

COMPOSITE MATERIALS

The invention relates to composite materials characterized by a substrate based on glass fibers, mineral fibers or derived timber products and by a nanocomposite which is in functional contact with said substrate and is obtainable by surface modification of

a) colloidal inorganic particles with

b) one or more silanes of the general formula (I)



where the radicals A are identical or different and are hydroxyl groups or groups which can be removed hydrolytically, except methoxy, the radicals R are identical or different and are groups which cannot be removed hydrolytically and x is 0, 1, 2 or 3, where $x \geq 1$ in at least 50 mol% of the silanes;

under the conditions of the sol-gel process with a sub-stoichiometric amount of water, based on the hydrolysable groups which are present, with formation of a nanocomposite sol, and further hydrolysis and condensation of the nanocomposite sol, if desired, before it is brought into contact with the substrate, followed by curing.

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The substrate may be of very different physical forms, and the nanocomposite may also be present in different forms of distribution. For example, the nanocomposite may cover the substrate partially or entirely in the form of a continuous covering or coating or it may be present between a plurality of substrates in lamellar form. Specific examples of composite materials of this type are fibers, twines, yarns, and semifinished products such as wovens, knits, braids and non-wovens provided with a thermally stable impregnation.

Alternatively the nanocomposite may form discontinuous or even point-shaped sites of contact between a plurality of substrates and may, for example, bind a particulate, flocculant or fibrous substrate in a matrix-like manner. Specific examples of composite materials of the latter type are insulating materials based on glass or mineral fibers and materials made of wood such as wood fiber slabs, particle boards, wood core plywood, plywood and wood-wool building slabs. For special purposes mixtures of glass fibers and timber materials may also be employed, e.g., for chip boards having flame-retardant properties.

Examples of suitable substrates are glass fibers, natural or man-made mineral fibers such as asbestos, mineral wool, slag wool, and fibers of ceramic materials including those of oxide ceramic; materials derived from timber in the form of cellulose, wood wool, wood flour, wood chips, paper, cardboard, wooden plates, wood borders and wood laminates.

The term fibrous substrates is taken to mean either individual fibers, including hollow fibers and whiskers, or corresponding fiber bundles, threads, ropes, twines and yarns, or semifinished products such as wovens, knits, braids, textiles, non-wovens, felts, webs, sheets and mats. Concrete examples of these are glass wool, glass fiber mats and mineral wool, e.g., slag wool, cinder wool, rock wool or basalt fibers.

The nanocomposite employed according to the invention is prepared by surface modification of colloidal inorganic particles (a) with one or more silanes (b), if desired in the presence of other additives (c) under the conditions of the sol-gel process.

Details of the sol-gel process are described in C.J. Brinker, G.W. Scherer: "Sol-Gel Science - The Physics and Chemistry of Sol-Gel-Processing", Academic

Press, Boston, San Diego, New York, Sydney (1990) and in DE 1941191, DE 3719339, DE 4020316 and DE 4217432.

Here, specific examples of the silanes (b) which can be employed according to the invention and of their radicals A which are hydrolytically removable and their radicals R which are not hydrolytically removable are given.

10 Preferred examples of groups A which are removable hydrolytically are hydrogen, halogen (F, Cl, Br and I, in particular Cl and Br), alkoxy (in particular C₂₋₄-alkoxy, such as ethoxy, n-propoxy, isopropoxy and butoxy), aryloxy (in particular C₆₋₁₀-aryloxy, such as
15 phenoxy), alkaryloxy (e.g. benzyloxy), acyloxy (in particular C₁₋₄-acyloxy, such as acetoxy and propionyloxy) and alkylcarbonyl (e.g. acetyl). Radicals A which are likewise suitable are amino groups (e.g. mono- or dialkyl-, -aryl- and -aralkylamino groups
20 having the abovementioned alkyl, aryl and aralkyl radicals), amide groups (e.g. benzamido) and aldoxime or ketoxime groups. Two or three radicals A may also together form a moiety which complexes the Si atom, as for example in Si-polyol complexes derived from glycol,
25 glycerol or pyrocatechol. Particularly preferred radicals A are C₂₋₄-alkoxy groups, in particular ethoxy. Methoxy groups are less suitable for the purposes of the invention, since they have an excessively high reactivity (short processing time of the nanocomposite
30 sol) and can give nanocomposites and/or composite materials with insufficient flexibility.

