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(54) Title: PRE-IMPREGNATED FIBRE-REINFORCED COMPOSITE MATERIAL AND FIBRE-REINFORCED COMPOSITE CERAMIC MATERIAL, OBTAINED BY FORMING AND SUBSEQUENT PYROLYSIS OF SAID PRE-IMPREGNATED MATERIAL

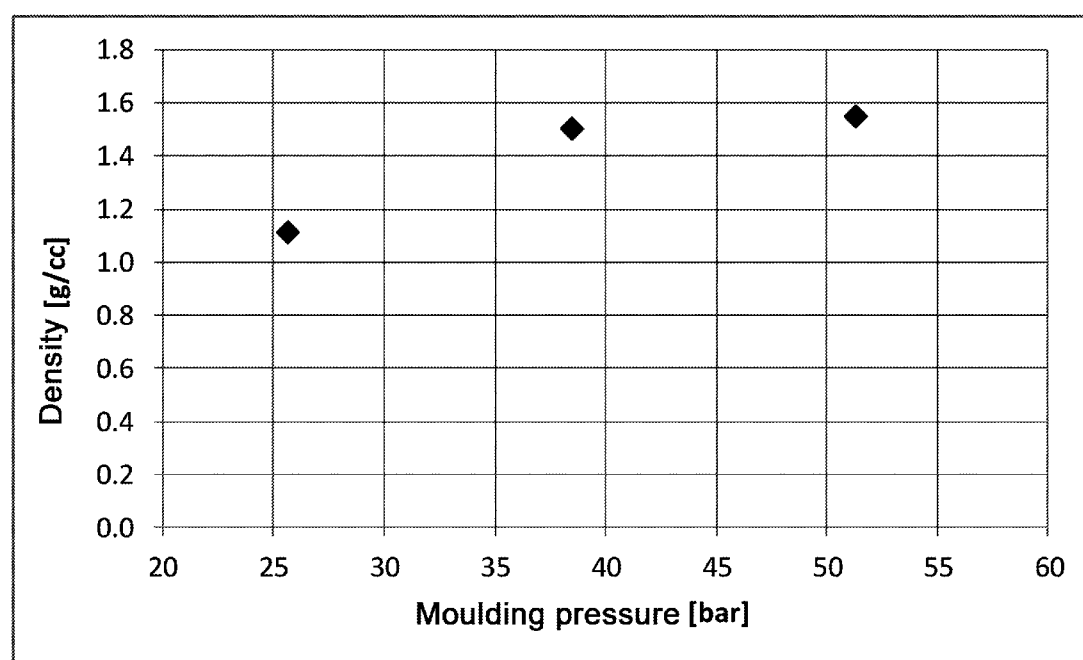


FIG.1

(57) Abstract: The invention relates to a pre-impregnated fibre-reinforced composite material in laminar form, obtained impregnating a fibrous mass with a polymeric binder composition and intended to be subjected to successive forming and pyrolysis operations to produce a fibre-reinforced composite ceramic material. The polymeric binder composition is based on one or more resins chosen from the group consisting of siloxane resins and silsesquioxane resins, and can optionally comprise one or more organic resins. The polymeric binder composition is a liquid with viscosity between 55000 and 10000 mPas at temperatures between 50°C and 70°C. The polymeric binder composition forms a polymeric binding matrix, not cross-linked or only partially cross-linked that fills the interstices of the fibrous mass. The invention also relates to a method for making said pre-impregnated fibre-reinforced composite material in laminar



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"PRE-IMPREGNATED FIBRE-REINFORCED COMPOSITE MATERIAL
AND FIBRE-REINFORCED COMPOSITE CERAMIC MATERIAL,
OBTAINED BY FORMING AND SUBSEQUENT PYROLYSIS OF SAID
5 PRE-IMPREGNATED MATERIAL"

Field of the Invention

[0001] The present invention relates to a pre-impregnated
fibre-reinforced composite material and a fibre-
reinforced composite ceramic material, obtained by
10 forming and subsequent pyrolysis of said pre-impregnated
(pre-preg) material.

[0002] The pre-impregnated fibre-reinforced composite
material according to the present invention (hereafter
also, more briefly, called "pre-preg") is intended to be
15 subjected to successive forming and pyrolysis operations
to obtain a fibre-reinforced composite ceramic material,
finding application as a basic material for the
production - through successive treatments and work
processes (forming, pyrolysis and possibly
20 densification) - of components intended to operate at
medium temperatures, even higher than 400°C, for example
heat-resistant bulkheads or other components intended to
operate at high temperatures.

State of the art

25 [0003] As is known, in the technical jargon a fibre-

reinforced composite material pre-impregnated with a polymeric binder composition is simply called "pre-preg".

[0004] A pre-preg consists of fibres, generally carbon
5 fibres and/or glass fibres and/or ceramic fibres, arranged to form a fabric or a nonwoven fabric, and impregnated with a thermosetting or thermoplastic polymeric composition. During any forming process, the polymeric composition, impregnating the fibres, forms a
10 binding matrix that fixes the fibres to each other.

[0005] Thermoplastic matrices are processed by heating to higher temperatures than the typical glass transition temperature of the material. This allows polymeric chains to move and slide on each other, until the
15 temperature is again brought below the glass transition temperature (T_g), in a reversible process.

[0006] In the case of thermosetting matrices, the work processes are carried out before an amount of chemical bonds is created between adjacent chains (cross-linking
20 or curing) such as to prevent their relative motion, bringing the polymer to be cured in a non-reversible process.

[0007] In pre-preg production, the thermosetting polymeric compositions used are based on organic resins, generally
25 epoxydic or phenolic, or resins based on vinyl ester or

cyanate ester. For these purposes, within these resin families, resins are used with such rheological characteristics (in particular viscosity) as to allow the obtainment of the desired degree of
5 integration/impregnation between fibres and resin during the impregnation phase.

[0008] In the production of pre-preg, the thermoplastic polymeric binder compositions used are, for example, polyetheretherketone (PEEK), polyetherimide (PEI) and
10 poly paraphenylene sulphide (PPS).

[0009] During the production of the pre-preg the thermosetting polymeric matrix is not crosslinked or is only partially crosslinked, so as to make the pre-preg manipulable, but still workable. For this purpose, the
15 pre-preg is preserved at low temperature to avoid the completion of cross-linking.

[0010] Operatively, the process for producing a pre-preg comprises an impregnating step in which the fibres are placed on flat surfaces and in this configuration they
20 are impregnated with the polymeric composition. During this step, the partial cross-linking of the thermosetting polymeric composition can take place at variable temperatures in the prior art according to the polymeric composition used. The material is then cooled
25 to ambient temperature. The pre-preg is then available

in the form of flat workable foils, which may then be worked to obtain components with far more complex shapes, for example by layering or rolling and subsequent shaping operations.

5 [0011] The organic resins provide the pre-preg with good mechanical resistance characteristics already after partial cross-linking.

[0012] However, pre-pregs made with organic resins have a series of limits that affect the characteristics of the materials obtained from them, or that make them unusable
10 in fact for determined applications.

[0013] For example, organic resins form, as a result of pyrolysis, a carbonaceous residue, which in the case of epoxy resins is also very limited and insufficient to
15 assure a good consistency of the composites. Said carbonaceous residue, moreover, is not suitable for applications with high temperatures in oxidising environment and does not have sufficient hardness to assure good abrasion resistance.

20 [0014] For example, the low yield of epoxy resins as a result of pyrolysis makes pre-pregs based on epoxy resins inadequate for the manufacture of preforms for densification processes.

[0015] A traditional pre-preg based on organic resins can
25 present, for example, the following limits:

- low operating temperature of the composites obtained after complete cross-linking of the resins; while these composites have excellent mechanical resistance characteristics, it is difficult for them to work above
5 200°C in oxidising atmosphere;
 - low resistance to wear by mechanical abrasion, due to the presence of carbonaceous matrices in the compounds obtained;
 - impossibility to generate amorphous and/or
10 crystalline inorganic structures as a result of pyrolysis;
 - low thermal conductivity of the composite, which makes is unsuitable for applications that require high heat dissipation capability
- 15 [0016] There is the need to obtain pre-pregs that can lead, as a result of pyrolysis of temperatures between 400°C and 1500°C, to the formation of amorphous and/or crystalline inorganic structures, such as to make the composite materials thus obtained:
- 20 - characterised by high thermal conductivity;
 - adequate to the manufacture of preforms for densification processes;
 - characterised by higher hardness so as to assure superior abrasion resistance.
- 25 [0017] To date, this need has not been met because

alternative resins, potentially able to satisfy the
aforesaid technical requirements, for example silicone-
organic preceramic resins (siloxane resins, silazane
resins, etc.), nevertheless have such rheological
5 characteristics as to make them unsuitable for the
impregnation of fibrous masses with common pre-preg
fabrication technologies.

