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**(54) Composite material for making sealing systems and method therefor**

Verbundstoffmaterial zur Herstellung von Versiegelungssystemen und Verfahren dafür

Matériau composite pour la fabrication de systèmes d'étanchéité et procédé correspondant

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**EP 2 728 046 B1**

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**Description**

**BACKGROUND OF THE INVENTION**

5 [0001] The present invention relates to a composite material for making sealing systems and a method therefor.  
 [0002] In the thermal insulation field the use of ceramics fibers is well known owing to their optimum thermal and chemical resistance.  
 [0003] However, the use of conventional ceramics fibers is limited because of their suspected toxicity.  
 [0004] For the above reasons, biosoluble ceramics fibers being characterized as unotoxic system have been developed.  
 10 [0005] In the present invention biosoluble ceramics fibers which will be hereinbelow referred to as "A" composite are exclusively used.  
 [0006] It is also known that mineral fillers have a sheet like microstructure and tend to overlap thereby providing structures which could be called "paling or palisade" constructions.  
 [0007] The above composite materials, which will be hereinbelow referred to as "B composites", comprise: muscovite and phlogophite mica, bentonite, montmorillonite, laponite, hydrotalcite, kaolin, lamellar structure silicates, phyllosilicates, thermally, ultrasonically and/or chemically foamed phlogophite mica.  
 15 [0008] Said B composites may also be used in any combinations and rates.  
 [0009] The A composite may be used as a fibrous reinforcement agent for composite materials, owing to its good mechanical and chemical properties; however, in the sealing or gasket system field it cannot be used per se, because  
 20 of its poor sealing capability.  
 [0010] In turn, the B composites may be used in the sealing system field, since they provide good sealing capabilities, but cannot be used per se, because of their poor mechanical characteristics.  
 [0011] Moreover, a simple composite A and B mixture cannot be used since the individual composites thereof are incompatible with one another and do not form blended systems of continuous and homogeneous properties.

**SUMMARY OF THE INVENTION**

25 [0012] Thus, the aim of the present invention is to provide a combined composite material the A composite of which is chemically bound to the B composite, through an organosilane based chemical process.  
 30 [0013] Moreover, the end product appears as consisting of an uneven weave of biosoluble ceramics fibers operating as structural support for inorganic compounds having a layered lamellar structure.  
 [0014] The invention also relates to a method for making plates, films and sheets even coupled to other materials such as metal and non-metal fiber fabrics, smooth, perforated and/or diamond shaped metal laminates, which will be hereinbelow referred to as "supports".  
 35 [0015] The above aim and objects, as well as yet other objects which will become more apparent hereinafter, are achieved by a method for making a composite material, as well as the related composite material consisting of biosoluble ceramics fibers and mineral fillers, particularly for making sealing or tightness systems.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

40 [0016] Further characteristics and advantages of the present invention will become more apparent hereinafter from the following disclosure of a preferred, though not exclusive, embodiment of the invention.  
 [0017] The method according to the present invention comprises the following method steps:  
 45 A step 1) of chemically pre-processing biosoluble ceramics fibers (A composite) in an aqueous solution with vinyltriethoxysilane and mineral fillers (B composite) with bis(triethoxysilylpropyl)polysulfide or vice-versa.  
 The B composite may comprise muscovite and phlogophite mica, bentonite, montmorillonite, laponite, hydrotalcite, kaolin, lamellar structure silicates, phyllosilicates, thermally, ultrasonically and/or chemically foamed phlogophite mica.  
 50 A step 2) of preferably slowly mixing the already processed A and B composites, with an elastomeric material solution as a process aid.  
 A step 3) of forming a plate and/or a coupling with the supports.  
 A step 4) of finally thermally curing the material from step 3).  
 A step 5) of preferably hot coating the material surface by an anti-adhering protective film having a thickness larger  
 55 than 5 µm, based on high temperature silica and PET, by a vacuum heated calender.

