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(54) Title: METHOD FOR THE PREPARATION OF A REINFORCED THERMOSET POLYMER COMPOSITE

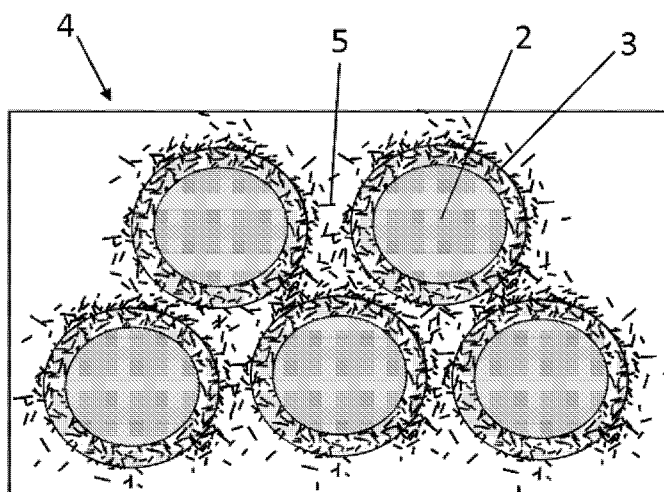


Fig. 2

(57) Abstract: The present invention refers to a method for the preparation of a reinforced thermoset polymer composite, said thermoset polymer composite comprising coated fibres, the coating being used as a vehicle for the introduction of carbon nanotubes into the thermoset polymer, the preparation of said reinforced thermoset polymer composite comprising the following steps: - providing fibres; - preparing a coating comprising carbon nanotubes and a polymeric binder; - applying said coating to said fibres to obtain coated fibres; - impregnating said coated fibres with a precursor of a thermoset polymer and letting part of the carbon nanotubes transfer from the coating into the precursor of the thermoset polymer; - curing said precursor containing the coated fibres and the transferred carbon nanotubes to achieve the reinforced thermoset polymer composite.



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**METHOD FOR THE PREPARATION OF A REINFORCED THERMOSET  
POLYMER COMPOSITE**

**Field of the invention**

10 [0001] The present invention is related to a method for the preparation of a reinforced thermoset polymer composite.

[0002] Another aspect of the invention is related to a fibre coating composition.

15

**State of the art**

[0003] The preparation of composites is generally based on processes wherein a substrate is impregnated by a polymer composition, which is solidified after impregnation  
20 by cross-linking, forming a polymeric matrix.

[0004] Usually, the substrate is in the form of fibres, like woven or non woven fibre mats.

[0005] The viscosity of the polymer composition (matrix) during the impregnation process is a critical  
25 parameter for most of the processes such as pre-impregnation (pre-preg), Resin Transfer Moulding (RTM), Resin Injection Moulding (RIM), Vacuum Assisted Resin Transfer Moulding (VARTM), Vacuum Infusion (VI), Hand lay-up, Pulltrusion, Pullwinding and filament winding, used to  
30 perform reinforced structural composites.

[0006] For all of these processes, the lower the viscosity of the polymer composition used to impregnate the fibres, the more homogeneous the resulting impregnation of the substrate, which leads to better final properties of

the composite structure and to a higher efficiency of the impregnation process (higher speed).

**[0007]** Generally for all type of matrixes, and especially for the thermosets, the lower the viscosity of the precursor of the polymeric matrix, the lower the resulting chemical and physical final properties of the solidified matrix (matrix brittleness, low Tg, low chemical resistance, etc.). The solidified matrixes with the highest physical and chemical properties usually also have the highest viscosity in the liquid precursor state, with the resulting restrictions in terms of their processability.

**[0008]** In some cases, it is possible to reduce the global viscosity of the precursor polymer composition used to impregnate the substrate by using solvents (e.g. prepreg, filament winding, pulltrusion and pullwinding). The drawback is due to the fact that the solvents need to be eliminated from the final composite, before the cross-linking of the precursor starts.

**[0009]** The solvent, which in some cases remains in the matrix, usually acts as a plasticizer and degrades the final properties of said matrix.

**[0010]** In other cases, the solvent evaporates from the matrix after its curing, resulting in a high porosity of the final composite (higher fragility and presence of micro-cracking in the matrix).