The abovementioned hydrolysable groups A may, if desired, carry one or more usual substituents, for
35 example halogen atoms or alkoxy groups.

The radicals R which are not hydrolytically removable are preferably selected from alkyl (in particular C₁₋₄-alkyl, such as methyl, ethyl, propyl and butyl),

alkenyl (in particular C₂₋₄-alkenyl, such as vinyl, 1-propenyl, 2-propenyl and butenyl), alkynyl (in particular C₂₋₄-alkynyl, such as acetylenyl and propargyl), aryl (in particular C₆₋₁₀-aryl, such as phenyl and naphthyl) and the corresponding alkaryl and arylalkyl groups. These groups may also, if desired, have one or more usual substituents, for example halogen, alkoxy, hydroxy, amino or epoxide groups.

10 The abovementioned alkyl, alkenyl and alkynyl groups include the corresponding cyclic radicals, such as cyclopropyl, cyclopentyl and cyclohexyl.

Particularly preferred radicals R are substituted or
15 unsubstituted C₁₋₄-alkyl groups, in particular methyl and ethyl, and substituted or unsubstituted C₆₋₁₀-aryl groups, in particular phenyl.

It is also preferable that x in the above formula (I)
20 is 0, 1 or 2, particularly preferably 0 or 1. It is also preferable if x = 1 in at least 60 mol%, in particular at least 70 mol%, of the silanes of the formula (I). In particular cases, it may be even more favourable if x = 1 in more than 80 mol%, or even more
25 than 90 mol% (e.g. 100 mol%), of the silanes of the formula (I).

The composite materials according to the invention may be prepared, for example, from pure methyltriethoxysilane (MTEOS) or from mixtures of MTEOS and
30 tetraethoxysilane (TEOS), as component (b).

Concrete examples of silanes of the general formula (I) are compounds of the following formulae:

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Si(OC₂H₅)₄, Si(O-n-or iso-C₃H₇)₄, Si(OC₄H₉)₄, SiCl₄,
Si(OOCCH₃)₄, CH₃-SiCl₃, CH₃-Si(OC₂H₅)₃, C₂H₅-SiCl₃,
C₂H₅-Si(OC₂H₅)₃, C₃H₇-Si(OC₂H₅)₃, C₆H₅-Si-(OC₂H₅)₃,
C₆H₅-Si(OC₂H₅)₃, (C₂H₅O)₃-Si-C₃H₆-Cl, (CH₃)₂SiCl₂,

5

$$\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$$

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40 good results are often achieved with from 0.35 to 0.45

mol of water per mole of the hydrolysable groups which are present.

Specific examples of colloidal inorganic particles (a) are sols and powders dispersible at the nano level (particle size preferably up to 300 nm, in particular up to 100 nm and particularly preferably up to 50 nm) of SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , Y_2O_3 , CeO_2 , SnO_2 , ZnO , iron oxides or carbon (carbon black and graphite), in particular of SiO_2 .

The proportion of component (a), based on the components (a), (b) and (c), is usually from 5 to 60% by weight, preferably from 10 to 40% by weight, and particularly preferably from 10 to 20% by weight.

For preparing the nanocomposite, other additives in amounts of up to 20% by weight, preferably up to 10% by weight, and in particular up to 5% by weight, may be employed as optional components (c); examples are curing catalysts, such as metal salts and metal alkoxides (e.g. aluminium alkoxides, titanium alkoxides or zirconium alkoxides), organic binders, such as polyvinyl alcohol, polyvinyl acetate, starch, polyethylene glycol and gum arabic, pigments, dyes, flame retardants, compounds of glass-forming elements (e.g. boric acid, boric acid esters, sodium methoxide, potassium acetate, aluminium sec-butoxide, etc.), anti-corrosion agents and coating aids. According to the invention, the use of binders is less preferred.

The hydrolysis and condensation is carried out under sol-gel conditions in the presence of acid condensation catalysts (e.g. hydrochloric acid) at a pH of preferably from 1 to 2, until a viscous sol is produced.