[0018] In the step 1) the A composite is processed with vinyltriethoxysilane in an aqueous or organic solution and with a concentration from 0.1 to 30% by weight, in which vinyltriethoxysilane is present starting from a rate from 0.5% up to

30% by weight, based on the A composite.

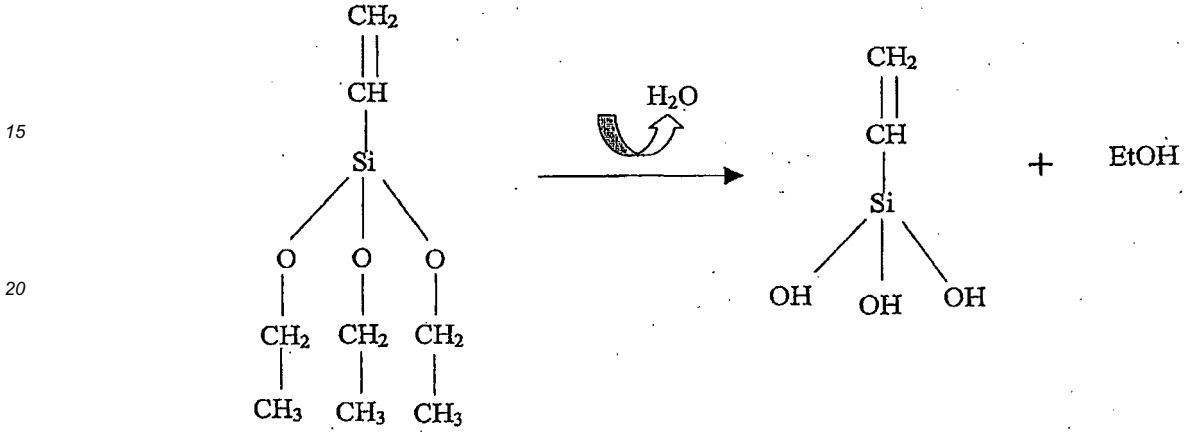
[0019] The B composite is processed with bis(triethoxy-silylpropyl)polysulfide in an aqueous or organic solution at a concentration from 0.1 to 60% by weight, wherein said bis(triethoxysilylpropyl)polysulfide is present from a rate of 0.5% to 30% by weight based on the B composite.

5 [0020] The above processes are carried out separately for the A and B composites, in a closed vessel and under slow stirring, at a temperature from 25°C to 80°C for 24 hours.

[0021] In this first step, the following chemical reaction occurs:

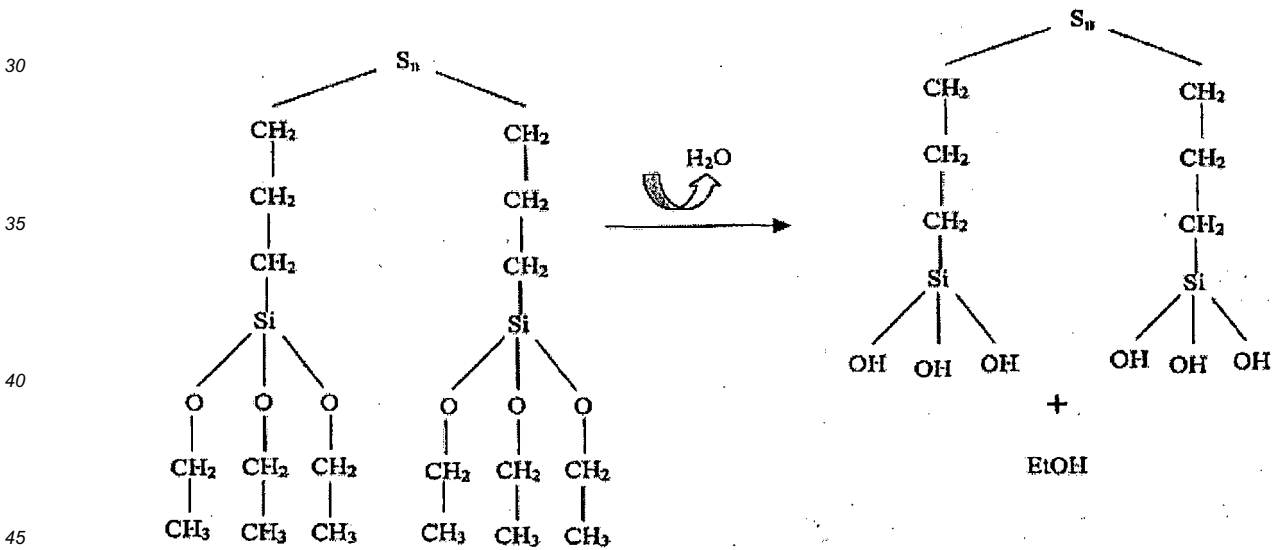
a) a vinyltriethoxysilane hydrolysis and an ethanol evolution