**[0011]** The solvent also needs additional energy to be completely evaporated after the support impregnation (higher costs compared to the hot-melt process for instance).

**[0012]** The organic solvent (e.g. Methyl Ethyl Ketone or Acetone) also needs to be recycled or burned after its evaporation, resulting in higher costs for the production and higher risks for the workers implicated in the substrate impregnation process.

[0013] For the processes which do not use solvents at all, the necessary viscosity for the processability of the precursor is achieved by a temperature increase. Nevertheless the temperature cannot be increased for the  
5 hand lay-up process or can only slightly be increased for all other processes. Depending on the type of polymers in the matrix, above a certain temperature limit, degradation starts or cross-linking starts (in case of thermoset matrixes), thereby reducing the impregnation time window.

10 [0014] Some additives used to increase the physical and chemical properties of the matrix also increase significantly the viscosity of the matrix precursor in the liquid state (e.g. poly(arylene ether sulphones) in epoxy matrixes), making such composition unsuitable for low  
15 viscosity processes. The additives which do not increase too much the viscosity of the matrix in the liquid state (e.g. PBS and phenoxy) reduce some of its physical properties after solidification, such as the Tg, and/or increase the Coefficient of Thermal Expansion (CTE).

20

#### **Aims of the invention**

[0015] The present invention aims to provide a method for the preparation of a reinforced thermoset polymer composite that does not present the drawbacks of  
25 the prior art.

[0016] More particularly, the present invention aims to provide a method to perform a reinforced composite material, improving some physical properties of said composite, such as mechanical properties and/or electrical  
30 conductivity, without increasing the difficulty of the impregnation process.

**Summary of the invention**

[0017] The present invention is related to a method for the preparation of a reinforced thermoset polymer composite, said thermoset polymer composite comprising  
5 coated fibres, the coating being used as a vehicle for the introduction of carbon nanotubes into the thermoset polymer, the preparation of said reinforced thermoset polymer composite comprising the following steps:

- providing fibres;
- 10 - preparing a coating comprising carbon nanotubes and a polymeric binder;
- applying said coating to said fibres to obtain coated fibres;
- impregnating said coated fibres with a precursor of a  
15 thermoset polymer and letting part of the carbon nanotubes transfer from the coating into the precursor of the thermoset polymer;
- curing said precursor containing the coated fibres and the transferred carbon nanotubes to achieve the  
20 reinforced thermoset polymer composite.

[0018] According to particular preferred embodiments, the invention further discloses at least one or a suitable combination of the following features:

- the thermoset polymer comprises a polymer selected from  
25 the group consisting of epoxy, vinylester, unsaturated polyester, phenolic and their blends and co-polymers;
- the weight ratio between the carbon nanotubes and the polymeric binder in the coating is higher than or equal to 1:9, more preferably higher than or equal to 1:4;
- 30 - the weight ratio between the carbon nanotubes and the thermoset polymer in the reinforced composite is higher than 1:1000;

- the polymeric binder is selected from the group consisting of aromatic poly(hydroxyl ether) (phenoxy), silanes and their blends and/or co-polymers;
- the carbon nanotubes are dispersed in a solvent before  
5 being dispersed in the coating;
- the precursor of the thermoset polymer comprises carbon nanotubes prior to impregnation;
- the fibres are selected from the group consisting of carbon, polyaramides, glass and mixture thereof;
- 10 - the fibres are selected from the group consisting of carbon fibres, glass fibres, and mixture thereof.

**[0019]** Another aspect of the invention is related to a fibre coating composition comprising:

- a polymeric binder selected from the group  
15 consisting of aromatic poly(hydroxyl ether) (phenoxy), silanes and their blends and/or co-polymers;
- carbon nanotubes,

wherein the weight ratio between the carbon nanotubes and  
20 the polymeric binder is higher than 1:9 and preferably higher than 1:4.

#### **Brief description of the drawings**

**[0020]** Fig. 1 represents a coated fibre according to  
25 the invention.

**[0021]** Fig. 2 represents a fibre-reinforced composite, with carbon nanotubes (CNT) which have partially migrated into the matrix (second polymer composition).