Description of the invention

[0018] Therefore, an object of the present invention is to
10 eliminate, or at least to reduce, the aforementioned
problems, relating to the prior art, making available a
pre-impregnated fibre-reinforced composite material
(pre-preg) with a polymeric binder composition that does
not contain, or at least does not exclusively contain
15 organic resins, such as epoxydic or phenolic resins or
resins based on vinyl ester or cyanate ester.

[0019] In particular, an object of the present invention
is to make available a pre-impregnated fibre-reinforced
composite material (pre-preg) with a polymeric binder
20 composition that does not contain, or at least does not
exclusively contain organic resins, such as epoxy resins
or phenolic resins, and that can lead, as a result of
pyrolysis at temperatures between 400°C and 1500°C, to
the formation of amorphous and/or crystalline inorganic
25 structures, such as to make the composite materials thus

obtained adequate for the production of preforms for high temperature processes.

[0020] In particular, an object of the present invention is to make available a pre-impregnated fibre-reinforced composite material (pre-preg) with a polymeric binder composition that does not contain, or at least does not exclusively contain organic resins, such as epoxy resins or phenolic resins based on vinyl ester or cyanate ester, and that can lead, as a result of pyrolysis at temperatures between 400°C and 1500°C, to the formation of amorphous and/or crystalline inorganic structures, such as to make the composite materials thus obtained adequate for manufacturing preforms for densification processes and characterised by higher hardness so as to assure superior abrasion resistance and high thermal conductivity.

Description of the drawings

[0021] The technical features of the invention can be clearly understood from the content of the claims that follow and its advantages shall be more readily apparent in the detailed description that follows, made with reference to the accompanying drawings, which represent one or more purely exemplifying and non-limiting embodiments, in which:

- Figure 1 shows the graph of density versus moulding

pressure of a fibre-reinforced composite material obtained by hot forming (through compression moulding) of a pre-preg and from which a fibre-reinforced composite ceramic material is obtained by pyrolysis.

5 Detailed description

[0022] The present invention refers to a pre-impregnated fibre-reinforced composite material in laminar form, obtained impregnating a fibrous mass with a polymeric binder composition, known in the jargon as pre-preg.

10 [0023] Said pre-impregnated fibre-reinforced composite material is intended to be subjected to successive subsequent forming and pyrolysis operations to obtain a fibre-reinforced composite ceramic material.

[0024] According to the invention, unlike traditional pre-
15 pregs impregnated exclusively with organic resins (phenolic or epoxydic resins or resins based on vinyl ester or cyanate ester), the polymeric binder composition is based on one or more resins selected in the group consisting of siloxane resins and
20 silsesquioxane resins.

[0025] The expression "based on ..." means that the resins selected in the group consisting of siloxane resins and silsesquioxane resins constitute at least 70% by weight of the polymeric binder composition.

25 [0026] Optionally, the aforesaid polymeric binder

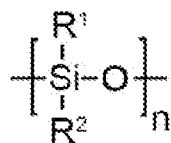
composition can comprise organic resins, preferably epoxy resins, phenolic resins and/or resins based on vinyl ester or cyanate ester. However, organic resins, if present, do not constitute more than 30% by weight of the polymeric binder composition.

[0027] Preferably, the aforesaid polymeric binder composition comprises only resins chosen in the group consisting of siloxane resins and silsesquioxane resins, and does not comprise organic resins.

[0028] Silsesquioxane resins are polymeric resins comprising polysiloxanes or are polysiloxane-based, while silsesquioxane resins are polymeric resins comprising polysilsesquioxanes or are polysilsesquioxane-based.

[0029] Polysiloxanes and polysilsesquioxanes are compounds characterised by the presence of silicon - oxygen bonds in the main chain.

[0030] polysiloxanes have the following basic structure



while polysilsesquioxanes have the following basic structure

[0031] According to $\left[\text{Si} \begin{smallmatrix} \text{R} \\ \text{O} \end{smallmatrix} \right]_{1.5n}$ another aspect of the present invention, the aforesaid polymeric binder composition is a liquid with
5 viscosity between 55000 and 10000 mPas at temperatures between 50°C and 70 °C.

[0032] In particular, viscosity is understood to be measured with a Brookfield viscometer, with a shear rate of 1 s⁻¹, unless otherwise indicated in the text.

10 [0033] In particular, the aforesaid polymeric binder composition is a pseudo-plastic liquid up to temperatures of approximately 60°C tending to a Newtonian behaviour beyond this temperature, with viscosity between approximately 55000 mPas at 50°C and
15 1 s⁻¹ and approximately 10000 mPas at 70°C regardless of shear rate.

[0034] In particular, the polymeric composition also has a pseudo-plastic behaviour (with viscosity decreasing as the shear rate increases) that increases as temperature
20 decreases. This feature allows the polymeric composition to behave like an elastic, flexible solid at ambient temperature, thus preventing it from dripping and being separated from the fibres. At growing temperatures, on the contrary, the polymeric composition tends to behave
25 progressively more like a fluid, until becoming nearly

Newtonian. Viscosity at 50°C is equal to approximately 55000 mPas applying a shear rate of 1s^{-1} and 25000 mPas applying a shear rate of 3s^{-1} . At 60°C, viscosity is approximately 18000 mPas at 3s^{-1} and measures 16000 mPas at 8.5s^{-1} , hence tending to the typical behaviour of a Newtonian fluid.

[0035] These rheological characteristics make the polymeric binder composition particularly suited to the impregnation of fibrous masses in the process of manufacturing a pre-impregnated fibre-reinforced composite material in laminar form, overcoming the limits that hitherto have prevented its use.

[0036] In the pre-impregnated fibre-reinforced composite material in laminar form according to the invention, the polymeric binder composition forms a binding matrix, not cross-linked or only partially cross-linked, which fills the interstices of the fibrous mass. In this way, the fibre-reinforced composite material in laminar form is on one hand manipulable, and on the other hand still flexible. The solidification of the polymeric binder composition in the pre-preg would entail its stiffening with consequent loss of the workability characteristics.

[0037] Advantageously, the pre-impregnated fibre-reinforced composite material in laminar form according to the invention can be obtained according to a

traditional production process for the manufacture of a pre-preg:

- arranging the fibrous mass in laminar form;
- impregnating step, in particular at temperatures
5 between 60 and 100°C, during which the fibrous mass is impregnated with the polymeric binder composition and the polymeric binder composition may be partially cross-linked; and
- cooling to ambient temperature the composite material
10 thus obtained.

[0038] In particular, application of the polymeric binder composition on the fibrous mass can be obtained depositing the polymeric composition beforehand on a transfer support (for example, made of paper). The
15 presence of the transfer support facilitates the deposition of the polymeric binder composition on the fibrous mass. The deposition of the polymeric composition on the transfer support is achieved in a so-called step of filming the polymeric binder composition.

20 [0039] Alternatively, the polymeric binder composition can be applied directly on the fibrous mass.

[0040] In particular, the pre-impregnated fibre-reinforced composite material according to the invention can be obtained in the form of flat workable foils, which may
25 then be subsequently processed to obtained components

with much more complex shapes, for example by stratification or rolling and subsequent shaping operations. These components are subsequently subjected to additional treatments (complete cross-linking, 5 pyrolysis, densification) to obtain final products with specific characteristics.

[0041] Siloxane and silsesquioxane resins have different characteristics from the organic (mainly epoxydic) resins normally used for manufacturing pre-pregs based 10 on carbon fibres or glass fibres or ceramic fibres.

[0042] A peculiar characteristic of siloxane resins and silsesquioxane resins is the ability to form, as a result of pyrolysis at temperatures between 400 and 900°C, amorphous structures consisting of Si-O-C chains. These 15 structures can be crystallised by heat treatments at higher temperatures, around 1300-1500°C. In this way it is possible to form, starting from resins selected from the group consisting of siloxane resins and silsesquioxane resins, silicon Carbide, a compound with 20 properties of technological interest, such as: very high hardness, high elastic modulus, high melting point and thermal stability, high thermal conductivity.

[0043] Instead, organic resins form, as a result of pyrolysis, a carbonaceous residue, which in the case of 25 epoxy resins is also very limited and insufficient to

assure a good consistency of the composites. Said carbonaceous residue, moreover, is not suitable for applications with high temperatures in oxidising environment and does not have sufficient hardness to
5 assure good abrasion resistance. For this reason, according to the invention, the polymeric binder composition preferably does not contain organic resins. In any case, the content of organic resins is no higher than 30% by weight of the polymeric binder composition,
10 so as to limit the negative effect given by the presence of the organic resins.

[0044] Organic resins are theoretically more suited for manufacturing pre-pregs to be used "as cured" and at low temperatures, because they provide the composite with
15 superior mechanical characteristics.