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a bis(triethoxysilylpropyl)polysulfide hydrolysis and an ethanol evolution

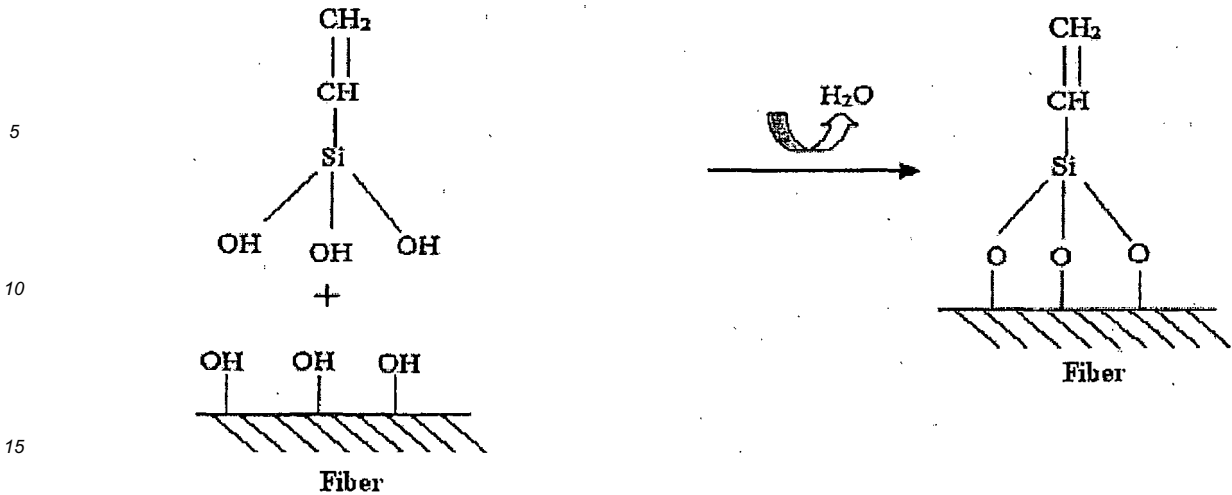
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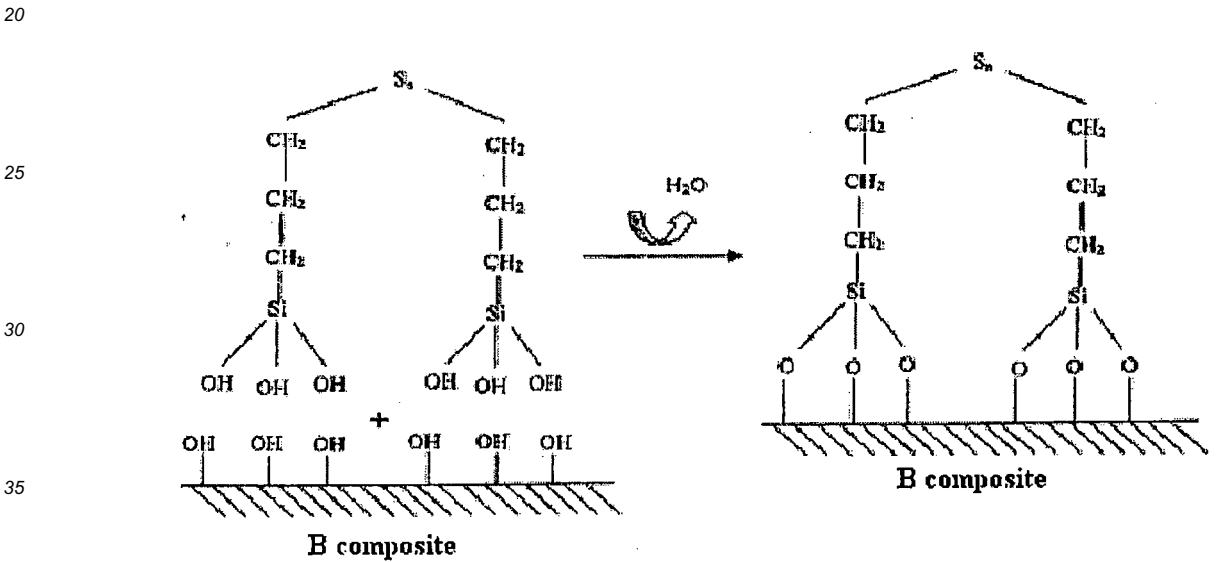
b) a condensation reaction of the A composite surface hydroxyls and the vinyltriethoxysilane hydroxyls