**[0022]** Fig. 3 represents a scanning electronic  
30 microscopy (SEM) of un-coated glass fibres.

**[0023]** Fig. 4 represents a scanning electronic microscopy (SEM) of coated glass fibres, according to the invention.

**Figure keys:**

- 1 Coated fibre.
- 2 Fibre.
- 3 Coating comprising carbon nanotubes (CNT).
- 5 4 Reinforced thermoset polymer composite.
- 5 Thermoset polymer matrix comprising CNT transferred from the fibre coating 3.

**Description of the invention**

10 [0024] The object of the present invention is a method to produce a final composite structure with enhanced static and dynamic mechanical and physical properties such as impact resistance, fracture toughness, compression, electrical conductivity etc., without affecting noticeably  
15 other physical characteristics of the impregnating polymer composition (matrix), such as the viscosity (processability restrictions) and of the final composite material, such as the glass transition temperature (Tg) (operational limitation).

20 [0025] The present invention refers to a method for the preparation of a reinforced thermoset polymer composite, said thermoset polymer composite comprising coated (sized) fibres, the coating (sizing) being used as a vehicle for the introduction of carbon nanotubes into the  
25 thermoset polymer, the preparation of said reinforced thermoset polymer composite comprising the following steps:

- providing fibres;
- preparing a coating (sizing) comprising carbon nanotubes and a polymeric binder;
- 30 - applying said coating to said fibres to obtain coated (sized) fibres;
- impregnating said coated fibres with a precursor of a thermoset polymer;



- transferring part of the carbon nanotubes from the coating into the precursor of the thermoset polymer;
- curing said precursor containing the coated fibres and the diffused carbon nanotubes to achieve the reinforced thermoset polymer composite.

**[0026]** The fibres are preferably in the form of non-woven or woven fibre mats.

**[0027]** The present invention also refers to a method in which carbon nanotubes are placed at the surface of fibres to be further impregnated by a precursor of a thermoset polymer, to obtain a final composite material reinforced with CNT in its matrix.

**[0028]** The fibres described in the present invention are preferably chosen from the group consisting of carbon, polyaramides and glass.

**[0029]** The carbon nanotubes described in the present invention can be single-wall (SWCNTs) or multi-wall (MWCNTs) and are characterized by a diameter between 0.5 and 75 nm.

**[0030]** Preferably, the polymeric binder described in the present invention comprises a polymer selected from the group consisting of poly(hydroxyl ether) (phenoxy), silanes and their blends.

**[0031]** The thermoset polymer used to impregnate the coated fibres is selected from the group consisting of epoxy, vinylester, unsaturated polyester, phenolic resins, their blends and co-polymers.

**[0032]** The most frequently used technologies to impregnate a support (substrate) with a thermoset precursor, especially if the support has a fibrous structure, can be divided in four categories, depending on the method used to impregnate the substrate and the curing process.

**[0033]** The first category is represented by the pre-impregnation (pre-preg) processes. In those processes, the fibrous support is impregnated by a thermoset polymer precursor (matrix), through a hot-melt process (the  
5 thermoset polymer precursor is molten to form a film which is then joined to the substrate) or through a solvent process (the thermoset polymer precursor is dissolved in a solvent to reduce its viscosity level and to improve the quality of the impregnation). The solvent process is often  
10 used when the matrix has a viscosity too high to be filmed by the hot-melt method.

**[0034]** Several layers of the impregnated support are then placed in a mould and the matrix is then cured. In case of a thermoset matrix, it is not fully cured at this  
15 stage (B-Stage) and it is later formed in a final shape in a mould for the further matrix consolidation (curing), normally under higher temperature and pressure.

**[0035]** The second category consists of processes using a closed mould, such as Resin Transfer Moulding  
20 (RTM), Resin Injection Moulding (RIM), Vacuum Assisted Resin Transfer Moulding (VARTM) and Vacuum Infusion (VI). In those processes, the fibrous substrate is first placed in a closed mould and the impregnating polymer composition (matrix) is injected under pressure (RTM and RIM), the  
25 impregnation is helped by an extra vacuum done in the mould to help the impregnation (VARTM) or the impregnating polymer composition(matrix) is only sucked by the vacuum created in the mould (VI). The impregnating polymer composition (precursor) is then consolidated by increasing  
30 the temperature of the mould (curing).