[0045] The pre-impregnated fibre-reinforced composite material with polymeric binder composition based on siloxane resins and/or silsesquioxane resins pyrolyzed and optionally densified according to the invention is
20 particularly indicated for applications at high temperatures, in conditions at which the compounds with exclusively organic base could not operate.

[0046] The materials obtained starting from a pre-impregnated fibre-reinforced composite material (pre-
25 preg) according to the invention can be used for

obtaining preforms to be pyrolyzed and densified.

[0047] Siloxane or silsesquioxane resins, given the reduced weight loss after pyrolysis and the possibility of forming silicon Carbide, are indicated to make
5 preforms to be densified. The term "densification" means processes such as: polymer impregnation and pyrolysis (PIP) or liquid silicon infiltration (LSI).

[0048] As will be described in more detail below, the characteristics of a composite obtained from a pre-preg
10 according to the invention after pyrolysis and optionally densification are:

- medium mechanical characteristics (ultimate tensile stress up to approximately 300-350 MPa, a value that is influenced by many factors, including fibres and types
15 and levels of densification);
- Low thermal conductivity ($>1 \text{ W/(m}\cdot\text{°K)}$);
- Good resistance to abrasion wear;
- Operating temperature up to 1000°C , in any case variable according to the densification processes.

20 [0049] Applications for which composites obtained in this way can be of interest are, for example, heat resistant bulkheads or other components intended to operate at high temperatures.

[0050] The above advantages are evident if the preform is
25 subjected to densification process with PIP techniques.

The use of resins containing silicon is the only way to generate silicon Carbide in matrix directly in the preform. This could in no way be obtained if the preform were produced from pre-preg based on organic resins.

5 This aspect allows to realise, with PIP techniques, composites with a significantly higher content of silicon Carbide in matrix than the composites obtained applying the same techniques to carbonaceous preforms obtained exclusively from organic resins.

10 [0051] These advantages instead are less evident in the case of densification with LSI technique. It should be recalled that the infiltration with silicon allows to form a high quantity of silicon Carbide in matrix also starting from a pre-preg with organic base (for example
15 a phenolic pre-preg).

* * *

[0052] According to a preferred embodiment of the invention, the aforesaid polymeric binder composition constitutes from 25% to 60% by weight of said pre-
20 impregnated fibre-reinforced composite material, while the fibrous mass constitutes from 40% to 75% by weight of said pre-impregnated fibre-reinforced composite material.

[0053] The content of fibres and of polymeric binder
25 composition can be varied according to the

characteristics to be obtained in the final materials to be produced starting from the pre-preg according to the invention.

[0054] A pre-preg with high fibre content is more indicated
5 for applications for which high mechanical characteristics are required. A higher percentage of polymeric binder composition can instead be more indicated for applications requiring higher operating temperatures, flameproof protection or resistance to
10 mechanical wear.

[0055] According to a preferred embodiment of the invention, the aforesaid polymeric binder composition comprises a mixture of:

- at least one resin selected from the group consisting
15 of siloxane and silsesquioxane resins, solid at room temperature, with melting point range of between 40 °C and 90 °C; and
- at least one resin selected from the group consisting of siloxane resins and silsesquioxane resins, liquid at
20 room temperature, with viscosity at ambient temperature of between 1 mPas and 5000 mPas.

[0056] In general, the weight ratio between solid resin at ambient temperature and liquid resin at ambient temperature is selected so that the polymeric binder
25 composition obtained is a liquid with viscosity between

55000 and 10000 mPas at temperatures between 50°C and 70°C.

[0057] In particular, the aforesaid polymeric binder composition is a pseudo-plastic liquid up to
5 temperatures of approximately 60°C tending to a Newtonian behaviour beyond this temperature, with viscosity between approximately 55000 mPas at 50°C and 1 s⁻¹ and approximately 10000 mPas at 70°C regardless of shear rate.

10 [0058] In particular, the polymeric composition also has a pseudo-plastic behaviour (with viscosity decreasing as the shear rate increases) that increases as temperature decreases. This feature allows the polymeric composition to behave like an elastic, flexible solid at ambient
15 temperature, thus preventing it from dripping and being separated from the fibres. At growing temperatures, on the contrary, the polymeric composition tends to behave progressively more like a fluid, until becoming nearly Newtonian. Viscosity at 50°C is equal to approximately
20 55000 mPas applying a shear rate of 1s⁻¹ and 25000 mPas applying a shear rate of 3 s⁻¹. At 60°C, viscosity is approximately 18000 mPas at 3 s⁻¹ and measures 16000 mPas at 8.5 s⁻¹, hence tending to the typical behaviour of a Newtonian fluid.

25 [0059] Preferably, the weight ratio between solid resin at

room temperature and liquid resin at room temperature is between 100/30 and 100/50.

[0060] Advantageously, the aforesaid polymeric binder composition can consist entirely of the aforesaid mixture of solid resin and liquid resin at ambient temperature.

[0061] Preferably, the solid resin at ambient temperature is selected from the group consisting of: a phenyl siloxane resin (for example, commercial products Silres 601 or RSN-0217), methyl siloxane resin, methyl phenyl silsequioxane resin (for example, the commercial product Silres H44), methyl silsesquioxane resin (for example, commercial product Silres MK).

[0062] Preferably, the liquid resin at ambient temperature is selected from the group consisting of: a methyl methoxy siloxane resin (for example, commercial product Silres MSE 100) and methyl phenyl vinyl siloxane resin (for example, commercial product Silres H62 C).

[0063] Advantageously, the liquid resin can be selected among the liquid siloxane resins with no solvent or with solvent content below 2% by weight.

[0064] According to a preferred embodiment of the invention, the solid resin is a phenyl siloxane resin, while the liquid resin is a methyl methoxy siloxane resin.

[0065] Advantageously, the aforesaid polymeric binder composition can further comprise at least one solvent, selected among the compounds able to solubilise polysiloxanes and polysilsesquioxanes. The function of the solvent is to maintain over time the rheological characteristics of the resin, thus making the pre-preg manipulable for a longer time, so that the pre-preg can be processed more easily and preserved for longer times.

[0066] Preferably, the aforesaid solvent is divinylbenzene, which has the advantage of having low vapor pressure (it tends to evaporate less) and not being flammable, unlike other solvents usable for the purpose, for example toluene or acetone.

[0067] Preferably, the solvent (if present) constitutes less than 1% by weight of the pre-impregnated fibre-reinforced composite material. Preferably, the solvent (if present) constitutes no less than 0.2% by weight of the pre-impregnated fibre-reinforced composite material.

[0068] Advantageously, the aforesaid polymeric binder composition can comprise at least one catalyst adapted to promote the cross-linking of the polymers (polysiloxanes and/or polysilsesquioxanes) of the polymeric binder composition at temperatures above 100°C.

[0069] The presence of the catalyst makes the processes

more suitable for industrial production because it reduces the times and temperatures necessary to form the pieces.

[0070] In particular, the catalyst can be inserted
5 directly in the polymeric composition or it can be added to the polymeric binder composition during the preparation of the pre-preg, at a temperature lower than 100°C, so that, during these steps, it remains latent and does not initiate the cross-linking reaction of the
10 polymeric binder composition. The catalyst then has to perform its function at the temperature at which the composite would subsequently be formed (for example 150-180°C).

[0071] Preferably, the catalyst is selected from the group
15 consisting of titanates, metal octoates and amines or a combination thereof.

[0072] Still more preferably, the catalyst is selected from the group consisting of: titanium tetrabutanolate (for example supplied by Wacker with the commercial name
20 "Catalyst TC 44"); zinc octoate; and N-[3-(Trimethoxysilyl)propyl]ethylenediamine (for example, supplied by Wacker with the commercial name "Geniosil GF 91").

[0073] The catalyst (if present) constitutes less than 1%
25 by weight of the polymeric matrix of the pre-impregnated

fibre-reinforced composite material.

[0074] According to an alternative embodiment of the invention, the aforesaid polymeric binder composition can comprise a mixture of:

- 5 - a single resin selected from the group consisting of siloxane resins and silsesquioxane resins, liquid at ambient temperature, with viscosity at ambient temperatures of between 1 mPas and 5000 mPas; and
- an inert filler in powder form, able to provide the
10 polymeric binder composition with the rheological characteristics necessary to allow the impregnation of the fibrous mass.

[0075] The term "inert" means a substance that does not participate in the curing reactions.

- 15 [0076] In particular, the inert filler in powder form is introduced to increase the viscosity of the liquid resin at ambient temperature.

[0077] In general, the volume ratio between inert filler in powder form and liquid polymer at ambient temperature
20 is selected so that the polymeric binder composition obtained from their mixture is a liquid with viscosity between 55000 and 10000 mPas at temperatures between 50°C and 70°C.

[0078] Preferably, the volume ratio of inert filler to
25 liquid polymer at room temperature is between 10/100 and

40/100.