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A condensation reaction between the B composite surface hydroxyls and the bis(trihydroxysilyl)propyl polysulfide hydroxyls



[0022] In said step 2) the A and B composites, as pre-processed in said step 1), are mixed with a solution polymer based binding system such as: NBR, chloroprene, SBR, polyisoprene, polybutadiene, butyl, silicone, fluorurated and urethane rubbers.

[0023] Preferably, the following solvents are herein used: toluene, xylene, dimethylketone methylethylketone, saturated C6-C10 linear and cyclic hydrocarbons.

[0024] The solutions contain the polymer in a rate up to 30% by weight.

[0025] The preferred mixing system comprises a "Z branch" or a planetary system.

[0026] The mixing time is preferably from 30 to 45 minutes, depending on the desired end viscosity.

[0027] The A composite may be introduced into the mixture in a rate up to 80% by weight.

[0028] The B composite may be introduced into the mixture in a rate up to 90% by weight.

[0029] This difference will depend on the required technical performance.

[0030] The process aid is introduced into the mixture in a rate up to 7% by weight.

[0031] As the A composite amount increases, a viscous creeping reduction in the gasket made from the plate is detected.

[0032] As the B composite amount increases, a decrease of the fluid loss (leakage) rate through the gasket made from the plate is detected.

[0033] In said step 3) the mixture of step 2) may be processed through calendaring or spreading and optionally coupled to a support, if either plates or continuous films are to be achieved.

[0034] In said step 4), the half-finished articles of step 3) are subjected to a thermal cycle up to 250°C depending on the used process aid polymer and solvent, with a heating rate from 1°C/minute.

[0035] The main reaction herein occurring are:

- a) a breaking of the polysulfide residue;
- b) a cross-linking reaction.

**Examples:**

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**Formulation 1**

**[0036]**

- 10 1) Treating 10 kg of biosoluble fiber with 100 g vinyltriethoxysilane in ethanol at 5%, in a mixer for 12-24 hours, while processing 5 kg muscovite mica, with a particle size from 10 to 50  $\mu\text{m}$  and 1 kg foamed phlogophite mica with a particle size from 200 to 500  $\mu\text{m}$ , with 150 g bis(triethoxysilylpropyl)polysulfide in ethanol at 5% in a mixer for 12-24 hours.
- 15 2) Drying the processed A and B composites, in a dryer, with a solvent abatement system for 4 hours at 50°C, in steel basins or vats.
- 3) Mixing the dried A and B composites with 200 g NBR in a toluene solution at 20% and 1.8 kg deionized water, in a planetary mixer for a minimum time of 20 minutes.
- 4) Depositing the mixture of step 3) on a stainless steel 321 grid metal support, by a calendaring process.
- 5) Thermally processing in an oven at 180°C for 180 minutes.
- 20 6) Coating the sheet element by a PET and silica protective film with a thickness larger than 5  $\mu\text{m}$ .