**[0036]** The third category of impregnation technologies is Hand lay-up (Thermosets). In this category, the fibrous support is placed in an open mould and impregnated by hand. The matrix is then consolidated at

room temperature, either by reactions with atmospheric components or by mixing the reactants just before impregnation.

**[0037]** The fourth category of impregnation technologies corresponds to pulltrusion, pullwinding and filament winding. In such technologies, the fibrous support is first impregnated by the thermoset polymer precursor and, immediately after that, placed around a rotating shape (filament winding) or extruded through a die (pulltrusion and pullwinding). The precursor is then consolidated (cured) immediately after the support impregnation, usually through the help of a temperature increase.

**[0038]** A reinforced structural composite comprising fibres (substrate) can be decomposed in three areas, each of those areas giving particular mechanical properties to the reinforced structural composite.

**[0039]** The first area is the part of the structural composite in which the fibres transfer the dominant mechanical properties to the reinforced structural composite. This first area is located in the volume occupied by the fibres themselves. The properties given by the fibres can be measured, in case of anisotropic fibres, by a test measuring the mechanical properties in a direction parallel to the orientation of the substrate (i.e. fibre direction).

**[0040]** The second area is the part of the structural composite wherein the matrix transfers the dominant mechanical properties to the reinforced structural material. This second area is located in the volume of the structural composite occupied by the matrix. The results of the Glc test, consisting in measuring the fracture toughness of the structural composite, are dominated by the properties of this second area (matrix).

[0041] Nevertheless, the Glc test only gives pertinent results in case of brittle matrixes, such as cured epoxy resin and the like. In case of tough matrixes such as polypropylene and usually thermoplastics above  
5 their Tg, the flexural modulus gives better indication of the matrix behaviour.

[0042] The third area is the part of the structural composite in which the mechanical properties of the structural composite are given by the interface between the  
10 substrate and the matrix. The mechanical properties given by the interface can be measured by Inter Laminates Shear Strength (ILSS).

[0043] Carbon nanotubes are well known products having interesting electrical, thermal and mechanical  
15 properties. CNT can transfer their interesting properties to a material, in which such CNT are (homogeneously) dispersed.

[0044] As previously mentioned, the viscosity of the impregnating precursor polymer composition (later forming  
20 the matrix) is also an important parameter to achieve a reinforced structural material with high mechanical performance. The level of viscosity can affect the use of processes to perform a reinforced structural composite.

[0045] High viscosity material can prevent the use  
25 of processes such as RTM, RIM, etc. that need low viscosity material to perform reinforced structural composites. During the impregnation step, the level of viscosity is given by the viscosity of the impregnating precursor polymer composition. As described before, the use of  
30 additives such as CNT affects the viscosity (increase of the viscosity of the impregnating precursor polymer composition).

[0046] The method described in the present invention allows to introduce CNT in a structural composite while

maintaining the viscosity level of the precursor close to that of the precursor of a virgin matrix.

**[0047]** In the present invention, the introduction of CNT is essentially made by the fibres with a coating  
5 containing carbon nanotubes. The CNT are placed on the surface of the substrate through this coating process.

**[0048]** The coating of the present invention further comprises a polymeric binder in which the carbon nanotubes are dispersed.

10 **[0049]** The polymeric binder with the CNT dispersed therein can be based on thermosets or thermoplastic polymers or their blends. The coating is preferably in the form of a dispersion or an emulsion.

**[0050]** The precursor of the thermoset polymer then  
15 used to impregnate the coated fibre substrate can be free or almost free of CNT before the impregnation process. During the impregnation process, thanks to the diffusion of the CNT from the coating into the matrix, the CNT are at least partially transferred into the thermoset polymer  
20 (matrix).

**[0051]** In such a process, the increase of the viscosity of the precursor of the thermoset polymer by the CNT is avoided during the impregnation step.

**[0052]** The transfer of the CNT properties to the  
25 structural material is achieved with the method of the present invention thanks to the dispersion (transfer) of CNT in the precursor of the thermoset polymer (matrix). The dispersion (transfer) of the CNT induces at least two different mechanisms:

30 - an increase of the interface properties (e.g. Interfacial Shear Strength IFSS), due to the CNT which remain localised in the coating, at the interface between the fibre substrate and the matrix and;

- an increase of the properties of the matrix (e.g. fracture toughness and/or flexural modulus), from the CNT which diffuse (migrate) in the thermoset polymer (matrix) after the impregnation step of the fibre support.

