

A PROCESS OF MELT IMPREGNATION

The present invention relates to a process of melt impregnation, in particular for preparing fibre-reinforced resin materials.

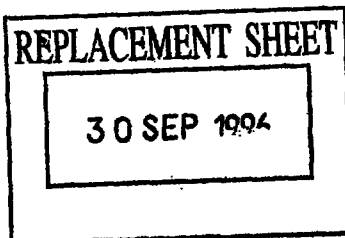
5 Fibre-reinforced resin materials are high in strength but light in weight, and are therefore highly desirable building materials in a number of industries.

10 A process of making such materials is described in EP-B-0167303, in which a fibre bundle is slid over a heated extruder head having an arcuate surface, and molten thermoplastic polymer is injected into the fibre bundle, from a slot in the arcuate surface, in a direction transverse to the array of filaments making up the fibre bundle.

15 When this process is used with relatively viscous materials, a significant operational problem is experienced, in that the extruded polymer tends to push the fibre bundles away from the surface of the extruder head rather than penetrating the bundle and thereby coating the individual fibres thereof. Fibres that are not encircled with polymer (wetted) do not contribute to the mechanical properties of the composite material. In further processing steps the fibre wetting can be improved but this often leads to a degradation in fibre length and consequently reduces the reinforced efficiency of the fibres. Attempting to overcome this problem by increasing fibre pressure onto the extruder head leads to unacceptably high friction over the extruder head.

20 EP-A-397506 discloses a process which differs from that of EP-B-167303 in the presence of two slit-like feed openings to the opposite sides of the arcuate surface, or more than 2 such openings. EP-A-397506 does not disclose any technical effect of having more than one slit-like opening.

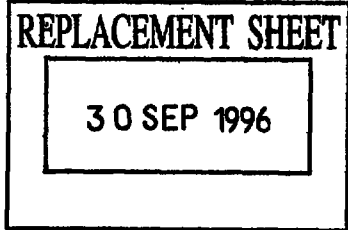
30 The present invention provides a process of making a fibre-reinforced polymeric material comprising the steps of sliding a fibre bundle over an arcuate support surface in the line of the arc, and injecting into the bundle a molten or liquid polymer,



AMENDED SHEET

- 1a -

characterized in that the polymer is injected through at least eight slots in the surface, each slot being substantially transverse to the bundle.



AMENDED SHEET

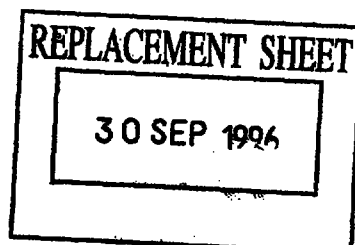
The process of the invention allows surprisingly effective impregnation of materials; for instance, it ensures that the individual fibres in the fibre bundle are encircled by polymer. It is therefore capable of producing more uniform materials than the prior art.

In addition, the process can be used to make fibre-reinforced polymeric resin materials at relatively high production speed and low capital costs.

Describing the process of the invention in more detail; a fibre bundle is slid over an arcuate surface. Use of an arcuate surface enables axial tension in the fibre to be converted into a radial force of the fibre towards the support surface. This radial force can be influenced by the axial pretension in the fibre, the contact angle of the fibre on the surface and the radius of the surface. Within these parameters, the surface geometry can be optimised for a certain pultrusion speed, fibre permeability and polymer viscosity.

The arcuate support can be provided by the surface of a support, for example, when the support is cylindrical. Alternatively, it can be provided by cutting an arcuate section, or trench, through a support. The remainder of the support can be any suitable shape to allow co-operation with other equipment with which it is to be used. For example, it may be mounted on an extruder. It is preferred that side walls extend upwardly from the surface, to facilitate handling of the fibre bundle passing over it and to prevent polymer from escaping sideways from under the fibre bundle.

Molten or liquid polymer, typically a thermoplastic polymer (though thermoset resins can be used), is pressed through a plurality of slots in the arcuate surface of the impregnation tool. These slots are substantially transverse to the direction of fibre alignment and bundle movement, since otherwise the fibres could become entrapped in the slots. There are at least eight slots in the arcuate surface but preferably there are more, for instance at least 12. The number of slots depends upon, for instance, the thickness of the bundle that has to be impregnated, the viscosity of the polymer used and the pultrusion speed required. The polymer



AMENDED SHEET

Apparatus suitable for use in the process of the invention can be designed suitably small for use in inline impregnation processes, such as pultrusion of profiles or filament winding.

5 Examples of suitable reinforcing fibres are glass, carbon and aramide fibres. Examples of suitable thermoplastic polymers, with which to impregnate these fibres, include polyolefin, such as polyethylene and polypropylene, polyesters such as polyethylene terephthalate (PET), and polyketones. Thermosetting polymers may also be used, such as phenolic and epoxy resins.