[0079] Advantageously, the aforesaid polymeric binder composition can consist entirely of the aforesaid mixture of liquid resin at ambient temperature and of
5 inert filler.

[0080] Advantageously, the aforesaid polymeric binder composition (even if it is defined by a mixture of multiple resins) can further comprise a thermal insulating inert filler, preferably selected from the
10 group consisting of oxides, silicates, phosphates or a combination thereof.

[0081] Preferably, the thermal insulating inert filler consists from 1% to 30% by volume of the pre-impregnated fibre-reinforced composite material.

15 [0082] The introduction of a thermal insulating inert filler in the polymeric binder composition is preferable if the pre-impregnated fibre-reinforced composite material is used to make materials to be used as thermal barriers.

20 [0083] Advantageously, the aforesaid fibrous mass can consist of fibres selected in the group consisting of: carbon fibres; glass fibres; ceramic fibres; or mixtures thereof.

[0084] In particular, carbon fibres are carbon fibres from
25 polyacrylonitrile (PAN) and/or carbon fibres from pitch.

[0085] In particular, glass or ceramic fibres consist of silica, alumina, zirconia or silicon Carbide.

[0086] According to a preferred embodiment, the aforesaid fibrous mass consists only of carbon fibres (PAN or
5 pitch).

[0087] Preferably, the fibrous mass consists of continuous fibres that form one or more layers of fabric or of nonwoven fabric.

[0088] Alternatively, the fibrous mass can consist of
10 broken fibres dispersed in the matrix formed by the aforesaid polymeric binder composition.

* * *

[0089] As stated, the content of fibres and of polymeric binder composition can be varied according to the
15 characteristics to be obtained in the final materials to be produced starting from the pre-preg according to the invention. A pre-preg with high fibre content is more indicated for indications for which high mechanical characteristics are required. A higher percentage of
20 resin can instead be more indicated for applications requiring higher operating temperatures, flameproof protection or resistance to mechanical wear.

[0090] Some formulations of the pre-impregnated fibre-reinforced composite material according to the
25 invention, without organic resins, are provided in the

following tables two tables 1 and 2.

Formulation 1	Pre-preg based on Pitch fibres [wt%]	Pre-preg based on PAN fibres [wt%]
Solid resin RSN-0217 (Dow Corning)	20 -40	20 -40
Liquid resin Silres MSE100 (Wacker)	<20	<20
Divinylbenzene (DVB)	< 1	< 1
fibre content	40- 70	40- 70

Table 1

Formulation 2	Pre-preg based on Pitch fibres [% by weight]	Pre-preg based on PAN fibres [% by weight]
Solid resin RSN-0217 (Dow Corning)	20 - 30	25 -35
Liquid resin Silres MSE100 (Wacker)	5 -15	5 -15
Divinylbenzene (DVB)	< 1	< 1
fibre content	55 - 65	50 -60

5

Table 2

[0091] Some general formulations of the pre-impregnated fibre-reinforced composite material according to the invention, also comprising at least one organic resin, are provided in Table 3 below.

10

Formulation 3	Pre-preg based on Pitch fibres	Pre-preg based on PAN fibres
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	[% by weight]	[% by weight]
Solid resin RSN-0217 (Dow Corning)	20 - 30	25 - 35
Liquid resin Silres MSE100 (Wacker)	0 - 5	0 - 5
Phenolic resin Norsophen 1203	5 - 10	5 - 10
Divinylbenzene (DVB)	< 1	< 1
fibre content	55 - 65	50 -60

Table 3

* * *

[0092] An object of the present invention is also a method for making a pre-impregnated fibre-reinforced composite material (intended to be subjected to subsequent forming and pyrolysis operations to make a fibre-reinforced composite material), in particular according to the present invention and in yet more detail as described above.

- 10 [0093] According to a general embodiment, said method comprises the following operating steps:
- arranging a fibrous mass in laminar form;
 - arranging a polymeric binder composition;
 - impregnating said fibrous mass with said polymeric binder composition obtaining a pre-impregnated fibre-reinforced composite material.
- 15

[0094] According to the invention, the aforesaid polymeric binder composition is based on one or more resins selected from the group consisting of siloxane resins and silsesquioxane resins.

20

[0095] As stated above, the expression "based on ..." means that the resins selected in the group consisting of siloxane resins and silsesquioxane resins constitute at least 70% by weight of the polymeric binder composition.

5 [0096] Optionally, the aforesaid polymeric binder composition can comprise organic resins, preferably epoxy resins, phenolic resins and/or resins based on vinyl ester or cyanate ester. However, organic resins, if present, do not constitute more than 30% by weight of
10 the polymeric binder composition.

[0097] Preferably, the aforesaid polymeric binder composition comprises only resins chosen in the group consisting of siloxane resins and silsesquioxane resins, and does not comprise organic resins.

15 [0098] As stated above, silsesquioxane resins comprise polysiloxanes, while silsesquioxane resins comprise polysilsesquioxanes.

[0099] According to the invention, the aforesaid polymeric binder composition is a liquid with viscosity between
20 55000 and 10000 mPas at temperatures between 50°C and 70 °C.

[00100] Following the impregnating step, the polymeric binder composition forms a binder polymeric matrix, not cross-linked or only partially cross-linked, which fills
25 the interstices of the fibrous mass.

[00101] What is described above in relation to the pre-impregnated fibre-reinforced composite material according to the invention also applies to the method for making said pre-impregnated material according to the invention. For the sake of brevity, this description is not repeated, however it is understood to be extended to the manufacturing method as well.

* * *

[00102] An object of the present invention is a fibre-reinforced composite ceramic material obtained by forming and pyrolysis of a pre-impregnated fibre-reinforced composite material (pre-preg) according to the invention, and in particular as described above.

[00103] The term "fibre-reinforced composite ceramic material" means, in general, a material having a ceramic or partially ceramic matrix within which are arranged reinforcing fibres.

[00104] The term "ceramic matrix" means the matrix obtained from the pyrolysis of the siloxane and/or silsesquioxane resins, which belong to the family of pre-ceramic resins. The partial or complete ceramization of the matrix can be obtained regulating the pyrolysis temperature. Pyrolysis treatments at low temperature (400-900°C) allow to obtain a partially pyrolyzed pyrolysis residue, still rich in organic structures.

Pyrolysis at higher temperatures entail the complete ceramization of the pyrolysis residue, which can form amorphous or crystalline inorganic structures (the latter at pyrolysis temperatures above approximately 5 1300°C).

[00105] The composition of the ceramic or partially ceramic matrix depends on the type of ceramic precursors used to produce the material.

[00106] In the specific case, the ceramic precursors 10 used are polysiloxanes or polysilsesquioxanes, contained in the polymeric binder composition of the pre-impregnated fibre-reinforced composite material (pre-preg) according to the invention, used as a starting base. The ceramic or partially ceramic matrix comprises 15 silicon oxycarbides (SiOC) and/or silicon Carbide (SiC). In particular, silicon oxycarbides (SiOC) can form amorphous structures consisting of Si-O-C chains of different lengths.

[00107] According to the invention, the pre-preg from 20 which the fibre-reinforced composite ceramic material is obtained by forming and pyrolysis comprises a fibrous mass impregnated with a polymeric binder composition based on one or more resins selected from the group consisting of siloxane resins and silsesquioxane resins, 25 with characteristics already described above and which,

for brevity, will not be set forth again.

[00108] In particular, the aforesaid polymeric binder composition can comprise organic resins, preferably epoxy resins, phenolic resins and/or resins based on vinyl ester or cyanate ester, although preferably it comprises only resins selected from the group consisting of siloxane resins and silsesquioxane resins, and does not comprise organic resins.

[00109] The fibre-reinforced composite ceramic material according to the invention comprises a ceramic or partially ceramic matrix that develops itself in the interstices of the aforesaid fibrous mass and that comprises silicon Carbide and amorphous structures consisting of chains of Si-O-C. The silicon Carbide and the chains of Si-O-C were generated by the pyrolysis process on said polysiloxanes and/or said polysilsesquioxanes.

[00110] The composite ceramic material fibre-reinforced and pyrolyzed according to the invention has a porosity generated by pyrolysis on the polymeric binder composition of the pre-preg. This porosity can be regulated by many variables, including types and contents of resins used to obtain the pre-preg, forming technique and parameters, pyrolysis temperature. Typically, composites are obtained that after pyrolysis

have porosity between 20 and 40%. Hereinafter, for simplicity, the expression "ceramic matrix" will be used instead of the expression "ceramic or partially ceramic matrix".

5 [00111] The pre-preg utilised according to the invention is then differentiated from a traditional pre-preg, by not being impregnated or at least not being exclusively impregnated with organic resins (in particular, phenolic or epoxy resins, or resins based on
10 vinyl ester or cyanate ester), but being impregnated with a polymeric binder composition based on one or more resins selected from the group consisting of siloxane resins and silsesquioxane resins.

