culms;
(c) at least partially separating individual fibers or fiber bundles from the sections or boards along the longitudinal axis of the sections or boards;
(d) contacting a solution with the sections or boards having separated individual fibers or fiber bundles, said solution comprising at least one metal-containing Lewis acid and/or at least one compound of an early transition metal;
(e) introducing the sections or boards having separated individual fibers or fiber bundles into a polymer resin matrix in such a way that the polymer resin matrix at least partially fills the interspaces between the individual fibers or fiber bundles; and
(f) hardening the polymer resin matrix with sections or boards having separated individual fibers or fiber bundles incorporated therein.

Preferably, the contacting of the solution with the sections or boards having separated individual fibers or fiber bundles precedes the incorporation of the sections or boards having separated individual fibers or fiber bundles into the polymer resin matrix.

Because of their high tensile strength with values of more than 400 MPa in some cases, the bamboo fiber-reinforced composite materials according to the present invention are particularly suitable as a substitute for steel reinforcements in concrete components, as what is called "green steel".

It will be appreciated that those remarks hereinafter which are made only with regard to one individual aspect of the present invention also apply equally to the other aspects of the present invention without any need for an explicit mention. With regard to the relative figures and percentages stated hereinafter, especially quantity figures based on weight, it should be noted that these should be selected by the person skilled in the art in the context of the present invention such that they add up – if appropriate with inclusion of optional further components or additives or ingredients or additions or constituents, especially as defined above – to 100% or 100% by weight. This will be self-evident to the person skilled in the art. Incidentally, it is the case that the person skilled in the art may depart from the quantity figures adduced hereinafter with regard to the application or as required by the individual case, without leaving the scope of the present invention.

The expression "bamboo fiber-reinforced composite material" in the context of the present invention shall encompass all bamboo fiber-containing composite materials having a polymer resin matrix. The fibers serve firstly as filler in order to reduce the polymer content in the composite material, and secondly, through specific selection of the type, amount and alignment of the fibers, the mechanical properties of the composite material are controlled in a specific manner.

In relation to the bamboo fiber-reinforced composite material of the invention, it is preferable when the polymer resin matrix is selected from the group consisting of polyolefins such as polyethylenes (PE) or polypropylenes (PP); vinyl polymers such as polystyrenes (PS), acrylonitrile-butadiene-styrene terpolymer (ABS) or polyvinyl ethers, acrylonitrile-styrene-acrylate terpolymer (ASA), polyvinyl chloride (PVC) or ethylene-vinyl acetate copolymer (EVA); polyesters such as polyethylene terephthalate (PET); polyamides such as nylon-6 (PA 6), nylon-6,6 (PA 6.6); acrylates such as poly(methyl methacrylate)

(PMMA) or poly(methylacrylate) (PMA); biopolymers, for example polylactic acid (PLA); polyurethanes (PU), phenolic resins; amino resins; epoxy resins; and melamine resins; and copolymers and blends thereof. It is possible to incorporate bamboo fibers into such polymer resin matrices with high compatibility. In this regard, particular preference is given to the use of an epoxy resin, especially Super Sap® CLR Epoxy and Super Sap® CPM Epoxy, each sourced from Entropy Resins Inc., and Araldite® 506, sourced from Sigma-Aldrich Corp., all in combination with at least one suitable hardener.

Bamboo fiber-reinforced composite materials that are of particularly good processibility can be obtained when the polymer resin matrix further comprises at least one additive selected from the group consisting of hardeners, UV stabilizers, other stabilizers, lubricants, plasticizers, dyes, processing aids, coupling agents, acid scavengers and mixtures thereof. Epoxidized vegetable oils are particularly preferred additives, for example as plasticizers, acid scavengers or stabilizers, or as unsaturated modified monomers in polymer resin matrices, for reasons of compatibility with the polymer resin matrix materials.