5 [0053] The CNT and the type of technique to place them on the surface of a fibre substrate are chosen in order to obtain a sufficient interaction between the CNT and the fibre substrates so that, after further impregnation of the fibres by the thermoset polymer precursor, a part of the CNT remains attached to the fibre surface and another part migrates in the precursor of the thermoset polymer (matrix).

[0054] The CNT remaining on the fibre surface also induce a high increase of the macroscopic conductivity of the reinforced composite, which can be of interest in applications, wherein electromagnetic shielding is necessary.

### **Examples of epoxy based composites**

#### 20 **Example 1**

[0055] Lab scale equipment was used to impregnate precut unidirectional glass fibre fabrics (300 mm by 300 mm) by first dipping them in a coating bath followed by squeezing the excess of coating.

25 [0056] Then, the impregnated fabrics were dried in the oven at 120°C for 3 minutes and then treated at 150°C for 3 minutes.

[0057] The coating was a water dispersion of phenoxy (tradename Hydrosize HP3-02) polymeric binder, wherein multi-wall carbon nanotubes were dispersed. The concentration of solid (Phenoxy + CNT) in the coating was about 32% and the ratio between the phenoxy binder and the carbon nanotubes was 2:1.

[0058] The final amount of dried coating on the surface of the fibre was about 1.12 wt% (Weight coating/Weight fibres). The final amount of the CNT on the surface of the glass fibres was therefore about 0.38%  
5 (Weight CNT/Weight fibres). The visual aspect of the sized glass fibres shows a homogeneous coating and a homogeneous dispersion of the CNT in the binder as shown in Figure 4.

[0059] These coated glass fibres (SGF) were then further impregnated with a standard bisphenol-A based epoxy  
10 resin used for the hot-melt pre-preg process, produced by Huntsman. The impregnation was performed through a drum winder device to obtain a unidirectional pre-preg leading to a resin content of about 50% by weight.

[0060] It was observed at that stage that the epoxy  
15 precursor resin had turned black during the impregnation process, indicating a transfer of at least a part of the carbon nanotubes from the fibre coating to the epoxy precursor resin.

[0061] The pre-pregs were cut into dimensions of  
20 300mm by 250mm and were cured at 120°C for 1 hour, followed by a post curing at 140°C for 2 hours. Composite laminate sheets with a thickness of about 2.0 mm were obtained with a final fibre volume fraction ranged between 45 and 50 %. The mechanical testing for fracture toughness (G<sub>IC</sub>) and  
25 flexural properties were conducted according to standards ASTM5528 and ASTM D790.

[0062] A rheometer (from Anton Paar) was used to analyse the viscosity. Parallel plate geometry with 1 mm gap and 25 mm diameter was used.

30 [0063] The samples were allowed to rest for 5 min after loading so that they could recover from any induced stress.

[0064] Measurements were taken in dynamic mode at room temperature (25°C) for epoxy. Dynamic strain sweeps at

a constant frequency were used to find the linear viscoelastic region (LVR) in which the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) were independent of strain amplitude.  $G'$  (MPa) and  $G''$  (MPa) and complex viscosity (Pas) values were measured.

[0065] The viscosity of the virgin epoxy resin was about 13 Pa.s. If the same quantity of carbon nanotubes had to be mixed in the matrix before impregnation, the epoxy resin/nanotubes mixture would have a nanotube concentration of about 0.6% nanotubes by weight. Such a concentration would increase the viscosity by more than one order of magnitude.

#### **Example 2 (comparative)**

15 The same procedure as in example 1 was used, except that no coating was applied to the fibres.

#### **Example 3 (comparative)**

20 The same procedure as in example 1 was used, except that no carbon nanotubes were added to the coating applied to the fibres.

#### **Example 4**

25 Carbon fibres, 100% unidirectional (UD), having an aerial weight of 300g/m<sup>2</sup> were used. The fibres were first dipped in a coating bath followed by squeezing the excess of coating.