It is preferable if no additional solvent is used besides the solvent produced in the hydrolysis of the

alkoxy groups. If desired, however, alcoholic solvents, such as ethanol, or other polar, protic or aprotic solvents, such as tetrahydrofuran, dioxane, dimethylformamide or butyl glycol, for example, may be employed.

In order to achieve a favourable sol particle morphology and sol viscosity, the resultant nanocomposite sol is preferably subjected to a special post-reaction step in which the reaction mixture is heated to temperatures of from 40 to 120°C over a period of from a number of hours to a number of days. Special preference is given to storage for one day at room temperature or heating for a number of hours at from 60 to 80°C. This gives a nanocomposite sol with a viscosity of preferably from 5 to 500 mPas, particularly preferably from 10 to 50 mPas. The viscosity of the sol can also, of course, be adjusted to suitable values for the specific application by adding solvents or removing side-products of the reaction (e.g. alcohols). The post-reaction step may preferably also be coupled with a reduction of the solvent content.

The proportion by weight of the nanocomposite in the composite material is preferably from 0.1 to 80% by weight, in particular from 1 to 40% by weight, and particularly preferably from 1 to 20% by weight.

The substrate and the nanocomposite or nanocomposite sol are combined after at least initial hydrolysis of component (b) and in any case before final curing. Before it is brought into contact with the substrate, the nanocomposite sol is preferably activated by feeding in a further amount of water.

The contact can be brought about by any means known to the person skilled in the art and deemed to be useful for the particular case, e.g. by simple mixing of

substrate and nanocomposite sol, dipping, spraying or showering, knife- or spin-coating, pouring, spreading, brushing, etc., into the or with the nanocomposite sol. In order to improve the adhesion between substrate and
5 nanocomposite, it may be advantageous in many cases to subject the substrate, before contact with the nanocomposite or its precursor, to a conventional surface pretreatment, e.g. corona discharge, degreasing, treatment with primers, such as
10 aminosilanes, epoxy silanes, sizes made from starch or silicones, complexing agents, surfactants etc.

Before final curing, a drying step at room temperature or slightly elevated temperature (e.g. up to about
15 50°C) may be undertaken.

The actual curing or a precuring can be carried out at room temperature, but preferably by heat treatment at temperatures above 50°C, preferably above 100°C and
20 particularly preferably at 150°C or above. The maximum curing temperature depends, inter alia, on the melting point and/or the heat resistance of the substrate, but is generally from 250 to 300°C. With mineral substrates, however, significantly higher curing
25 temperatures are also possible, e.g. from 400 to 500°C and above. Curing times are generally in the range from minutes to hours, e.g. from 2 to 30 minutes.

Besides conventional curing by heat (e.g. in a
30 circulating air oven) other curing methods may be used, for example curing with IR beams or laser beams. If desired, the composite prepared may also be subjected to a shaping process before curing.

35 The invention also relates to the use of the abovementioned nanocomposite for the coating and/or consolidation of the abovementioned substrates. The term "consolidation" is intended here to include any measure which is suitable for providing the substrate

in consolidated and/or compacted form, and thus includes, for example, impregnation of the substrate with nanocomposite, embedding of the substrate into a matrix of nanocomposite or cementation or binding of
5 substrates or pieces of substrate with nanocomposite. The term "coating" is taken to mean in particular a partial or complete encapsulation of a substrate with a nanocomposite in order to give this substrate, or pieces thereof, particular properties, for example
10 oxidation resistance, flame retardancy, hydrophobic or oleophobic character, hardness, impermeability, or electrical or thermal insulation.