In addition, it may be beneficial when the metal-containing Lewis acid is selected from the group consisting of aluminum(III) halides, iron(III) halides and titanium(IV) halides, and/or the compound of an early transition metal is selected from the group consisting of titanium(IV) alkoxides and zirconium(IV) alkoxides. Such Lewis acids or compounds of an early transition metal give bamboo fiber-reinforced composite materials of the invention having particularly high tensile strengths. In this context, the term "halides" comprehends the anions of the halogens, i.e. fluoride, chloride, bromide and iodide, and the term "alkoxides" anions obtained by the deprotonation of alcohols, in particular of alkanols, especially methoxide, ethoxide, n-propoxide, isopropoxide, n-butoxide, s-butoxide, isobutoxide, tert-butoxide and the like. It is of further preference that the metal-containing Lewis acid is iron(III) chloride and/or iron(III) bromide and/or the compound of an early transition metal is a compound, preferably an alkoxide and/or acetylacetonate, of a metal of transition group IV to VIII of the Periodic Table of the Elements.

Typically, bamboo composite materials are produced from bamboo culms having a period of growth of at least three years. It is possible to use various bamboo species and culms of different durations of growth. For production of the bamboo fiber-reinforced composite material of the invention, the culms of a preferably fast-regrowing bamboo species, preferably *Gigantochloa apus*, may be cut first into elements having a length in the range

from 50 cm to 150 cm, preferably 60 cm to 100 cm, and especially having a length of about 80 cm.

Optionally, the bamboo elements obtained or the non-comminuted bamboo culms may be pretreated by boiling or simmering them in a heated water bath over a period of 6 hours to 72 hours, especially over a period of about 24 hours. The temperature of the water bath is preferably within a range of 60°C to 100°C and is especially about 92°C. Such a pretreatment stage removes sugar molecules from the bamboo material and improves the processibility of the bamboo material in further processing stages, for example cutting.

Thereafter, the optionally pretreated bamboo elements or the non-comminuted bamboo culms are preferably cut into sections or boards in a cutting apparatus in such a way that the longitudinal axis of the sections or boards at least approximately coincides with the fiber direction of the optionally pretreated bamboo elements or the non-comminuted bamboo culms. In this context, it is within the scope of the present invention that the sections or boards obtained from the optionally pretreated bamboo elements or the non-comminuted bamboo culms may have different sizes and/or size ratios. It is preferable, however, that the sections or boards have a length in the range from about 40 cm to 5 m, preferably about 60 cm to 2 m, a width in the range from about 5 cm to 1.5 m, preferably about 10 cm to 80 cm, and a thickness in the range from about 0.1 cm to about 1 cm, preferably about 0.3 cm to 0.8 cm. While the sizes and/or size ratios of the sections or boards obtained from the optionally pretreated bamboo elements or the non-comminuted bamboo culms may vary, it is important in accordance with the invention that the longitudinal axis of the sections or boards at least approximately coincides with the fiber direction of the optionally pretreated bamboo elements or the non-comminuted bamboo culms.

Subsequently, the sections or boards thus obtained can be dried in an optional drying stage. This drying stage can be effected in a customary drying oven at temperatures in the range from 50°C to 80°C, preferably at about 60°C, over a drying time of about 6 hours to 72 hours, especially over a period of about 24 hours. This preferably establishes a moisture content of the sections or boards of about 2% by weight to 15% by weight, especially of about 5% by weight to 10% by weight and more preferably of about 6% by weight to 8% by weight. Through a reduction in the moisture content of the bamboo fibers the risk of inhomogeneous changes in volume of fibers and polymer resin matrix in the composite materials to be produced is reduced, as a result of which the adhesion between bamboo

fibers and polymer resin matrix could possibly be damaged or in the extreme case could even be destroyed.

In addition, it is possible that the bamboo fibers are fibrillated. Fibrillated fibers have a much increased fiber surface area compared to non-fibrillated fibers. The use of fibrillated fibers is advantageous especially because fewer impurities adhere to the fibrillated fibers and the fibrillated fibers, because of their structure, have another increase in mechanical properties in the composite material, especially another increase in mechanical durability.

Subsequently, at least some individual fibers or fiber bundles are separated from the sections or boards. For this purpose, the individual sections or boards are divided along their longitudinal axis in sections or boards having separated individual fibers or fiber bundles, preferably having a width of about 0.2 mm to about 2 cm, preferably of about 0.3 mm to about 1 cm and more preferably of about 0.5 mm to about 2 mm.