10 The invention will now be described in more detail by way of example only with reference to the accompanying drawings, in which:

Fig. 1 is a perspective view of part of apparatus suitable for use in the process of the invention; and

15 Fig. 2 is a part cross-section of the apparatus of Fig. 1 in use, with a fibre bundle passing over its surface.

Referring to Fig. 1, a support 1 has an arcuate surface 2 having side walls 3, i.e. in the form of trench in the support. At least eight slots 4 are provided in the arcuate surface, through which polymer is injected into the fibre bundle. The support is typically connected to an extruder (not shown) which supplies polymer to a central bore 5 in the support, the bore being in connection with the slots 4.

25 Referring to Fig. 2, a fibre bundle 6 is passed over the arcuate surface 2 in a direction 7. Polymer is injected into the fibre bundle through channels 8, which are in turn supplied with polymer through central bore 5 connected to an extruder. The polymer that exits from channels 8 tends to create a film 9 of polymer over the contact area between the fibre bundle 6 and the arcuate surface 2, and this acts to reduce the friction between them.

30 The following example illustrates the invention:

Example

35 A 2400 tex glass fibre, with an appropriate sizing, is impregnated with a polypropylene matrix according to the process. The polypropylene has a melt flow index (MFI) of 25 gr/10 min and a relative viscosity of 2.1 (measured according to ASTM D 1601-86 in

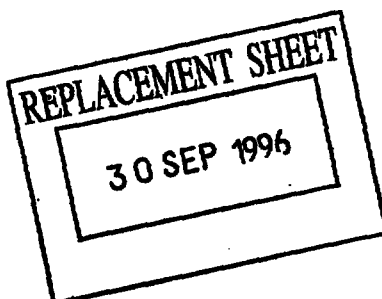
REPLACEMENT SHEET

30 SEP 1996

AMENDED SHEET

C L A I M S

1. A process of making a fibre-reinforced polymeric material, comprising the steps of sliding a fibre bundle (6) over an extruder die having an arcuate support surface (2) in the line of the arc, and injecting into the bundle a molten or liquid polymer,
5 characterized in that the polymer is injected through at least eight slots (4) in the arcuate surface (2), each slot being substantially transverse to the bundle (6).
2. The process as claimed in claim 1 wherein at least 12 transverse slots (4) are present in the arcuate support surface (2).
- 10 3. The process as claimed in claim 1 or 2 wherein the spacing between successive slots (4) increases in the direction of bundle movement (7).
4. The process as claimed in any one of claims 1-3, wherein the width of each slot (4), in the direction along the fibre bundle (6),
15 is in the range 0.2 to 1.5 mm.
5. The process as claimed in any one of claims 1-4, wherein the relative viscosity of the polymer is less than 50.
6. The process as claimed in any one of claims 1-5, wherein the polymer is a thermoplastic polymer selected from polyolefins,
20 polyesters and polyketones.
7. Extruder die suitable for use in the process of any one of claims 1-6 which comprises an axial bore (5), communicating through radial channels (8) with slots (4) on an arcuate external surface, characterized in that there are at least eight of said slots.



0-0751132

AMENDED SHEET



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

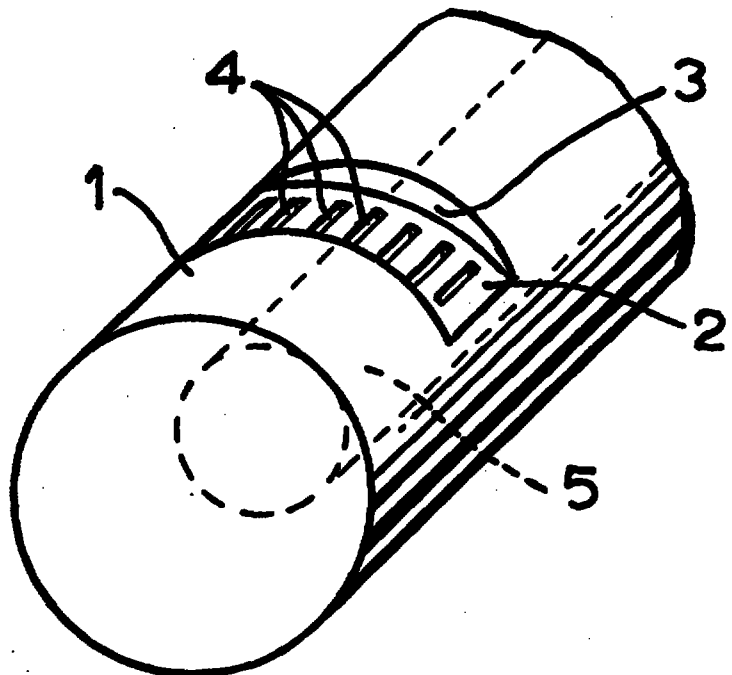
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29B 15/12, B29C 47/30	A1	(11) International Publication Number: WO 95/25000 (43) International Publication Date: 21 September 1995 (21.09.95)
(21) International Application Number: PCT/EP95/01024 (22) International Filing Date: 16 March 1995 (16.03.95) (30) Priority Data: 94301920.8 17 March 1994 (17.03.94) EP (34) Countries for which the regional or international application was filed: AT et al. (71) Applicant (for all designated States except US): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventor; and (75) Inventor/Applicant (for US only): VLUG, Marc, Andrew [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).	(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SG SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments. RTMP + annexes	

