The invention relates to an apparatus and a method of manufacturing a composite sheet, the method comprising:

a. irradiating a sheet of fibres (20) and/or a matrix (11, 13) at an irradiation zone (33) with a plasma at substantially atmospheric pressure, and

b. impregnating the sheet of fibres with the matrix at an adhesion zone (32); wherein processes a. and b. are performed simultaneously.
METHOD OF MANUFACTURING COMPOSITE MATERIAL AND APPARATUS THEREFORE

FIELD OF THE INVENTION

The present invention relates to a method and apparatus for manufacturing a composite material.

BACKGROUND OF THE INVENTION

In US5 108780 a single fibre of reinforcing filament is irradiated with a plasma in a vacuum chamber prior to being coated with a thermoplastic coating. Immediate coating of the plasma treated fibre with the thermoplastic produces stronger interfacial shear strength than when the fibre is exposed to air or other free-radical-quenching species before it is coated.

The abstract of JP2005171432 describes a method of manufacturing fibres for polymer composite reinforcement. The fibres are subjected to a first plasma treatment under ordinary pressure followed by a second plasma treatment in a medium containing a gaseous alkene or alkyne at ordinary pressure. An adhesive is imparted after the plasma treatments.

SUMMARY OF THE INVENTION

A first aspect of the invention provides a method of manufacturing a composite sheet, the method comprising:

a. irradiating a sheet of fibres and/or a matrix at an irradiation zone with a plasma at substantially atmospheric pressure, and

b. impregnating the sheet of fibres with the matrix at an adhesion zone;

wherein processes a. and b. are performed simultaneously.

The first aspect of the invention irradiates a sheet of fibres (instead of a single fibre) and simultaneously runs an impregnation process to produce a sheet of fibres impregnated with matrix (commonly known in the art as a "prepreg"). This can be contrasted with the prior
art above which only produces a single filament of fibre. The method enables a sheet to be formed without having to treat the fibres with an intermediate product (for example the thermoplastic in US5108780 or the alkene/alkyne in JP2005171432).

The sheet of fibres may be fully impregnated, or only partially impregnated to form a so-called "partial prepreg".

Irradiating at substantially atmospheric pressure means that no special containment system is required for the irradiation zone.

Typically process b. is also performed at substantially atmospheric pressure, typically in air. This runs contrary to the teaching of US5 108780 which requires coating of the fibre in a controlled environment (that is, either in a vacuum or an inert gas).

The sheet of fibres may be impregnated by application of a fluid matrix melt, or the matrix may be in a sheet form during process b. Direct application of a fluid matrix melt provides the advantage that a process step (formation of the matrix sheet) can be omitted. However, the use of a sheet of matrix is preferred because this requires less modification of conventional manufacturing processes, enables the matrix to be irradiated more easily, and enables the preparation of a partial prepreg, if desired.

Preferably the sheet of fibres and/or the matrix are moving during step a, and preferably the sheet of fibres is moving during step b. This enhances the speed of the method, and ensures uniform irradiation.

Preferably the method further comprises moving the sheet of fibres and/or the matrix from the irradiation zone to the adhesion zone in less than 30 seconds.

A second aspect of the invention provides apparatus for manufacturing a composite prepreg, the apparatus comprising:

- a plasma source for irradiating a sheet of fibres and/or a matrix with a plasma at substantially atmospheric pressure, and
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means for impregnating the sheet of fibres with the matrix.

A third aspect of the invention provides a method of manufacturing a composite material, the method comprising:

irradiating a matrix with a plasma, and

coating a filler with the irradiated matrix.

The third aspect of the invention recognises that irradiation of the matrix may be used (optionally in conjunction with irradiation of the filler) to enhance adhesion between the filler and the matrix. The filler may be a sheet of fibres (in common with the first aspect of the invention) or may be a non-fibrous material or a single fibre.

A fourth aspect of the invention provides apparatus for manufacturing a composite material, the apparatus comprising:

a plasma source for irradiating a matrix with a plasma, and

means for coating a filler with the irradiated matrix.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described with reference to the accompanying drawings, in which:

FIG. 1 shows a first step in a method of manufacturing a composite prepreg; and

FIG. 2 shows a second step in the method.

DETAILED DESCRIPTION OF EMBODIMENT(S)

Referring to Figure 1, apparatus 1 for manufacturing a matrix film is shown. A coating head 2 comprises a funnel 3 filled with liquid matrix material 4: either a "melt" or a dispersion. The opening of the funnel 3 is positioned between a pair of rollers 5. The liquid matrix material 4 is applied by the rollers 5 to the upper face of a sheet of release
paper 6 which is fed continuously from a release paper roll 7. The sheet of matrix film 8 and release paper 6 are wound onto a roller 10. When a roll of desired size has been formed, the flow of matrix 4 from the coating head is stopped, and the roller 10 is reversed. The matrix film 8 is wound onto a roller via a guide roller 12 to form a roll 11 of matrix film. At the same time the release paper 6 is wound back onto the release paper roll 7. The roll 11 is then removed and the process is repeated to form a second roll 13 of matrix film shown in Figure 2.