This is followed by a further treatment stage in which, in accordance with the present invention, a solution with at least one metal-containing Lewis acid and/or at least one compound of an early transition metal present therein is contacted with the sections or boards having separated individual fibers or fiber bundles. In principle, it is possible in accordance with the present invention to use a great variety of metal-containing Lewis acids and/or compounds of an early transition metal. However, metal-containing Lewis acids used are preferably aluminum(III) halides (AlF_3, $AlCl_3$, $AlBr_3$, AlI_3), iron(III) halides (FeF_3, $FeCl_3$, $FeBr_3$, FeI_3) and titanium(IV) halides (TiF_4, $TiCl_4$, $TiBr_4$, TiI_4) and compounds of an early transition metal used are compounds, especially alkoxides and acetylacetonates, of metals of transition groups IV to VIII of the Periodic Table of the Elements, especially titanium(IV) alkoxides and zirconium(IV) alkoxides as wellas mixed titanium(IV) halide alkoxides and zirconium(IV) halide alkoxides. Alkoxides in this context are especially methoxide, ethoxide, n-propoxide, isopropoxide, n-butoxide, s-butoxide, isobutoxide, tert-butoxide and the like.

Preference is given here to using a diluted solution, especially having a proportion of the at least one metal-containing Lewis acid and/or at least one compound of an early transition metal of about 0.2% by weight to 5% by weight and preferably of about 1% by weight to 3% by weight in a suitable solvent. Particularly suitable solvents are aliphatic alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, tert-butanol and the like.

For this purpose, the contacting is preferably effected by dipping the sections or boards having separated individual fibers or fiber bundles into the appropriate solution, or by applying the appropriate solution to the sections or boards having separated individual fibers or fiber bundles, for example with a brush or paintbrush.

It is then possible to subject the sections or boards having separated individual fibers or fiber bundles thus treated to an additional drying stage, in which they are dried over a drying period of about 6 hours to 72 hours, especially over a drying time of about 24 hours, preferably in a standard drying oven at temperatures in the range from 50°C to 80°C, preferably at about 60°C, to a moisture content of about 2% by weight to 15% by weight, especially of about 5% by weight to 10% by weight and more preferably of about 6% by weight to 8% by weight.

The optionally dried sections or boards having separated individual fibers or fiber bundles are then incorporated into a polymer resin matrix in such a way that the polymer resin matrix at least partially fills the interspaces between the individual fibers or fiber bundles. This gives rise to an intimate and durable bond between the bamboo fibers and the polymer resin matrix in the fiber-reinforced composite materials according to the present invention, such that, firstly, a fiber-reinforced composite material having high mechanical stability, especially having high tensile strength, is formed and, secondly, the penetration of moisture into the composite material of the present invention is prevented, such that swelling of the bamboo fibers brought about by ingress of moisture and ultimately possible destruction of the composite material of the invention is effectively prevented.

Preferably, the optionally dried sections or boards having separated individual fibers or fiber bundles are incorporated into a polymer resin matrix by placing the sections or boards into a mold, preferably made from metal or wood, of a mold press, with initial preliminary alignment in such a way that the fiber direction of the bamboo fibers essentially corresponds to the longitudinal direction of the mold, and then the mold is filled with the liquid polymer resin matrix. It is preferable first to place two or three layers of the sections or boards into the mold in preliminary alignment, to pour the polymer resin matrix over them, then to place a further two or three layers of the sections or boards into the mold in preliminary alignment, to pour the polymer resin matrix over them in turn, and to repeat this operation until the desired thickness has been attained.

Alternatively, the incorporation of the optionally dried sections or boards having separated individual fibers or fiber bundles into a polymer resin matrix can also be accomplished by placing all the required sections or boards in initial preliminary alignment into a mold, preferably made from metal or wood, of a mold press with a vacuum film disposed at the base thereof, disposing a further vacuum film atop the sections or boards and sealing the arrangement airtight with the inflow and outflow each closed. Thereafter, a vacuum pump is connected to the outflow, a hose dipped into a vessel containing the liquid polymer resin matrix is connected to the inflow, the outflow and inflow are opened after the vacuum pump has been started and the reduced pressure generated draws the polymer resin matrix into the bamboo fibers, such that all the bamboo fibers are wetted by the liquid polymer resin matrix. Then the vacuum films are removed.

The liquid polymer resin matrix may have been diluted with a suitable diluent, especially ethyl acetate or n-butyl acetate. The amounts of the diluent in the liquid polymer resin matrix may be about 0.5% by weight to about 15% by weight.