**[0037]** It has been found that the invention fully achieves the intended aim and objects.

**[0038]** In fact, the invention has provided a method of making a composite material, particularly suitable for making sealing systems, comprising a combination of biosoluble ceramics fibers and mineral fillers.

25 **[0039]** The method according to the present invention provides an end product consisting of an uneven weave of biosoluble ceramics fibers, operating as a structural support for inorganic composites having a lamellar layered structure.

**[0040]** The sealing system composite material according to the present invention comprises a biosoluble fiber matrix having a thermal resistance up to 1000°C, with lamellar layered structure inorganic composites having a particle size from 1  $\mu\text{m}$ .

30 **[0041]** The use of organosilanes in the subject method provides a mechanically continuous phase between the biosoluble fiber structure and the lamellar structure inorganic composites.

**[0042]** Moreover, the method according to the present invention provides semifinished sheets, plates, films or sheet elements coupled to other materials such as metal and non-metal fiber fabrics, smooth, perforated and/or diamond shaped metal laminates and other articles.

35 **[0043]** The composite material made by the present invention may be used at high temperatures up to 1,000°C, even in the presence of strongly oxidizing agents.

**[0044]** Moreover, the inventive composite material may also be used for high temperature sealing systems.

**[0045]** Furthermore, the inventive composite material may also be used as a protective film coated on surfaces of the sheet elements.

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**Claims**

- 45 1. A method for making a composite material for sealing systems, said composite material comprising a biosoluble ceramics fiber matrix operating as a structural support for inorganic composites having a lamellar layered structure, said method comprising the steps of:

chemically pre-processing biosoluble ceramics fibers in an aqueous solution with vinyltriethoxysilane and mineral fillers with bis(triethoxysilylpropyl)-polysulfide or vice versa;

50 slowly mixing the chemically pre-processed biosoluble ceramics fibers and mineral fillers by an elastomeric material solution;

forming a plate and/or a laminate structure with said structural support;

thermally curing said plate and/or laminated structure; and

55 hot coating, by vacuum calendaring, on a surface of said plate and/or laminated structure, an anti-adhering protective film having a thickness larger than 5 $\mu\text{m}$ , based on high temperature silica and PET.

- 2. A method, according to claim 1, **characterized in that** said mineral fillers comprise one or more of mica, muscovite and phlogophite, bentonite, montmorillonite, laponite, hydrotalcite, kaolin, lamellar structure silicates, phyllosilicates,

and thermally, ultrasonically and/or chemically foamed, phlogopite mica.

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3. A method, according to claim 1, **characterized in that** said vinyltriethoxysilane is in a form of an aqueous or organic solution at a concentration from 0.1 to 30% by weight, said vinyltriethoxysilane being applied in an amount from 0.5% to 30% by weight based on the biosoluble ceramics fibers, said bis(triethoxysilylpropyl)polysulfide being in a form of an aqueous or organic solution at a concentration from 0.1 to 60% by weight, said bis(triethoxysilylpropyl)polysulfide being applied in an amount from 0.5% to 30% by weight with respect to said mineral fillers, said pre-processing being carried out separately in a closed pre-processing vessel and under stirring at a temperature from 25°C to 80°C for 24 hours.
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4. A method, according to claim 1, **characterized in that** said elastomeric material solution is a solution of a polymeric material selected from one or more of NBR, chloroprene, SBR, polyisoprene, polybutadiene, butyl, silicone, and fluorinated and urethane rubbers.
- 15
5. A method, according to claim 1, **characterized in that** in said method solvents selected from toluene, xylene, dimethylketone, methylethylketone, saturated C6-C10 linear and cyclic hydrocarbons are used.
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6. A composite material for making sealing systems by a method according to claim 1, **characterized in that** said biosoluble ceramics fiber matrix consists of an uneven weave arrangement of biosoluble fibers.
- 25
7. A composite material, according to claim 6, **characterized in that** said biosoluble ceramics fiber matrix has a thermal resistance less than 1,000°C and said inorganic lamellar layered structure composites have a particle size larger than 1 µm.