The matrix material 4 is typically a polymer, and may be thermosetting (for example epoxy resin) or thermoplastic (for example polyetheretherketone - PEEK).

Referring to Figure 2, a sheet of fibres 20 is fed from a roller (not shown) via a pair of guide rollers 21,22. The fibres making up the sheet 20 may be made of any organic or inorganic material such as carbon, glass, natural fibre or thermoplastic. The sheet 20 may be in the form of a unidirectional tape or a woven fabric. A pair of matrix films are unwound from the matrix film rolls 11,13 via rollers 22,23. The three-layer assembly is then heated by a heater 24 and compressed between three pairs of consolidation rollers 25. This causes the sheet to be impregnated with the matrix material to form a sheet of prepreg 26. The prepreg 26 is shown in Figure 2 as two layers, but in reality will effectively be a single layer of matrix-impregnated fibre. The prepreg 26 is then wound on to a roller 27 along with a layer of release paper 28 which is unwound from a release paper roll 29 and applied to the prepreg by a pair of rollers 30,31.

Prior to entering an adhesion zone (indicated generally at 32, and defined by the rollers 22,33, heater 24 and consolidation rollers 25) the fibre sheet 20 and/or the matrix films from rolls 11,13 are irradiated with plasma in an irradiation zone (indicated generally at 33). Three plasma sources are shown in Figure 2:

- a first source 40 which is directed at the nip of the roller 22 so as to irradiate the opposed faces of the fibre sheet and the lower matrix film;
• a second source 41 which is directed at the nip of the roller 23 so as to irradiate the opposed faces of the fibre sheet and the upper matrix film; and

• a third source 42 which is directed at the upper matrix film only.

Although three sources are shown in Figure 2, more or less plasma sources may be used as required. Thus in general, plasma sources may be used to irradiate the fibre sheet only; one or both of the matrix films only; or the fibre sheet and one or both of the matrix films (as in Figure 2).

Each plasma sources may be for example:

• a "Plasmatec" plasma unit supplied by Plasmatec Inc. of Montreal, Canada;

• a "Tantec" plasma unit supplied by Dyne Technology Ltd, of Tamworth, UK; or

• an "AX Series" plasma unit supplied by Adtec Europe Ltd (UK) of Hounslow Business Park, UK.

The plasma sources generate plasma at substantially atmospheric pressure. This means that the plasma sources do not need to be housed in a vacuum chamber as in US5 108780, but instead may be housed under normal conditions (that is, in air at atmospheric pressure) along with the rest of the apparatus.

The irradiation and impregnation process are run simultaneously, instead of being run in series as batch processes. This enables the fibre sheet to be impregnated quickly after irradiation, while the active free radicals are still present.

The rollers are run continuously, so that the fibre sheet and matrix films are moving during irradiation and impregnation.

The plasma may be generated at ambient or elevated temperature and may be any mixture of gases such as oxygen, argon and nitrogen mixed in any proportion to form the required ionic species for treating the material. For example, the plasma may be:
• nitrogen/argon
• nitrogen/oxygen
• nitrogen/oxygen/argon
• air

Although only three plasma sources are shown in Figure 2, depending on the width of the sheet 20, further plasma sources may be arranged in an array (that is, out of the plane of Figure 2) to irradiate the full width of the fibre sheet and/or matrix films. The width may range between 3mm and 20 metres.

The irradiation of the fibres and/or matrix generates free radicals on their surfaces and enhances adhesion between these components in the prepreg. These free radicals have a limited dwell time, so the plasma sources 40-42 are positioned sufficiently close to the rollers 22,23, and the rollers are run at a sufficient speed, to ensure that the layers are brought together by the rollers 22,23 as soon as possible after irradiation, typically less than 30 seconds after irradiation and preferably less than one second after irradiation.

Typically the process is run at 2-10 metres per minute, although speeds of up to 400 metres per minute may be possible.

No separate adhesive is applied to the fibre sheet prior to combination with the matrix.

The prepreg can be used in the formation of aircraft components such as wing skins, stringers, spars, wing access panels, or spoilers; or non-aircraft components such as bicycle frames, industrial goods, sports goods, automotive products, wind energy products, or marine products such as boat hulls.

Although the invention has been described above with reference to one or more preferred embodiments, it will be appreciated that various changes or modifications may be made without departing from the scope of the invention as defined in the appended claims.
CLAIMS

1. A method of manufacturing a composite sheet, the method comprising:
   a. irradiating a sheet of fibres and/or a matrix at an irradiation zone with a plasma at substantially atmospheric pressure, and
   b. impregnating the sheet of fibres with the matrix at an adhesion zone;

wherein processes a. and b. are performed simultaneously.