In both alternatives, it is preferable to preheat the mold to a temperature of 60°C to 120°C, especially to about 100°C. Thereafter, a pressure of about 12 to 15 MPa is applied to the arrangement of the sections/boards and the polymer resin matrix at this temperature for about 30 minutes, then a pressure of about 2.5 MPa is exerted at the same temperature for about a further 20 minutes. The composite material obtained, for cooling and further hardening, can then be transferred into an oven having a temperature of about 42°C, where the composite materials remain for about 24 hours to about 96 hours, preferably about 48 hours.

In general, the bamboo fiber-reinforced composite material of the present invention contains the fibers in amounts of 1% by weight to 90% by weight, especially 20% by weight to 85% by weight, preferably 25% by weight to 80% by weight, based on the composite material. In the context of the present invention, it is thus possible to produce composite materials having only a low polymer content, as a result of which the composite materials of the present invention can be produced inexpensively and with a good carbon footprint. In general, the bamboo fiber-reinforced composite material of the present invention contains the polymer matrix in amounts of 10% by weight to 99% by weight, in particular 15% by weight to 80% by weight, preferably 20% by weight to 75% by weight, based on the composite material.

According to the invention, the polymer material of the polymer resin matrix is selected from the group consisting of polyolefins such as polyethylenes (PE) or polypropylenes (PP); vinyl polymers such as polystyrene (PS), acrylonitrile-butadiene-styrene terpolymer (ABS) or polyvinyl ethers, acrylonitrile-styrene-acrylate terpolymer (ASA), polyvinyl chloride (PVC) or ethylene-vinyl acetate copolyer (EVA); polyesters such as polyethylene terephthalate (PET); polyamides such as nylon-6 (PA 6), nylon-6,6 (PA 6.6); acrylates such as polymethylmethacrylate (PMMA) or polymethylacrylate (PMA); biopolymers, for example polylactic acid (PLA); polyurethanes (PU), phenolic resins; amino resins; epoxy resins; and melamine resins; and copolymers and blends thereof. Particular preference is given in accordance with the invention to an epoxy resin, especially Super Sap® CLR Epoxy and Super Sap® CPM Epoxy, each sourced from Entropy Resins Inc., and Araldite® 506, sourced from Sigma-Aldrich Corp., all in combination with at least one suitable hardener.

In addition, in the context of the present invention, it may be the case that the polymer resin matrix contains at least one further additive. Possible additives here include hardeners, UV stabilizers, other stabilizers, lubricants, plasticizers, dyes, processing aids, coupling agents, acid scavengers and mixtures thereof.

The additive(s) may be present in the polymer resin matrix in an amount of about 0.5% by weight to 60% by weight, especially of about 5% by weight to 50% by weight and more preferably of about 10% by weight to 45% by weight. Particularly good results are obtained when the polymer resin matrix comprises at least one hardener. In that case, the hardener(s) may preferably be present in the polymer resin matrix in an amount of about 15% by weight to 50% by weight, especially of about 20% by weight to 50% by weight and more preferably of about 25% by weight to 40% by weight.

The present invention is explained in detail hereinafter with reference to working examples and comparative examples. It will be appreciated that these examples should not be considered to restrict the invention in any way at all. Unless stated otherwise, in the present application including the claims, all percentages and proportion figures are based on weight.

Comparative example and working examples

There follows a description of formulations or compositions and production methods for i modification of fibers in accordance with the present invention and for production of fiber-reinforced composite materials of the invention, and comparison with reference samples.

1. Production of bamboo boards with separated individual fibers or fiber bundles

For production of bamboo boards having separated individual fibers or fiber bundles, bamboo culms from the fast-regrowing bamboo species *Gigantochloa apus*, after a period of growth of more than three years, were cut into sections having a length of about 80 cm. The sections were placed into a water bath having a temperature of 92°C for about 48 hours. Immediately after the removal from the water bath, the sections were processed to boards with a cutting apparatus in such a way that the longitudinal axis of the boards essentially corresponded to the fiber direction of the bamboo sections. The boards had a length of 80 cm, a width of not more than 65 cm and a thickness in the range from 0.3 mm to 0.5 mm. If required, the boards were cut to a width of 15 cm and then dried to a moisture content between 6% by weight and 8% by weight in a drying oven at 60°C for 48 hours. To separate individual fibers or fiber bundles from the boards, the individual boards are then at least partially divided in a manual manner along the longitudinal axis thereof into boards having a width of about 0.5 mm to about 2 mm, with individual fibers or fiber bundles pulled out of the boards.