[0066] Then, the coated fibres were dried in an oven at 120°C for 3 minutes and then treated at 150°C for 30 minutes.

[0067] The coating was a water dispersion of phenoxy (tradename Hydrosise HP3-02) polymeric binder and carbon nanotubes. The concentration of solid (Phenoxy + CNT) in



the coating was about 32% and the ratio between the phenoxy binder and the carbon nanotubes was 2:1.

[0068] The fibres were then put in a mould and impregnated by RTM with an epoxy resin (Epikote 828). The epoxy precursor resin was mixed with a hardener at room temperature followed by a degassing step for 15-30 min. In the beginning, the resin was introduced by applying vacuum and later by a combination of vacuum and pressure.

[0069] It was again observed that the epoxy resin had turned black during the impregnation process, indicating a transfer of at least part of the carbon nanotubes from the coating into the epoxy precursor resin.

[0070] The testing samples produced had the same dimensions as in example 1.

[0071] The weight fraction of the carbon fibres in the final composite was estimated to be 56 wt%. The concentration of carbon nanotubes in the final composite was 0.2 wt%.

#### 20 **Example 5 (comparative)**

The same procedure as in example 4 was used, except that no coating was applied to the fibres.

#### **Example 6**

25 The same procedure as in example 4 was used, except that polyethylene terephthalate (PET) textile having an aerial weight of 250g/m<sup>2</sup> were used instead of the glass fibres. No Glc measurement was performed, due to the inherent high toughness of PET. The fibres represented 57 wt% of the total composite, and the carbon nanotubes represented 0.2 wt% of the composite.

**Example 7 (comparative)**

The same procedure as in example 6 was used, except that no coating was applied to the fibres.

Example	Glc Crack initiation $J/m^2$	Electrical Resistance Fibre in direction (k ohm/m)
1	474	2142
2	375	(insulator)
3	414	(insulator)
4	460	0.32
5	370	1.7
6	-	42857
7	-	(insulator)

5     **Table 1** mechanical and electrical measurement results of epoxy based composites

**[0072]**             In the Glc test presented in table 1, the laminates obtained with the coated glass fibres (SGF/EP) showed better results than the uncoated glass fibres (VGF/EP). The presence of carbon nanotubes in the coating of the glass fibres is found to be improving the energy for delamination initiation.

**[0073]**             The interlaminar fracture energy (GI) for coated glass fibres in the reinforced thermoset polymer composite also shows an improvement of 10% with respect to the composite with uncoated glass fibres. This is attributed to the strong fibre/matrix interfacial adhesion due to a CNT network.

20   **[0074]**             The presence of CNT prevents the initiation and further propagation of delamination of the fibre/matrix interface. It is interesting to observe that with further addition of CNT in the matrix (0.5% by weight in the

matrix) along with CNT in the fibre coating the fracture initiation energy shows a further improvement (SGF/EP-CNT).

**[0075]** Additional examples, varying the level of carbon nanotubes, indicate that an improvement of Glc is  
5 observed for ratios of CNT/polymeric binder in the fibre coating as low as 1:9.

**[0076]** The flexural modulus and flexural strength of the composite of the examples 6 and 7 comprising PET fibres have been additionally tested. The presence of the coating  
10 comprising CNT in example 6 improves the flexural modulus by 10%, from 3.3 GPa in example 7 to 3.5 GPa in example 6. The flexural strength was improved by 20%, from 93 MPa in example 7 to 122 MPa in example 6.

**CLAIMS**

1. A method for the preparation of a reinforced thermoset polymer composite, said thermoset polymer composite comprising coated fibres, the coating being used as a vehicle for the introduction of carbon nanotubes into the thermoset polymer, the preparation of said reinforced thermoset polymer composite comprising the following steps:
- providing fibres;
  - 10 - preparing a coating comprising carbon nanotubes and a polymeric binder;
  - applying said coating to said fibres to obtain coated fibres;
  - impregnating said coated fibres with a precursor of a thermoset polymer and letting part of the carbon nanotubes transfer from the coating into the precursor of the thermoset polymer;
  - 15 - curing said precursor containing the coated fibres and the transferred carbon nanotubes to achieve the reinforced thermoset polymer composite.
2. The method according to claim 1, wherein the thermoset polymer comprises a polymer selected from the group consisting of epoxy, vinylester, unsaturated polyester, phenolic and their blends and co-polymers.
- 25 3. The method according to any of the claims 1 or 2, wherein the weight ratio between the carbon nanotubes and the polymeric binder in the coating is higher than or equal to 1:9.
4. The method according to any of the previous claims, wherein the weight ratio between the carbon nanotubes and the polymeric binder in the coating is higher than or equal to 1:4.
- 30

5. The method according to any of the previous claims, wherein the weight ratio between the carbon nanotubes and the thermoset polymer in the reinforced composite is higher than 1:1000.