#### Patentansprüche

- 30
1. Verfahren zur Herstellung eines Verbundstoffmaterials für Versiegelungssysteme, wobei das Verbundstoffmaterial eine biolösliche Keramikfasermatrix umfasst, die als ein struktureller Träger für anorganische Verbundstoffe fungiert, die eine lamellenförmige Schichtstruktur aufweisen, wobei das Verfahren die folgenden Schritte umfasst:
- 35
- chemisches Vorverarbeiten von biolöslichen Keramikfasern in einer wässrigen Lösung mit Vinyltriethoxysilan und mineralischen Füllstoffen mit Bis(triethoxysilylpropyl)-polysulfid oder umgekehrt;  
langsameres Mischen der chemisch vorverarbeiteten biolöslichen Keramikfasern und mineralischen Füllstoffe durch eine Elastomermateriallösung;  
Bilden einer Platte und/oder einer Laminatstruktur mit dem strukturellen Träger;  
Wärmehärten der Platte und/oder der laminierten Struktur; und  
Heißbeschichten durch Vakuumkalandrieren auf einer Oberfläche der Platte und/oder laminierten Struktur eines Antihafschutzfilms mit einer Dicke von mehr als 5 µm basierend auf Hochtemperatur-Siliciumdioxid und PET.
- 40
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die mineralischen Füllstoffe einen oder mehrere von Glimmer, Muskovit und Phlogopit, Bentonit, Montmorillonit, Laponit, Hydrotalkit, Kaolin, Silikaten mit lamellenförmiger Struktur, Phyllosilikaten und thermisch, durch Ultraschall und/oder chemisch geschäumtem Phlogopit-Glimmer umfasst.
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3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** das Vinyltriethoxysilan in Form einer wässrigen oder organischen Lösung in einer Konzentration von 0,1 bis 30 Gew.-% vorliegt, wobei das Vinyltriethoxysilan in einer Menge von 0,5 Gew.-% bis 30 Gew.-% basierend auf den biolöslichen Keramikfasern angewendet wird, wobei das Bis(triethoxysilylpropyl)polysulfid in Form einer wässrigen oder organischen Lösung in einer Konzentration von 0,1 bis 60 Gew.-% vorliegt, wobei das Bis(triethoxysilylpropyl)polysulfid in einer Menge von 0,5 Gew.-% bis 30 Gew.-% in Bezug auf die mineralischen Füllstoffe angewendet wird, wobei das Vorverarbeiten getrennt in einem geschlossenen Vorverarbeitungsbehälter und unter Rühren 24 Stunden lang bei einer Temperatur von 25 °C bis 80 °C ausgeführt wird.
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4. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die Elastomermateriallösung eine Lösung eines Polymermaterials ist, das ausgewählt ist aus einem oder mehreren von NBR, Chloropren, SBR, Polyisopren, Polybutadien, Butyl, Silikon und fluorierten und Urethankautschuken.
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## EP 2 728 046 B1

5. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** in dem Verfahren Lösungsmittel verwendet werden, die ausgewählt sind aus Toluol, Xylol, Dimethylketon, Methylethylketon, gesättigten linearen und cyclischen C6-C10-Kohlenwasserstoffen.
- 5 6. Verbundstoffmaterial zur Herstellung von Versiegelungssystemen durch ein Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** die biolösliche Keramikfasermatrix aus einer ungleichmäßigen Webanordnung biolöslicher Fasern besteht.
- 10 7. Verbundstoffmaterial nach Anspruch 6, **dadurch gekennzeichnet, dass** die biolösliche Keramikfasermatrix einen Wärmewiderstand von weniger als 1.000 °C aufweist und die anorganische Verbundstoffe mit lamellenförmiger Schichtstruktur eine Teilchengröße von mehr als 1 µm aufweisen.