2. Comparative example

The bamboo boards having separated individual fibers or fiber bundles that have been obtained in this way were placed into the metal mold of a mold press which has been preheated to 100°C in such a preliminary alignment that the fiber direction of the bamboo fibers of the boards essentially coincided with the longitudinal direction of the metal mold. For this purpose, some of the boards were initially placed into the metal mold in two layers.

A mixture of 100 g of bisphenol A epoxide (poly(bisphenol A-co-epichlorohydrin) having glycidyl end caps, average M_n ~ 348; purchased from Sigma-Aldrich Corp.) as liquid polymer resin matrix and 40 g of diethylenetriamine (purchased from Sigma-Aldrich Corp.) as hardener was poured over the bamboo boards having separated individual fibers or fiber bundles and penetration of the liquid polymer resin matrix through the bamboo boards was awaited. Then further liquid polymer resin matrix (32 g of bisphenol A epoxide and 13 g of diethylenetriamine) was poured over the bamboo boards having separated individual fibers or fiber bundles until the bamboo boards were completely covered. Then two further layers of the bamboo boards were placed into the metal mold in preliminary alignment as

described and covered with liquid polymer resin matrix, likewise as described. This operation was repeated three times more.

For hardening, the mold press was then used to exert a pressure of 14 MPa on the mixture of boards and polymer resin matrix at 100°C for 30 minutes, then a pressure of 2.5 MPa for a further 20 minutes. For gradual cooling and complete hardening, the bamboo fiber-reinforced composite material obtained was transferred into an oven heated to 42°C and left therein at this temperature for 72 hours.

This procedure was conducted with various liquid polymer resin matrices, with variation of the proportion of the hardener within the range from 5% by weight to 40% by weight.

After cooling to room temperature, the tensile strength of the resulting bamboo fiber-reinforced composite materials was measured in accordance with ASTM D3039-08 (Standard Test Method for Tensile Properties of Polymer Matrix Composite). The tensile strengths measured on the bamboo fiber-reinforced composite materials were in the range from 160 MPa to 190 MPa.

3. Examples according to the present invention

3.1 Pretreatment with a compound of an early transition metal

Bamboo boards having separated individual fibers or fiber bundles were produced as described in section 1. above and dipped into a solution of 2% by weight of tetraethoxytitanate(IV) (sourced from Sigma-Aldrich Corp.) in isopropanol. After they had dripped dry, treated bamboo boards were dried to a moisture content between 6% by weight and 8% by weight in a drying oven at 60°C for 48 hours.

The same procedure was used to treat the individual fibers or fiber bundles separated as described in section 1. above in a solution containing 1% by weight of titanium(IV) bis(ammonium lactato) dihydroxide (sourced from Sigma-Aldrich Corp.) in isopropanol.

3.2 Pretreatment with a Lewis acid

Bamboo boards having separated individual fibers or fiber bundles were produced as described in section 1. above and dipped into a solution of 1.5% by weight of iron(III)

chloride hexahydrate (sourced from Fluka) in isopropanol. After they had dripped dry, the treated bamboo boards were dried to a moisture content between 6% by weight and 8% by weight in a drying oven at 60°C for 48 hours.

The same procedure was applied to the individual fibers or fiber bundles separated as described in section 1. above with 5% and 10% by weight solutions of iron(III) chloride hexahydrate (sourced from Fluka) in isopropanol.

3.3 Production of bamboo fiber-reinforced composite materials of the present invention

The resulting bamboo boards having separated individual fibers or fiber bundles pretreated according to section 3.1 above were placed into the metal mold, preheated to 100°C, of a mold press, in such a preliminary alignment that the fiber direction of the bamboo fibers of the boards essentially coincided with the longitudinal direction of the metal mold. At the same time, some of the boards were first placed into the metal mold in two layers.