[00112] Siloxane and silsesquioxane resins have
15 different characteristics from the organic (mainly epoxydic) resins normally used for manufacturing pre-pregs, in particular pre-pregs based on carbon fibres or glass fibres or ceramic fibres.

[00113] In the first place, siloxane and
20 silsesquioxane resins exhibit a far greater temperature stability, thanks to their lower weight loss, both in oxidising atmosphere and in inert atmosphere.

[00114] A second peculiar characteristic of siloxane resins and silsesquioxane resins is the ability to form,
25 as a result of pyrolysis at temperatures between 400 and

900°C, amorphous structures consisting of Si-O-C chains. These structures can be crystallised by heat treatments at higher temperatures, around 1300-1500°C. In this way it is possible to form, starting from resins selected
5 from the group consisting of siloxane resins and silsesquioxane resins, silicon Carbide, a compound with properties of technological interest, such as: very high hardness, high elastic modulus, high melting point and thermal stability, high thermal conductivity.

10 [00115] Instead, organic resins form, as a result of pyrolysis, a carbonaceous residue, which in the case of epoxy resins is also very limited and insufficient to assure a good consistency of the composites. Said carbonaceous residue, moreover, is not suitable for
15 applications with high temperatures in oxidising environment and does not have sufficient hardness to assure good abrasion resistance.

[00116] For this reason, as stated above, according to the invention, the polymeric binder composition
20 preferably does not contain organic resins. In any case, the content of organic resins is no higher than 30% by weight of the polymeric binder composition, so as to limit the negative effect given by the presence of the organic resins.

25 [00117] Siloxane or silsesquioxane resins, given the

reduced weight loss after pyrolysis and the possibility of forming silicon Carbide, are indicated to make preforms to be densified. The term "densification" means processes such as: polymer impregnation and pyrolysis (PIP) or liquid silicon infiltration (LSI).

[00118] As will be described in more detail below, the characteristics of the fibre-reinforced composite ceramic material obtained from a pre-preg according to the invention after forming and pyrolysis and optionally densification are:

- medium mechanical characteristics (ultimate tensile stress up to approximately 300-350 MPa, a value that is influenced by many factors, including fibres and types and levels of densification);
- Thermal conductivity ($>1 \text{ W}/(\text{m} \cdot ^\circ\text{K})$);
- Good resistance to abrasion wear;
- Operating temperature up to 1000°C , in any case variable according to the densification processes.

[00119] Applications for which composites obtained in this way can be of interest are in particular structure components intended to operate at high temperatures, even above 400°C .

[00120] The above advantages are evident if the preform is subjected to densification process with PIP techniques. The use of resins containing silicon is the

only way to generate silicon Carbide in matrix directly in the preform. This could in no way be obtained if the preform were produced from pre-preg based exclusively on organic resins. This aspect allows to realise, with PIP
5 techniques, composites with a significantly higher content of silicon Carbide in matrix than the composites obtained applying the same techniques to carbonaceous preforms obtained exclusively from organic resins.

[00121] These advantages instead are less evident in
10 the case of densification with LSI technique. It should be recalled that infiltration with silicon allows to form a high quantity of silicon Carbide in matrix even starting from a pre-preg with organic base (for example a phenolic pre-preg).

15 [00122] According to a preferred embodiment, the ceramic matrix constitutes from 15% to 70% by weight of the fibre-reinforced composite ceramic material, while the fibrous mass constitutes from 30% to 85% by weight of that material.

20 [00123] The content of fibres and of ceramic matrix can be varied according to the characteristics to be obtained in the fibre-reinforced composite material according to the invention.

[00124] A material with high fibre content is more
25 indicated for applications for which high mechanical

characteristics are required. A higher percentage of ceramic matrix can instead be more indicated for applications requiring higher operating temperatures or resistance to mechanical wear.

5 [00125] In particular, the fibrous mass can consist of fibres selected from the group consisting of carbon fibres, glass fibres, ceramic fibres or mixtures thereof. In particular, carbon fibres are carbon fibres from polyacrylonitrile (PAN) and/or carbon fibres from
10 pitch, while glass or ceramic fibres consist of alumina, zirconia or silicon Carbide.

[00126] According to a preferred embodiment, the fibrous mass consists only of carbon fibres, PAN or pitch.

15 [00127] Preferably, the fibrous mass consists of continuous fibres that form one or more layers of fabric or of nonwoven fabric.

[00128] Alternatively, the fibrous mass can consist of chop fibres dispersed in the matrix formed by the
20 aforesaid polymeric binder composition.

[00129] Advantageously, the aforesaid ceramic matrix can comprise a thermal insulating inert filler in powder form.

[00130] Preferably, the inert thermal insulating
25 filler in the form of powder is selected from the group

consisting of oxides, silicates and phosphates or a combination thereof.

[00131] Advantageously, the thermal insulating inert filler can be in aerogel form.

5 [00132] The presence of this filler is functional to reduce the thermal conductivity of the material, increasing its thermal insulating properties.

[00133] The presence of a thermal insulating filler in the fibre-reinforced composite material is to be
10 preferred if the manufactured article is a thermal or flameproof barrier or a component with structural function that has to operate at high temperatures.

* * *

[00134] An aspect that influences the characteristics
15 of the fibre-reinforced composite ceramic material according to the invention is the technique for forming the pre-preg, because it influences the final density of the composite thus obtained and hence the mechanical resistance characteristics.

20 [00135] Two forming techniques were evaluated:

- Compression moulding:
- Vacuum Bagging followed by curing in autoclave.

[00136] The different forming techniques typically work at different pressures. A greater pressure allows
25 to obtain greater density of the "as cured" composite

material (i.e. at the end of the forming operation, before pyrolysis) and hence superior mechanical characteristics.

[00137] In the case of compression moulding, pressures
5 from 20 to approximately 80-100 bar; in the case of vacuum bagging (followed by curing in autoclave), pressures of the order of 2-14 bar can be applied.

[00138] In case of forming by compression moulding, it has been observed that the density of the composite after
10 forming (but before pyrolysis) increases as the moulding pressure increases. The graph of Figure 1 shows the density of the fibre-reinforced composite material as a function of moulding pressure, if the material was obtained from a pre-preg based on PAN fibres (with
15 characteristics indicated in Table 2 above) with forming by compression moulding. Above approximately 50 bar, the maximum densification of the composite, and hence the optimal mechanical characteristics, are obtained.

[00139] It can be affirmed that compression moulding
20 is indicated for:

- forming composites with superior mechanical characteristics;
- making pieces with planar and simple shape;
- more rapid process times.

25 [00140] Vacuum bagging instead is more indicated for

forming pieces with complex shapes and when high moulding densities are not required. In particular, if the pre-preg is used to manufacture preforms to be densified, perfect compacting of the pre-preg in the moulding phase is not necessary. A determined degree of porosity could be sought with the purpose of avoiding the emergence of delaminations or bulges during the subsequent pyrolysis. These porosities can then be closed during the subsequent densification processes (PIP or LSI).

10 [00141] Preferably, the fibre-reinforced composite ceramic material according to the invention is obtained subjecting the pre-preg to forming by vacuum bagging technique and subsequent curing heat treatment.

[00142] Preferably, the vacuum bagging process is
15 carried out at a pressure of between 2 and 14 bar and at a temperature between 150°C and 300°C for a time of 1 to 6 hours, which may be followed by a post-curing cycle at a temperature between 250°C and 300°C for a time of 1 to 3 hours.

20 [00143] Alternatively, the fibre-reinforced composite ceramic material according to the invention is obtained subjecting the pre-preg to hot forming by compression moulding technique.

[00144] Preferably, hot forming by compression
25 moulding is carried out with a pressure of no less than

40 bar and at a temperature of no less than 200°C for a time between 60 and 150 minutes.

[00145] It is possible to carry out the forming operation at temperatures below 200°C, preferably around 5 180°C, providing a subsequent post-curing treatment. However, it has been observed experimentally that the best characteristics are obtained with forming at 300°C.

[00146] The vacuum bagging technique and the compression moulding technique are both well known to 10 the person skilled in the art and will not be described in detail herein.

* * *

[00147] An object of the present invention is a manufactured article fully or partly obtained with a 15 fibre-reinforced composite ceramic material according to the present invention, in particular as described above.

[00148] Preferably, the aforesaid manufactured article is a preform to be subjected to densification processes, preferably with Polymer Infiltration Pyrolysis (PIP) 20 technique, to obtain a heat barrier or a structural component intended to operate at high temperatures.

* * *

[00149] An object of the present invention is also a method for producing the fibre-reinforced composite 25 ceramic material according to the present invention and

in particular as described above.