5 6. The method according to any of the previous claims, wherein the polymeric binder is selected from the group consisting of aromatic poly(hydroxyl ether) (phenoxy), silanes and their blends and/or co-polymers.

7. The method according to any of the previous  
10 claims, wherein the carbon nanotubes are dispersed in a solvent before being dispersed in the coating.

8. The method according to any of the previous claims, wherein the precursor of the thermoset polymer comprises carbon nanotubes prior to impregnation.

15 9. The method according to any of the previous claims, wherein the fibres are selected from the group consisting of carbon, polyaramides, glass and mixture thereof.

10. The method according to any of the previous  
20 claims, wherein the fibres are selected from the group consisting of carbon fibres, glass fibres, and mixture thereof.

11. A fibre coating composition comprising:

25 - a polymeric binder selected from the group consisting of aromatic poly(hydroxyl ether) (phenoxy), silanes and their blends and/or co-polymers;

- carbon nanotubes,

wherein the weight ratio between the carbon nanotubes and  
30 the polymeric binder is higher then 1:9.

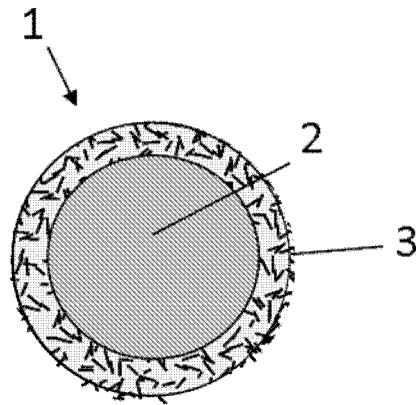


Fig. 1

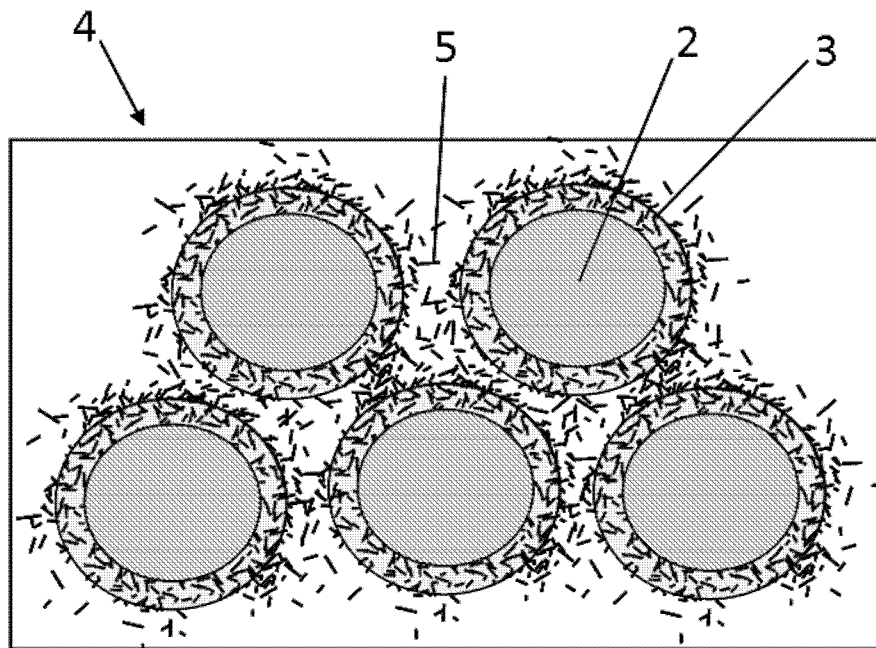


Fig. 2

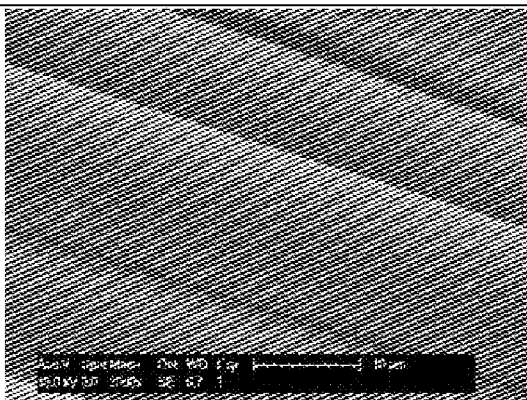


Fig.3

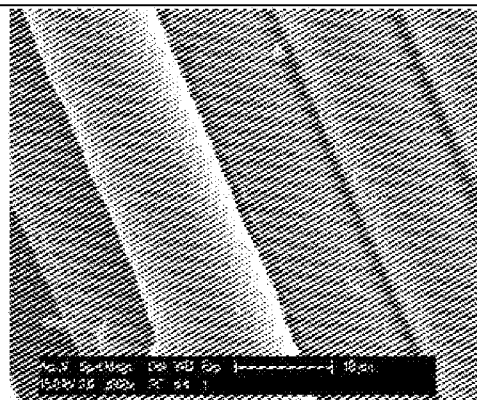


Fig.4

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2009/059247

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J5/06 C08J5/10 C08J5/24 C09D171/10 D06M11/74  
D06M13/513 D06M15/53 D06M15/643

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)

C08J C09D D06M

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 practical, 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.
A	<p>WO 2007/130979 A2 (ROHR INC [US]; GOODRICH CORP [US]; KRUCKENBERG TERESA M [US]; HILL VAL) 15 November 2007 (2007-11-15) page 2, paragraph 7 - paragraph 10 page 4, paragraph 19 - paragraph 23 page 8, paragraph 41 page 13, paragraph 60 page 16, paragraph 69 - paragraph 70; claims</p> <p style="text-align: center;">----- -/--</p>	1-11

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

☒ See patent family annex.

### \* Special categories of cited documents:

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