A mixture of a 4:1 mixture of an epoxy resin (Super Sap® CPM Epoxy (56 g, sourced from Entropy Resins Inc.)) and poly[(phenyl glycidyl ether)-co-formaldehyde] (14 g, sourced from Sigma-Aldrich) as liquid polymer resin matrix and Super Sap® CPL hardener (28 g, sourced from Entropy Resins Inc.) as hardener was poured over the bamboo boards having separated individual fibers or fiber bundles and penetration of the liquid polymer resin matrix through the bamboo boards was awaited. Then further liquid polymer resin matrix (20 g of Super Sap® CPM Epoxy, 5 g poly[(phenyl glycidyl ether)-co-formaldehyde] and 10 g of Super Sap® CPL hardener) was poured over the bamboo boards having separated individual fibers or fiber bundles until the bamboo boards were completely covered. Then two further layers of the bamboo boards were placed into the metal mold in preliminary alignment as described and covered with liquid polymer resin matrix, likewise as described. This operation was repeated three times more.

For hardening, the mold press was then used to exert a pressure of 14 MPa on the mixture of boards and polymer resin matrix at 100°C for 30 minutes, then a pressure of 2.5 MPa for a further 20 minutes. For gradual cooling and complete hardening, the bamboo fiber-reinforced composite material obtained was transferred into an oven heated to 42°C and left therein at this temperature for 72 hours.

This procedure was conducted with various liquid polymer resin matrices, with variation of the proportion of the hardener within the range from 3% by weight to 50% by weight.

After cooling to room temperature, the tensile strength of the resulting bamboo fiber-reinforced composite materials of the invention was measured in accordance with ASTM D3039-08 (Standard Test Method for Tensile Properties of Polymer Matrix Composite). The tensile strengths measured on the bamboo fiber-reinforced composite materials were in the range from 360 MPa to 420 MPa.

The same process was used to produce bamboo fiber-reinforced composite materials of the present invention with bamboo boards having separated individual fibers or fiber bundles pretreated according to section 3.2 above. The polymer resin matrix used was a bisphenol A epoxy resin (Araldite® 506, sourced from Sigma-Aldrich Corp.) with Super Sap® INF epoxy hardener (sourced from Entropy Resins Inc.), with variation of the proportion of the hardener in the range from 4% by weight to 45% by weight.

In addition, bamboo fiber-reinforced composite materials of the present invention were produced from the bamboo boards having separated individual fibers or fiber bundles pretreated according to section 3.2 above. The polymer resin matrix used was an epoxy resin (Super Sap® CLR Epoxy, sourced from Entropy Resins Inc.)) with Super Sap® INF epoxy hardener (sourced from Entropy Resins Inc.), with variation of the proportion of the hardener in the range from 6% by weight to 33% by weight.

Lastly, also produced using the same process were bamboo fiber-reinforced composite materials of the presnt invention with bamboo boards having separated individual fibers or fiber bundles pretreated according to section 3.2 above, using a 4:1 mixture of a poly(bisphenol A-co-epichlorohydrin) having glycidyl end caps (average M_n ~ 348; sourced from Sigma-Aldrich Corp.) and poly[(phenyl glycidyl ether)-co-formaldehyde] (sourced from Sigma-Aldrich.) with diethylenetriamine (sourced from Sigma-Aldrich Corp.) as polymer resin matrix. The proportion of the hardener was varied within the range from 4% by weight to 40% by weight.

The tensile strength of the resulting bamboo fiber-reinforced composite materials of the present invention was measured in accordance with ASTM D3039-08 (Standard Test Method for Tensile Properties of Polymer Matrix Composite). The tensile strengths

measured on the bamboo fiber-reinforced composite materials were in the range from 365 MPa to 445 MPa.

The present invention has been described above with reference to examples and comparative examples. However, it will be clear to the person skilled in the art that the invention is not restricted to these examples; instead, the scope of the present invention is apparent from the appended claims.

- Claims -

Claims

1. A bamboo fiber-reinforced composite material comprising a polymer resin matrix incorporating sections or boards of bamboo culms having separated individual fibers or fiber bundles, the polymer resin matrix at least partly filling the interspaces between the individual fibers or fiber bundles,

   characterized in that

   the sections or boards have been treated with a solution comprising at least one metal-containing Lewis acid and/or at least one compound of an early transition metal.