[00150] According to a general embodiment, said method comprises the following operating steps:

- arranging a pre-impregnated fibre-reinforced composite material (pre-preg) impregnated with a polymeric binder composition according to the invention, and in particular as described above; and
- forming pre-impregnated fibre-reinforced composite ceramic material (pre-preg) bringing said polymeric binder composition at least to a partial curing obtaining a fibre-reinforced composite ceramic material;
- subjecting the aforesaid fibre-reinforced composite material to pyrolysis at a temperature between 400°C and 1,500°C.

15 [00151] According to the invention, forming leads to curing said one or more resins of the polymeric binder composition of the pre-preg and hence to the formation of a solid polymeric binding matrix that develops itself in the interstices of the fibrous mass of the pre-preg and it is based on polysiloxanes and/or polysilsesquioxanes, mutually cross-linking as a result of the cross-linking induced by the curing of the aforesaid one or more resins of the polymeric binder composition of the pre-preg.

25 [00152] Preferably, forming is carried out by vacuum

bagging and subsequent curing thermal treatment.

[00153] Preferably, the vacuum bagging process is carried out at a pressure of between 2 and 14 bar and at a temperature between 150°C and 300°C for a time of 1 to 5 6 hours, which may be followed by a post-curing cycle at a temperature between 250°C and 300°C for a time of 1 to 3 hours.

[00154] Alternatively, hot forming is achieved by compression moulding.

10 [00155] Preferably, hot forming by compression moulding is carried out with a pressure of no less than 40 bar and at a temperature of no less than 200°C for a time between 60 and 150 minutes.

[00156] It is possible to carry out the forming 15 operation at temperatures below 200°C, preferably around 180°C, providing a subsequent post-curing treatment. However, it has been observed experimentally that the best characteristics are obtained with forming at 300°C.

[00157] According to the invention, pyrolysis causes 20 the formation of porosities in the solid binder polymeric matrix because of a partial degradation of the solid binder polymeric matrix and the at least partial transformation of said polysiloxanes and/or of said polysilsesquioxanes into silicon Carbide and into 25 amorphous structures consisting of Si-O-C chains, so as

to obtain a fibre-reinforced composite ceramic material from said fibre-reinforced composite material.

[00158] The pyrolysis treatment can be carried out in inert atmosphere, for example in nitrogen or in argon,
5 or in a vacuum. Typically, treatments are executed with up ramps between 0.2 and 1 °C/min. Pyrolysis temperatures are usually between 400 and 1500°C.

[00159] Advantageously, the method can comprise a step of densifying the fibre-reinforced composite ceramic
10 material. Said densifying step is conducted after the pyrolysis step.

[00160] Preferably, the densifying step is conducted with Polymer Infiltration Pyrolysis (PIP) technique.

[00161] Alternatively, the densifying step can be
15 conducted by liquid silicon infiltration (LSI).

[00162] Preferably, the polymeric binder composition constitutes from 25% to 60% by weight of the pre-preg, while the fibrous mass constitutes from 40% to 75% by weight of the pre-preg.

20 [00163] The polymeric binder composition to be used in the present invention and the method for producing the pre-impregnated fibre-reinforced composite material (pre-preg) according to the invention have already been described above in relation to the fibre-reinforced
25 composite ceramic material according to the invention.

For simplicity of description, these characteristics are not repeated again, but they are understood also to be referred to the method for producing the ceramic composite material according to the invention.

5

APPLICATION EXAMPLES

[00164] As stated, the pre-impregnated fibre-reinforced composite material according to the present invention finds particular application as a basic material for the production (through subsequent
10 treatments and processing) of components intended to operate at high temperatures (even higher than 400°C), for example heat-resistant bulkheads or other components intended to operate at high temperatures.

[00165] It was possible to verify experimentally that
15 the pre-impregnated fibre-reinforced composite material according to the invention, lacking organic resins or, at least, not impregnated exclusively with organic resins, such as epoxy or phenolic resins, can lead, following pyrolysis at temperatures between 400°C and
20 1500°C, to the formation of such amorphous and/or crystalline inorganic structures as to make the composite materials thus obtained adequate for the production of preforms for densification processes and characterised by greater hardness, so as to assure
25 superior abrasion resistance and high thermal

conductivity.

[00166] In particular, it has been verified experimentally that the fibre-reinforced composite ceramic material according to the invention, obtained by forming and pyrolysis of a pre-preg that does not contain or, at least, does not exclusively contain organic resins, and impregnated with a polymeric binder composition based on one or more siloxane resins and/or silsesquioxane resins, has such silicon Carbide and amorphous inorganic structures consisting of chains of Si-O-C, as to make it adequate to the production of preforms for densification processes, and it is characterised by high thermal conductivity and by greater hardness, so as to assure a superior resistance and abrasion.

[00167] Fibre-reinforced composite materials according to the present invention were tested, starting from pre-pregs impregnated with two different formulations of the polymeric binder composition, lacking organic resins. The two formulations differ essentially in that a formulation is made with carbon fibres from pitch and the other formulation is made with carbon fibres from polyacrylonitrile (PAN).

[00168] In both formulations, the same resins were used, changing the weight ratios to maintain constant

the ratios by volume between resins and fibres. This became necessary because the different types of fibres have different densities.

[00169] The two formulations correspond to the two
5 formulations indicated in table 2 above.

[00170] As polymeric binder composition, a mixture of two siloxane resins was used, of which one that is solid at ambient temperature and one that is liquid at ambient temperature. The weight ratio between solid resin and
10 liquid resin is between 100/30 and 100/50.

[00171] The solid resin used was the resin RSN-0217 (marketed by Dow Corning); it is a phenyl siloxane resin, solid at ambient temperature, with melting point of approximately 80°C.

15 [00172] The liquid resin used was the resin Silres MSE100 (marketed by Wacker); it is a methyl methoxy siloxane resin, liquid at ambient temperature, characterised by low viscosity, around 25-40 mPas at ambient temperature.

20 [00173] The solid resin is soluble in the liquid resin and a solution with weight ratios between 100/30 and 100/50 respectively between solid and liquid has optimal properties for the production of a pre-preg. In particular, the mixture has a semi-solid and sticky
25 appearance at ambient temperature, whereas at 50-70°C it

is a highly viscous liquid (between 55000 and 10000 mPas), ideal characteristic to impregnate a fabric.

[00174] Carbon fibres were used in the form of a unidirectional laminate, i.e. consisting of fibres
5 oriented along only one direction.

[00175] The laminate of fibres (Pitch or PAN fibres) was impregnated with the polymeric binder composition at a temperature between 70 and 75°C obtaining the pre-preg.

10 [00176] The impregnated laminate (pre-preg) thus obtained was then subjected to forming, inducing the curing (cross-linking) of the resins, obtaining a fibre-reinforced composite material.

[00177] In particular, hot forming was carried out by
15 compression moulding. Tests were conducted at two different pressures: 51 bar and 26 bar. Forming was conducted at 300°C for a minimum time of 150 minutes, without conducting a post-curing step.

[00178] The samples of fibre-reinforced composite
20 material according to the invention obtained from the formulation with fibre pitch (in the form of unidirectional laminate), after forming (with compression moulding at 50 bar) and complete cross-linking of the resins, were subjected to pyrolysis and
25 densification by Polymer Infiltration Pyrolysis process

(PIP; 3 cycles).

[00179] The pyrolysis treatments were conducted at 1500°C in vacuum. Densification was carried out with a liquid siloxane resin. The impregnation process was
5 carried out at ambient temperature, at a vacuum level of approximately 40 mbar.

[00180] The samples were characterized in terms of thermal conductivity and mechanical resistance.

[00181] Table 4 shows the values of thermal
10 conductivity of a sample of fibre-reinforced composite ceramic material, after pyrolysis and densification by PIP process (3 cycles). The characterization was carried out with Laserflash technique, in accordance with ASTM E-1461, in an orthogonal direction to the planes of the
15 pre-preg and at 400°C in nitrogen.

Preform	Composite density [g/cm ³]	Specific heat [J/(g·K)]	Thermal diffusivity [mm ² /s]		Thermal conductivity [W/(m·°K)]	
		Mean	Mean	St. Dev.	Mean	St. Dev.
laminated	1,83	1,68	1,38	0,01	4,25	0,02

UD pitch						
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Table 4

[00182] The level of conductivity of the composite, higher than $4 \text{ W}/(\text{m} \cdot ^\circ\text{K})$, derives from the conductivity of the matrix, which was partly crystallized to silicon Carbide.

[00183] Table 5 shows the values of some mechanical resistance properties of the same composite that was thermally characterized. The characterisation was conducted with 3-point flexural test in accordance with the ASTM C-1341 standard, testing the composite with fibre orientation at 0° . The measurement was conducted on only one specimen.

Preform	MOR [MPa]		MOE [GPa]		Deformation at break [%]	
	Mean	St. Dev.	Mean	St. Dev.	Mean	St. Dev.
UD pitch	342	--	175	--	0,21	--

Table 5

[00184] The test confirmed that the fibre-reinforced composite ceramic material according to the present invention - after forming and subsequent pyrolysis and

densification can lead to the production of components intended to operate at high temperatures (even higher than 400°C), for example thermal barriers, flameproof barriers or structural components.