### Revendications

- 15 1. Procédé de fabrication d'un matériau composite pour des systèmes d'étanchéité, ledit matériau composite comprenant une matrice de fibres de céramique biosolubles fonctionnant comme un support structurel pour les composites inorganiques ayant une structure stratifiée lamellaire, ledit procédé comprenant les étapes de :
- 20 prétraitement chimique de fibres de céramique biosolubles dans une solution aqueuse avec du vinyltriéthoxysilane et de charges minérales avec du polysulfure de bis(triéthoxysilylpropyle) ou inversement ; mélange lentement des fibres de céramique biosolubles et des charges minérales chimiquement prétraitées par une solution de matériau élastomère ;
- 25 formation d'une plaque et/ou d'une structure lamellaire avec ledit support structurel ; durcissement thermique de ladite plaque et/ou de ladite structure stratifiée ; et revêtement à chaud, par calandrage à vide, sur une surface de ladite plaque et/ou de ladite structure stratifiée, d'un film protecteur antiadhésif ayant une épaisseur supérieure à 5 µm, basé sur une silice à température élevée et du PET.
- 30 2. Procédé selon la revendication 1, **caractérisé en ce que** lesdites charges minérales comprennent un ou plusieurs éléments choisis parmi le mica, la muscovite et la phlogopite, la bentonite, la montmorillonite, la laponite, l'hydrotalcite, le kaolin, les silicates de structure lamellaire, les phyllosilicates et un mica phlogopite expansé thermiquement, par ultrasons et/ou chimiquement.
- 35 3. Procédé selon la revendication 1, **caractérisé en ce que** ledit vinyltriéthoxysilane est sous la forme d'une solution aqueuse ou organique à une concentration de 0,1 à 30 % en poids, ledit vinyltriéthoxysilane étant appliqué en une quantité de 0,5 % à 30 % en poids par rapport aux fibres de céramique biosolubles, ledit polysulfure de bis(triéthoxysilylpropyle) étant sous la forme d'une solution aqueuse ou organique à une concentration de 0,1 à 60 % en poids, ledit polysulfure de bis(triéthoxysilylpropyle) étant appliqué en une quantité de 0,5 % à 30 % en poids par
- 40 rapport auxdites charges minérales, ledit prétraitement étant réalisé de manière séparée dans un récipient de prétraitement fermé et sous agitation à une température de 25 °C à 80 °C pendant 24 heures.
- 45 4. Procédé selon la revendication 1, **caractérisé en ce que** ladite solution de matériau élastomère est une solution d'un matériau polymère choisi parmi un ou plusieurs de NBR, chloroprène, SBR, polyisoprène, polybutadiène, butyle, silicone et caoutchoucs d'uréthane et fluorés.
- 50 5. Procédé selon la revendication 1, **caractérisé en ce que** lesdits solvants du procédé choisis parmi le toluène, le xylène, la diméthylcétone, la méthyléthylcétone, les hydrocarbures en C6-C10 linéaires et cycliques saturés sont utilisés.
- 55 6. Matériau composite pour la préparation de systèmes d'étanchéité par un procédé selon la revendication 1, **caractérisé en ce que** ladite matrice de fibres de céramique biosolubles se compose d'un arrangement tissé irrégulier de fibres biosolubles.
7. Matériau composite selon la revendication 6, **caractérisé en ce que** ladite matrice de fibres de céramique biosolubles a une résistance thermique inférieure à 1 000 °C et lesdits composites inorganiques de la structure stratifiée lamellaire ont une granulométrie supérieure à 1 µm.