The following examples further illustrate the present
15 invention. In the following examples, the silica sol employed is an aqueous silica sol from BAYER ("Levasil 300/30") with a solids content of 30% by weight and a particle size of from 7 to 10 nm. The following abbreviations are furthermore used in the examples:

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MTEOS	=	Methyltriethoxysilane
TEOS	=	Tetraethoxysilane
PTEOS	=	Phenyltriethoxysilane

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EXAMPLE 1

A mixture of 65 mole% of MTEOS, 15 mole% of PTEOS and 20 mole% of TEOS (or, alternatively, of 80 mole% of
30 MTEOS and 20 mole% of TEOS) is vigorously stirred with silica sol and hydrochloric acid as catalyst in order to prepare a nanocomposite sol by hydrolysis and condensation of the silanes. The amount of water introduced by means of the silica sol is such that 0.8
35 moles of water are present per mole of hydrolysable group. About 5 minutes after the preparation of the sol the above silane mixture is added thereto so that the total water content of the resulting mixture is 0.4 moles of water per mole of alkoxy groups. The silica

sol accounts for about 14 wt.% of the total solids content.

5 Following a post-reaction phase of about 12 hours at room temperature, water is added to the above mixture in an amount which results in a total water content of the sol of 0.5 moles of water per mole of alkoxy groups. After about 5 minutes the mixture is ready for use.

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The ready-for-use mixture is sprayed onto dampened glass wool through an atomizing ring and cured for about 5 to 10 minutes in a circulating air oven at about 200°C. Thereby an elastic insulating material
15 showing highly improved flame properties in comparison to glass wool bonded with phenolic resin is obtained.

EXAMPLE 2

20 68.7 ml of MTEOS (corresponding to 80 mole%) and 19.2 ml of TEOS (corresponding to 20 mole%) are mixed and half of said mixture is vigorously stirred with 11.7 ml of silica sol (corresponding to a proportion of 14.3 % by weight of silica sol) and 0.386 ml of concentrated
25 hydrochloric acid. Five minutes later the second half of the silane mixture is added to the run, whereafter stirring is continued for a further 5 minutes. Subsequently the resulting sol is subjected to a post-reaction step (allowing it to stand at room temperature
30 for 2 hours). Thereby a storage-stable precondensate having a SiO₂ solids content of about 300 g/l and 0.4 moles of water per mole of hydrolysable group is obtained. By concentration on a rotary evaporator the solids content is adjusted to 60 wt.%.

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Prior to the application of the binder, 3.0 ml of titanium isopropylate and about 2.5 ml of water are added thereto in order to reach a water content of 0.5 moles of water per mole of hydrolysable group. The

5 mixture thus prepared is mixed with wood chips in an
amount which results in 15% of the composition
consisting of SiO_2 . Subsequently the composition is
bonded in a hot press at 180°C for 10 minutes to form a
10 shaped body. Thereby a shaped body resembling a common
glaced insulating press board is obtained; which body
is, however, prepared without organic binder. The flame
properties of a corresponding plate are significantly
improved in comparison to those of a conventional
glaced insulating press board.

EXAMPLE 3

1. Preparation of the sol

15 172 ml of MTEOS are mixed with 48 ml of TEOS. 29 ml of
silica sol and 2 ml of sulfuric acid (35%) are added
thereto with vigorous stirring. Five minutes thereafter
an opaque sol has formed which is allowed to post-react
for 4 hours at room temperature. Following the addition
20 of a further 3 ml of water with stirring the mixture is
ready for use after about 5 minutes.

2. Application of the sol

2.1

25 100 g of wood chips are mixed with 60 ml of sol and
molded under a pressure of 7.1 mPa in a press mold
having a diameter of 12 cm for 10 minutes. Subsequently
the molding is pressed in a heatable press (upper and
lower mold heated) at a pressure of 2.6 mPa and a
30 temperature of 100°C for about 3 hours. Thereby a
mechanically stable shaped body having a wood chips
content of 82 wt.% is obtained.

2.2

35 300 g of rock wool granules are mixed with 10 ml of the
above sol and are pressed at a pressure of 4.4 mPa in a
press mold having a diameter of 12 cm for 5 minutes.
Subsequently the molding is exposed to a temperature of
 80°C for 8 hours in a circulating air dryer. Thereby a

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mechanically stable shaped body having a content of rock wool granules of 1 wt.% is obtained.