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

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

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

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

7 October 2009

Date of mailing of the international search report

20/10/2009

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Authorized officer

Masson, Patrick



## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/059247

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	BEKYAROVA E; THOSTENSON E T; YU A; KIM H; GAO J; TANG J; HAHN H T; CHOU T-W; ITKIS M E; HADDON R C: "Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites" LANGMUIR, vol. 23, no. 7, 27 March 2007 (2007-03-27), pages 3970-3974, XP002549140 page 3970 - page 3971 -----	1-11
A	DATABASE WPI Week 200673 Thomson Scientific, London, GB; AN 2006-701319 XP002549141 & JP 2006 274211 A (ARISAWA MFG CO LTD) 12 October 2006 (2006-10-12) abstract -----	1-11
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A	GAO S-L; MADER E; PLONKA R: "Nanocomposite coatings for healing surface defects of glass fibers and improving interfacial adhesion" COMPOSITES SCIENCE AND TECHNOLOGY, vol. 68, no. 14, 23 October 2007 (2007-10-23), pages 2892-2901, XP002549143 page 2893 -----	1-11

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International application No

PCT/EP2009/059247

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2005/114324 A2 (UNIV DAYTON [US]; DAI LIMING [US]; CHEN WEI [US]; LIN RENHE [US]) 1 December 2005 (2005-12-01) claims; examples -----	1-11
A	WO 2008/046165 A2 (NANOCYL S A [BE]; BEIGBEDER ALEXANDRE [FR]; BONDUEL DANIEL [BE]; CLAES) 24 April 2008 (2008-04-24) claims -----	1-11
A	GAO ET AL: "Nanostructured coatings of glass fibers: Improvement of alkali resistance and mechanical properties" ACTA MATERIALIA, ELSEVIER, OXFORD, GB, vol. 55, no. 3, 4 January 2007 (2007-01-04), pages 1043-1052, XP005822646 ISSN: 1359-6454 page 1045, left-hand column page 1046, left-hand column -----	1-11

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Information on patent family members

International application No

PCT/EP2009/059247

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