5 [00185] As a result of the fact that the polymeric binder composition is based on siloxane resins and/or silsesquioxane resins, following pyrolysis between 400 and 1500°C, the composite material has silicon Carbide and amorphous structures consisting of Si-O-C chains,
10 which assure operating temperatures up to 1000°C (variable according to the densification processes). The formation at least in part of silicon Carbide as a result of pyrolysis treatments at temperatures up to 1500°C, provides the composite with properties of technological
15 interest, such as: high hardness, high elastic modulus, high thermal stability, high thermal conductivity.

[00186] In particular, it is worth stressing the high thermal conductivity, well above 1 W/(m·°K).

[00187] Mechanical resistance values are medium. In
20 particular, it is worth stressing the flexural strength (MOR), which reaches values of approximately 300-350 MPa (this value is affected by many factors, including fibres and types and levels of densification).

[00188] Lastly, the presence of silicon Carbide in the
25 matrix assures good resistance to abrasion wear.

* * *

[00189] The invention thus conceived therefore achieves the pre-set purposes.

[00190] Obviously, in its practical embodiment the
5 invention may also assume different shapes and configurations from the one illustrated above, without thereby departing from the present scope of protection.

[00191] In addition, all details may be replaced by technically equivalent elements and the dimensions, the
10 shapes and the materials used may be any, according to the needs.

CLAIMS

1. Pre-impregnated fibre-reinforced composite material in laminar form, obtained by impregnating a fibrous mass with a polymeric binder composition and
5 destined to be subjected to subsequent forming and pyrolysis operations to obtain a fibre-reinforced composite ceramic material, **characterized in that** said polymeric binder composition is based on one or more resins selected from the group consisting of siloxane
10 resins and silsesquioxane resins, and may optionally comprise one or more organic resins, said siloxane resins comprising polysiloxanes and said silsesquioxane resins comprising polysilsesquioxanes, **and in that** said polymeric binder composition is a liquid having
15 viscosity of between 55000 and 10000 mPas at temperatures of between 50 °C and 70 °C, wherein the polymeric binder composition forms a polymeric binding matrix not crosslinked or only partially crosslinked which fills the interstices of the fibrous mass.
- 20 2. Material according to claim 1, wherein said polymeric binder composition comprises only resins chosen in the group consisting of siloxane resins and silsesquioxane resins, and does not comprise organic resins.

3. Pre-impregnated fibre-reinforced composite material according to claim 1 or 2, wherein said polymeric binder composition constitutes from 25% to 60% by weight of said pre-impregnated fibre-reinforced composite material and wherein said fibrous mass constitutes from 40% to 75% by weight of said pre-impregnated fibre-reinforced composite material.

4. Pre-impregnated fibre-reinforced composite material according to claim 1, 2 or 3, wherein said polymeric binder composition comprises a mixture of:

- at least one resin selected from the group consisting of siloxane resins and silsesquioxane resins, solid at room temperature, with melting point range of between 40 °C and 90 °C; and
- 15 - at least one resin selected from the group consisting of siloxane resins and silsesquioxane resins, liquid at room temperature, with viscosity at room temperatures of between 1 mPas and 5000 mPas;

the weight ratio between solid resin at room temperature and liquid resin at room temperature is between 100/30 and 100/50.

5. Pre-impregnated fibre-reinforced composite material according to claim 4, wherein said solid resin

at ambient temperature is selected in the group consisting of a phenyl siloxane, methyl siloxane, methyl methoxy silsequioxane, methyl silsequioxane resin and wherein said liquid resin at ambient temperature is
5 selected from the group consisting of a methyl methoxy siloxane and methyl phenyl vinyl siloxane resin.

6. Pre-impregnated fibre-reinforced composite material according to claim 1, 2 or 3, wherein said polymeric binder composition comprises a mixture of:
- 10 - a single resin selected from the group consisting of siloxane resins and silsesquioxane resins, liquid at ambient temperature, with viscosity at ambient temperatures of between 1 mPas and 5000 mPas and
- an inert filler in powder form,
- 15 the volume ratio of inert filler to liquid polymer at room temperature is between 10/100 and 40/100.

7. Pre-impregnated fibre-reinforced composite material according to one or more of the preceding claims, wherein said polymeric binder composition
20 further comprises at least one **solvent**, selected from the compounds able to solubilize the polysiloxanes and polysilsesquioxanes, preferably said solvent being divinylbenzene.

8. Pre-impregnated fibre-reinforced composite material according to one or more of the preceding claims, wherein said polymeric binder composition further comprises at least one **catalyst** adapted to
5 promote the cross-linking of the polymers of said polymeric composition at temperatures higher than 100 °C, preferably said catalyst being selected from the group consisting of titanates, metal octoates and amines, and even more preferably said catalyst being
10 selected from the group consisting of titanium tetrabutanolate, zinc octoate and N-3-(trimethoxysilyl)propyl)ethylenediamine, preferably said catalyst constituting less than 1% by weight of the polymeric matrix of said pre-impregnated fibre-
15 reinforced composite material.

9. Pre-impregnated fibre-reinforced composite material according to one or more of the preceding claims, wherein said polymeric binder composition further comprises a **thermo-insulating inert filler**,
20 preferably selected from the group consisting of oxides, silicates and phosphates or a combination thereof, preferably said thermo-insulating inert filler constituting from 1% to 30% by volume of said pre-impregnated fibre-reinforced composite material.

10. Pre-impregnated fibre-reinforced composite material according to one or more of the preceding claims, wherein said fibrous mass consists of fibres selected from the group consisting of carbon fibres, glass fibres, ceramic fibres or mixtures thereof, preferably the carbon fibres being carbon fibres from polyacrylonitrile (PAN) and/or carbon fibres from pitch, the glass or ceramic fibres preferably consisting of silica, alumina, zirconia or silicon Carbide.
- 10 11. Pre-impregnated fibre-reinforced composite material according to one or more of the preceding claims, wherein said fibrous mass consists of continuous fibres forming one or more layers of fabric or nonwoven fabric.
- 15 12. Pre-impregnated fibre-reinforced composite material according to one or more of claims 1 to 14, wherein said fibrous mass consists of chopped fibres dispersed in the matrix formed by said polymeric binder composition.
- 20 13. Method for making a pre-impregnated fibre-reinforced composite material destined to be subjected to subsequent forming and complete curing operations to make a fibre-reinforced composite material, comprising the following operating steps:

- arranging a fibrous mass in laminar form;
- arranging a polymeric binder composition;
- impregnating said fibrous mass with said polymeric binder composition obtaining a pre-impregnated fibre-

5 reinforced composite material

characterized in that said polymeric binder composition is based on one or more resins selected from the group consisting of siloxane resins and silsesquioxane resins, and may optionally comprise one or more organic resins, 10 said siloxane resins comprising polysiloxanes and said silsesquioxane resins comprising polysilsesquioxanes, **and in that** said polymeric binder composition is a liquid having viscosity of between 55000 and 10000 mPas at temperatures of between 50 °C and 70 °C, wherein 15 following the impregnation step the polymeric binder composition forms a polymeric binding matrix not crosslinked or only partially crosslinked which fills the interstices of the fibrous mass.

14. Fibre-reinforced composite ceramic material, 20 obtained by forming and subsequent pyrolysis of a pre-impregnated fibre-reinforced composite material according to one or more of the claims from 1 to 12, wherein said fibre-reinforced composite ceramic material comprises a ceramic or partially ceramic matrix that

develops itself in the interstices of the fibrous mass of said pre-impregnated fibre-reinforced composite ceramic material and that comprises silicon Carbide and amorphous structures consisting of Si-O-C chains, said
5 silicon Carbide and said Si-O-C chains having been generated by the pyrolysis process on said polysiloxanes and/or said polysilsesquioxanes, said fibre-reinforced composite ceramic material having a porosity generated by pyrolysis on the polymeric binder composition of the
10 pre-preg.

15. Fibre-reinforced composite ceramic material according to claim 14, wherein said ceramic or partially ceramic matrix constitutes from 15% to 70% by weight of said fibre-reinforced composite ceramic material and
15 wherein said fibrous mass constitutes from 30% to 85% by weight of said fibre-reinforced composite ceramic material.

16. Fibre-reinforced composite ceramic material according to claim 14 or 15, wherein said ceramic or
20 partly ceramic matrix comprises a **thermo-insulating inert filler in powder form**, preferably selected from the group consisting of oxides, silicates and phosphates or a combination thereof.

17. Fibre-reinforced composite ceramic material

according to one or more of the claims from 14 to 16,
wherein said forming is carried out by vacuum bagging
and subsequent heat treatment of curing, preferably said
vacuum bagging being carried out at a pressure of between
5 2 and 14 bar and a temperature of between 180 °C and 300
°C for a time of between 60 and 150 minutes.