CLAIMS

1. Composite material, characterized by a substrate based on glass fibers, mineral fibers or derived timber products and by a nanocomposite which is in functional contact with said substrate and is obtainable by surface modification of

a) colloidal inorganic particles with

b) one or more silanes of the general formula (I)



- where the radicals A are identical or different and are hydroxyl groups or groups which can be removed hydrolytically, except methoxy, the radicals R are identical or different and are groups which cannot be removed hydrolytically and x is 0, 1, 2 or 3, where $x \geq 1$ in at least 50 mol% of the silanes;

under the conditions of the sol-gel process with a below-stoichiometric amount of water, based on the hydrolysable groups which are present, with formation of a nanocomposite sol, and further hydrolysis and condensation of the nanocomposite sol, if desired, before it is brought into contact with the substrate, followed by curing.

2. Composite material according to Claim 1, characterized in that the surface modification has been carried out in the presence of an acid condensation catalyst at a pH of from 1 to 2.

3. Composite material according to Claim 1 or 2, characterized in that the nanocomposite sol has been subjected, over a period of from a number of





hours to a number of days, to a post-reaction at temperatures from room temperature to 120°C.

4. Composite material according to any one of Claims 1 to 3, characterized in that the colloidal inorganic particles (a) are selected from the group consisting of sols and dispersible powders of nano-scaled SiO_2 , TiO_2 , ZrO_2 , Al_2O_3 , Y_2O_3 , CeO_2 , SnO_2 , ZnO , iron oxides or carbon.
5. Composite material according to any one of Claims 1 to 4, characterized in that, for preparing the nanocomposite sol, other additives (c) have been used, for example curing catalysts, organic binders, pigments, dyes, flame retardants, compounds of glass-forming elements, anti-corrosion agents and/or coating aids.
6. Composite material according to any one of Claims 1 to 5, characterized in that from 5 to 60% by weight, preferably from 10 to 40% by weight, and particularly preferably from 10 to 20% by weight, of component (a) have been employed for preparing the nanocomposite.
7. Composite material according to any one of Claims 1 to 6, characterized in that from 20 to 95% by weight, preferably from 40 to 90% by weight, and particularly preferably from 70 to 90% by weight, of component (b), expressed as polysiloxane of the formula: $\text{R}_x\text{SiO}_{(2-0.5x)}$ have been employed for preparing the nanocomposite.
8. Composite material according to any one of Claims 5 to 7, characterized in that not more than 20% by weight, preferably not more than 10% by weight, and particularly preferably not more than 5% by weight, of the other additives (c) have been employed for preparing the nanocomposite.



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9. Composite material according to any one of Claims 1 to 8, characterized in that the radicals A in formula (I) are C₂₋₄-alkoxy groups, preferably ethoxy groups.
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10. Composite material according to any one of Claims 1 to 9, characterized in that R in formula (I) is an unsubstituted or substituted C₁₋₄-alkyl group and/or a substituted or unsubstituted C₆₋₁₀-aryl group, preferably a methyl, ethyl and/or phenyl group.
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11. Composite material according to any one of Claims 1 to 10, characterized in that x in formula (I) is 0, 1 or 2, preferably 0 or 1.
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12. Composite material according to any one of Claims 1 to 11, characterized in that at least 60 mol% and preferably at least 70 mol% of component (b) is silanes of the formula (I) where $x \geq 1$, and preferably $x = 1$.
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13. Composite material according to any one of Claims 1 to 12, characterized in that the surface modification has been carried out using from 0.1 to 0.9 mol, preferably from 0.25 to 0.75 mol, of water per mole of hydrolysable groups which are present.
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14. Composite material according to any one of Claims 1 to 13, characterized in that the proportion by weight of the nanocomposite is from 0.1 to 80% by weight, preferably from 1 to 40% by weight, and particularly preferably from 1 to 20% by weight.
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15. Composite material according to any one of Claims 1 to 14, characterized in that the curing is carried out thermally, preferably at temperatures from 50°C to 300°C.
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16. Composite material according to any one of Claims
1 to 15 in the form of a substrate coated with the
nanocomposite, a fabric impregnated with the
nanocomposite or a shaped article comprising a
5 substrate material consolidated with the
nanocomposite.
17. Use of a nanocomposite as defined in Claims 1. to
13 for coating and/or consolidation of substrates
10 based on glass fibers, mineral fibers or derived
timber products.