2. The bamboo fiber-reinforced composite material as claimed in claim 1, characterized in that the polymer resin matrix is selected from the group consisting of polyolefins such as polyethylenes (PE) or polypropylenes (PP); vinyl polymers such as polystyrenes (PS), acrylonitrile-butadiene-styrene terpolymers (ABS) or polyvinyl ethers, acrylonitrile-styrene-acrylate terpolymers (ASA), polyvinyl chloride (PVC) or ethylene-vinyl acetate copolymers (EVA); polyesters such as polyethylene terephthalate (PET); polyamides such as nylon-6 (PA 6), nylon-6,6 (PA 6.6); acrylates such as polymethylmethacrylate (PMMA) or polymethylacrylate (PMA); biopolymers, for example polylactic acid (PLA); polyurethanes (PU), phenolic resins; amino resins; epoxy resins; and melamine resins; and copolymers and blends thereof.

3. The bamboo fiber-reinforced composite material as claimed in claim 2, characterized in that the polymer resin matrix comprises at least one epoxy resin.

4. The bamboo fiber-reinforced composite material as claimed in any of claims 1 to 3, characterized in that the polymer resin matrix further comprises at least one additive selected from the group consisting of hardeners, UV stabilizers, other stabilizers, lubricants, plasticizers, dyes, processing aids, coupling agents, acid scavengers and mixtures thereof.

5. The bamboo fiber-reinforced composite material as claimed in any of claims 1 to 4, characterized in that the metal-containing Lewis acid is selected from the group consisting of aluminum(III) halides, iron(III) halides and titanium(IV) halides, and/or the

compound of an early transition metal is selected from the group consisting of titanium(IV) alkoxides and zirconium(IV) alkoxides.

6. The bamboo fiber-reinforced composite material as claimed in claim 5, characterized in that the metal-containing Lewis acid is iron(III) chloride and/or iron(III) bromide and/or the compound of an early transition metal is a compound, preferably an alkoxide and/or acetylacetonate, of a metal of transition group IV to VIII of the Periodic Table of the Elements.

7. The use of a bamboo fiber-reinforced composite material as claimed in any of claims 1 to 6 in construction materials, especially in reinforcements for concrete components, doors and/or door frames, doors and/or window frames, or in water drain tanks or water drain gutters; indoor and outdoor floor coverings; automobile accessories and/or automobile constituents; and sports equipment.

8. A method for producing a bamboo-reinforced composite material, in particual as claimed in any of claims 1 to 6, comprising the following steps:
   (a) providing bamboo culms;
   (b) separating sections or boards from the bamboo culms in such a way that the longitudinal axis of the sections or boards essentially corresponds to the fiber direction of the bamboo culms;
   (c) at least partly separating individual fibers or fiber bundles from the sections or boards along the longitudinal axis of the sections or boards;
   (d) contacting a solution with the sections or boards having separated individual fibers or fiber bundles, said solution comprising at least one metal-containing Lewis acid and/or at least one compound of an early transition metal;
   (e) introducing the sections or boards having separated individual fibers or fiber bundles into a polymer resin matrix in such a way that the polymer resin matrix at least partially fills the interspaces between the individual fibers or fiber bundles; and
   (f) hardening the polymer resin matrix with sections or boards having separated individual fibers or fiber bundles incorporated therein.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/098335

A. CLASSIFICATION OF SUBJECT MATTER

B27N 3/00(2006.01)i

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)

B27N

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

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

CNABS,SIPOABS,DWPI,CNKI: bamboo, fiber, fibre, composite material, resin, matrix, section?, boards, Lewis acid, metal, early transition

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014137294 A1 (EIDGENOESSISCHE TECH HOCHSCHULE ZUERICH) 12 September 2014 (2014-09-12) description, page 5, line 21 to 27, and claims 1-39	1-8
Y	CN 101234499 A (UNIV CENT SOUTH FORESTRY & TECHNOLOGY) 06 August 2008 (2008-08-06) description, page 2, line 1 to page 3, line 17	1-8
Y	US 6576331 B1 (RYAN D B) 10 June 2003 (2003-06-10) claims 1-10	1-8

☐ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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	Date of mailing of the international search report
29 August 2016	**29 September 2016**

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/098335

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2014137294	A1	12 September 2014	SG	11201506646	A1	29 September 2015
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				CN	105189065	A	23 December 2015
CN	101234499	A	06 August 2008	CN	101234499	B	15 September 2010
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				WO	0051796	A1	08 September 2000
				AU	2887899	A	21 September 2000
				US	2003049428	A1	13 March 2003
				US	2003207098	A1	06 November 2003