18. Fibre-reinforced composite ceramic Materia
according to one or more of the claims from 14 to 16,
wherein said forming is carried out under heat by
10 compression moulding, preferably carried out at a
pressure not lower than 40 bar and at a temperature not
lower than 200 °C for a time between 60 and 150 minutes.

19. Manufactured article characterised in that it
is made with a fibre-reinforced composite ceramic
15 material according to one or more of the claims from 14
to 18, preferably said manufactured article being a
preform intended to be subjected to densification
processes, preferably with Polymer Infiltration
Pyrolysis (PIP) technique, for the manufacture of a heat
20 barrier or of a structural component intended to operate
at high temperatures.

20. Method for producing a fibre-reinforced
composite ceramic material, comprising the following
operating steps:

- arranging a fibre-reinforced composite ceramic material pre-impregnated with a polymeric binder composition according to one or more of claims 1 to 12; and
- 5 - forming said pre-impregnated fibre-reinforced composite ceramic material bringing said polymeric binder composition at least to a partial curing obtaining a fibre-reinforced composite material;
- subjecting said fibre-reinforced composite material to
- 10 pyrolysis at a temperature between 400°C and 1,500°C,
characterised in that said forming leads to the curing of said one or more resins of the polymeric binder composition of said pre-impregnated fibre-reinforced composite ceramic material and hence to the formation of
- 15 a solid polymeric binding matrix that develops itself in the interstices of the fibrous mass of said pre-impregnated fibre-reinforced composite ceramic material and is based on polysiloxanes and/or polysilsesquioxanes, mutually cross-linked as a result
- 20 of the cross-linking induced by the curing of said one or more resins of the polymeric binder composition, and wherein said pyrolysis causes the formation of porosities in said solid polymeric binding matrix because of a partial degradation of the solid polymeric

binding matrix and the at least partial transformation of said polysiloxanes and/or of said polysilsesquioxanes into silicon Carbide and into amorphous structures consisting of Si-O-C chains, so as to obtain a fibre-reinforced composite ceramic material from said fibre-reinforced composite material.

21. Method according to claim 20, wherein said forming is carried out by vacuum bagging and subsequent heat treatment of curing, preferably said vacuum bagging being carried out at a pressure between 2 and 14 bar and a temperature of between 180 °C and 300 °C for a time between 60 and 150 minutes.

22. Method according to claim 20, wherein said forming is carried under heat out by compression moulding technique, preferably carried out at a pressure not lower than 40 bar and at a temperature not lower than 200 °C for a time between 60 and 150 minutes.

23. Method according to one or more of the claims from 20 to 22, comprising a step of densifying said fibre-reinforced composite ceramic material, conducted after said pyrolysis step, preferably said densifying step being conducted with Polymer Infiltration Pyrolysis (PIP) technique.

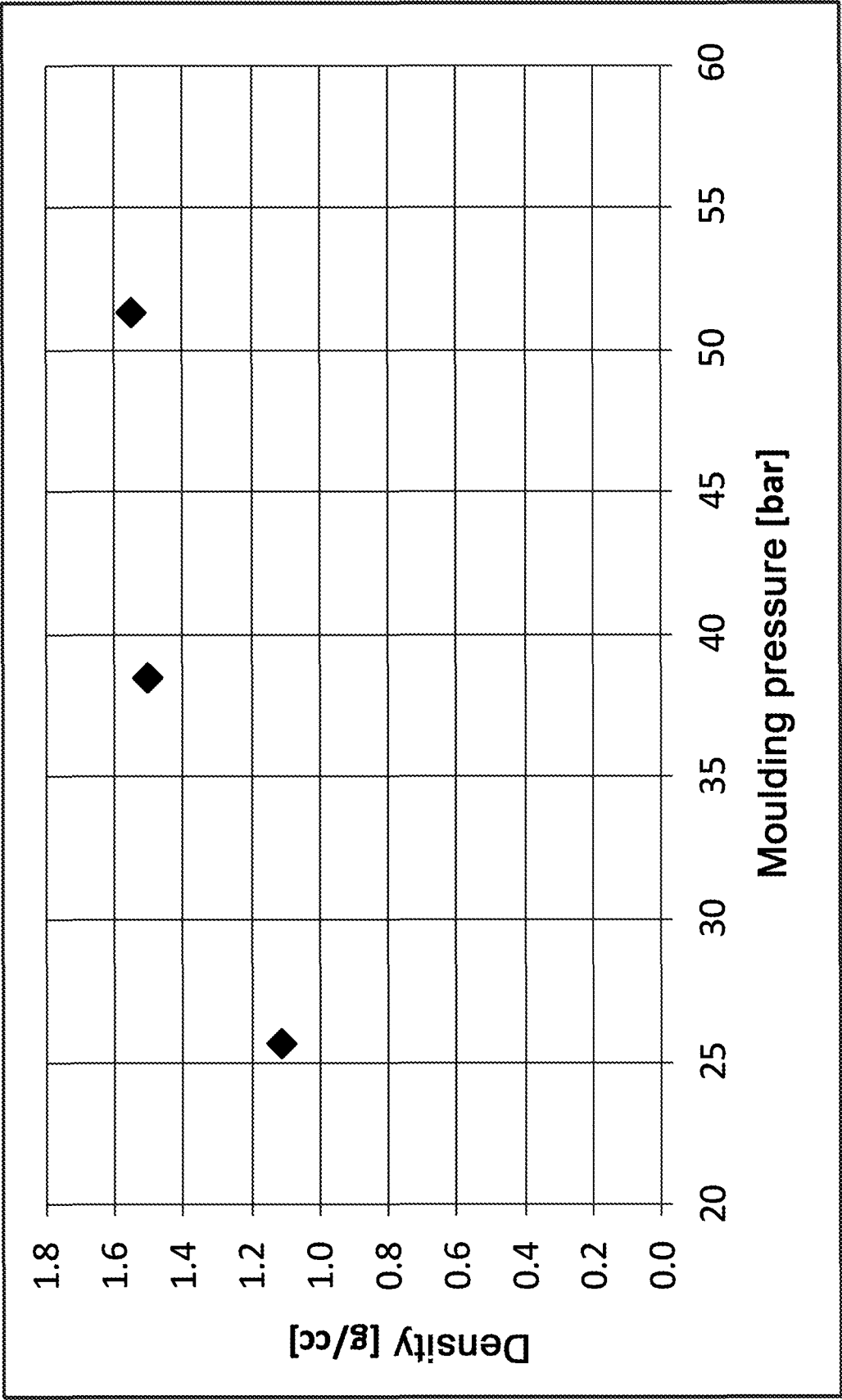


FIG.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/055842

A. CLASSIFICATION OF SUBJECT MATTER

INV. C04B35/571 B28B3/02 C04B35/626 C04B35/632 C04B35/80
C04B35/82

ADD.

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)

C04B B28B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 40 16 052 A1 (DORNIER LUFTFAHRT [DE]) 21 November 1991 (1991-11-21)	1,2,7, 9-11,13, 14,16-20
Y	column 1, line 58 - column 2, line 38; claims 1,3	5,12,22
X	----- US 2012/034428 A1 (CLARKE WILLIAM A [US]) 9 February 2012 (2012-02-09)	1-4, 6-11, 13-20
Y	paragraphs [0096], [0102], [0180]; claims 1-3; figure 4; tables 3,4,7 ----- -/-	5,12,22

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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"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

22 October 2018

Date of mailing of the international search report

30/10/2018

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INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2018/055842

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Sr 355s: "Technical Data Sheet SR 355S", 30 July 2011 (2011-07-30), XP055460099, Retrieved from the Internet: URL:https://www.momentive.com/products/show-technical-datasheet.aspx?id=10062 [retrieved on 2018-03-16] the whole document -----	1-22
A	Jens Schröter: "Handbuch Medienwissenschaft", 11 April 2014 (2014-04-11), XP055460111, Stuttgart DOI: 10.1007/978-3-476-05297-1 ISBN: 978-3-476-02412-1 Retrieved from the Internet: URL:http://www.dcproducts.com.au/Technical_Library/Fluids.pdf pages 6,14 -----	1-22
A,P	Anonymous: "1166 - BGF Industries, Inc. - BGF Industries, Inc.", 1 January 2018 (2018-01-01), XP055460152, Retrieved from the Internet: URL:http://www.bgf.com/datasheet/1166/ [retrieved on 2018-03-16] the whole document -----	1-22
X	EP 0 549 224 A1 (DOW CORNING [US]) 30 June 1993 (1993-06-30)	1,2,7, 9-11,13, 14, 16-21,23
Y	example 13 -----	5,12,22

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Information on patent family members

International application No

PCT/IB2018/055842

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