2. The method of claim 1 wherein process b. is performed at substantially atmospheric pressure.

3. The method of any preceding claim wherein the matrix is in a sheet form during process b.

4. The method of any preceding claim wherein the sheet of fibres and/or the matrix are moving during process a.

5. The method of any preceding claim wherein the sheet of fibres is moving during process b.

6. The method of any preceding claim wherein process b. is performed in air.

7. The method of any preceding claim further comprising moving the sheet of fibres and/or the matrix from the irradiation zone to the adhesion zone in less than 30 seconds.


9. Apparatus for manufacturing a composite sheet, the apparatus comprising:
   a. a plasma source for irradiating a sheet of fibres and/or a matrix with a plasma at substantially atmospheric pressure, and
b. means for impregnating the sheet of fibres with the matrix.

10. A method of manufacturing a composite material, the method comprising:
   a. irradiating a matrix with a plasma, and
   b. coating a filler with the irradiated matrix.

11. The method of claim 10 wherein process a. is performed at substantially atmospheric pressure.

12. The method of claim 10 or 11 wherein process b. is performed at substantially atmospheric pressure.

13. The method of any of claims 10 to 12 wherein the filler comprises a sheet.

14. The method of any of claims 10 to 13 wherein the matrix comprises a sheet.

15. The method of any of claims 10 to 14 wherein the matrix is irradiated in process a. as it moves through an irradiation zone; and coats the filler in process b. as it moves through an adhesion zone.

16. The method of any of claims 10 to 15 wherein process a. and process b. are performed simultaneously.

17. The method of any of claims 10 to 16 wherein process b. is performed in air.

18. The method of any of claims 10 to 17 wherein the matrix is irradiated in process a. at an irradiation zone, and coats the filler in process b. at an adhesion zone, and wherein the method further comprising moving the matrix from the irradiation zone to the adhesion zone in less than 30 seconds.

19. A composite material manufactured by the method of any of claims 10 to 18.

20. Apparatus for manufacturing a composite material, the apparatus comprising:
a. a plasma source for irradiating a matrix with a plasma, and

b. means for coating a filler with the irradiated matrix.
INTERNATIONAL SEARCH REPORT

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)
B29C  B29B  D06M

Documentation searched other than minimum documentation & the extent to which 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

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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</thead>
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<tr>
<td>X</td>
<td>US 5 895 622 A (RAMANI KARTHIK [US] ET AL) 20 April 1999 (1999-04-20)</td>
<td>1,2,4-6, 8-12, 15-17, 19,20</td>
</tr>
<tr>
<td></td>
<td>column 5 , line 24 - column 6 , line 65; figures 1,2</td>
<td>3,7,13, 14,18</td>
</tr>
<tr>
<td>X</td>
<td>EP 0 191 680 A (SHINETSU CHEMICAL CO [JP]) 20 August 1986 (1986-08-20)</td>
<td>8,19</td>
</tr>
<tr>
<td></td>
<td>claims 1,4</td>
<td>1-7, 9-18,20</td>
</tr>
<tr>
<td></td>
<td>cited in the application</td>
<td>1-7, 9-18,20</td>
</tr>
<tr>
<td></td>
<td>column 5 , line 20 - line 63; figure 1</td>
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</tbody>
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X Further documents are listed in the continuation of Box C. E See patent family annex.

* Special categories of cited documents :

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*A document member of the same patent family

Date of the actual completion of the international search
13 November 2007

Date of mailing of the international search report
20/11/2007

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
Tel. +31-70 340-2040, Tx. 31 651 epo nl.
Fax: +31-70 340-3016

Authorized officer

Pierre, Nathalie
<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>DE 196 10 113 A1 (REINHAUSEN MASCHF SCHEUBECK [DE]) 18 September 1997 (1997-09-18) column 6, line 23 - column 7, line 50; claims 1,2,7; figure 5</td>
<td>1-20</td>
</tr>
<tr>
<td>A</td>
<td>US 5 266 139 A (YOKOTA MICHAEL J [US] ET AL) 30 November 1993 (1993-11-30) column 6, line 22 - line 29; figure 1 column 11, line 26 - line 31</td>
<td>1-20</td>
</tr>
</tbody>
</table>
## INTERNATIONAL SEARCH REPORT

### Information on patent family members

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 5895622 A</td>
<td>20-04-1999</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>US 5180780 A</td>
<td>19-01-1993</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>DE 19610113 A1</td>
<td>18-09-1997</td>
<td>AU 1925897 A</td>
<td>01-10-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>WO 9734307 A1</td>
<td>18-09-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0886872 A1</td>
<td>30-12-1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZA 9702130 A</td>
<td>25-09-1997</td>
</tr>
<tr>
<td>US 5266139 A</td>
<td>30-11-1993</td>
<td>NONE</td>
<td></td>
</tr>
</tbody>
</table>

Form PCT/IBA/210 (patent family annex) (April 2005)