(54) Title: **A PROCESS OF MELT IMPREGNATION**

(57) Abstract

A process of making a fibre-reinforced polymeric material comprises sliding a fibre bundle over an arcuate support surface (2) in the line of the arc, and injecting into the bundle a molten or liquid polymer through a plurality of slots (4) in the surface, each slot being transverse to the bundle. The process allows effective impregnation of materials, at relatively high production speed and low capital cost.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

THIS SHEET HAS BEEN
REPLACED

- 1 -

This Sheet Has Been Replaced



A PROCESS OF MELT IMPREGNATION

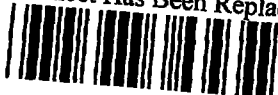
The present invention relates to a process of melt impregnation, in particular for preparing fibre-reinforced resin materials.

5 Fibre-reinforced resin materials are high in strength but light in weight, and are therefore highly desirable building materials in a number of industries.

A process of making such materials is described in EP-B-0167303, in which a fibre bundle is slid over a heated extruder head having an arcuate surface, and molten thermoplastic polymer is
10 injected into the fibre bundle, from a slot in the arcuate surface, in a direction transverse to the array of filaments making up the fibre bundle.

When this process is used with relatively viscous materials, a significant operational problem is experienced, in that the extruded
15 polymer tends to push the fibre bundles away from the surface of the extruder head rather than penetrating the bundle and thereby coating the individual fibres thereof. Fibres that are not encircled with polymer (wetted) do not contribute to the mechanical properties of the composite material. In further processing steps the fibre
20 wetting can be improved but this often leads to a degradation in fibre length and consequently reduces the reinforced efficiency of the fibres. Attempting to overcome this problem by increasing fibre pressure onto the extruder head leads to unacceptably high friction over the extruder head.

25 The present invention provides a process of making a fibre-reinforced polymeric material comprising the steps of sliding a fibre bundle over an arcuate support surface in the line of the arc, and injecting into the bundle a molten or liquid polymer, characterized in that the polymer is injected through a plurality of
30 slots in the surface, each slot being substantially transverse to the bundle.

THIS SHEET HAS BEEN
REPLACED

- 2 -

5 The process of the invention allows surprisingly effective impregnation of materials; for instance, it ensures that the individual fibres in the fibre bundle are encircled by polymer. It is therefore capable of producing more uniform materials than the prior art.

In addition, the process can be used to make fibre-reinforced polymeric resin materials at relatively high production speed and low capital costs.

10 Describing the process of the invention in more detail; a fibre bundle is slid over an arcuate surface. Use of an arcuate surface enables axial tension in the fibre to be converted into a radial force of the fibre towards the support surface. This radial force can be influenced by the axial pretension in the fibre, the contact angle of the fibre on the surface and the radius of the surface.

15 Within these parameters, the surface geometry can be optimised for a certain pultrusion speed, fibre permeability and polymer viscosity.

The arcuate support can be provided by the surface of a support, for example, when the support is cylindrical.

20 Alternatively, it can be provided by cutting an arcuate section, or trench, through a support. The remainder of the support can be any suitable shape to allow co-operation with other equipment with which it is to be used. For example, it may be mounted on an extruder. It is preferred that side walls extend upwardly from the surface, to facilitate handling of the fibre bundle passing over it and to

25 prevent polymer from escaping sideways from under the fibre bundle.

Molten or liquid polymer, typically a thermoplastic polymer (though thermoset resins can be used), is pressed through a plurality of slots in the arcuate surface of the impregnation tool. These slots are substantially transverse to the direction of fibre

30 alignment and bundle movement, since otherwise the fibres could become entrapped in the slots. There are at least two slots in the arcuate surface but preferably there are more, for instance at least 8 or 12. The number of slots depends upon, for instance, the thickness of the bundle that has to be impregnated, the viscosity of

35 the polymer used and the pultrusion speed required. The polymer

- 3 -

creates a film between the surface of the tool and the glass fibre. This polymer film simultaneously lubricates the process and impregnates the glass fibre. Since the fibre is impregnated from one side, air is expelled through the other side of the fibre bundle, reducing the void content of the composite. The thickness of the polymer film is an important parameter. If the film is too thin the fibres will touch the tool surface, resulting in frictional forces between the tool surface and the fibre, and no more impregnation of the fibre will occur. If the film thickness is too high the polymer will push the fibre aside and flow other than through the fibre bundle, creating excessive amounts of voids in the composite. Typical film thicknesses are in the range of 0.05 to 1 mm.

When a fibre is passing over a slot in the tool surface an amount of polymer is delivered through the slot forming a film with a certain thickness. This film thickness is limited as explained above and, in case of high viscosity polymers, does not contain enough polymer to wet-out all the filaments in the fibre bundle when operating according to prior art methods. Following the surface of the tool the polymer is pressed into the fibre bundle increasing the degree of impregnation and reducing the polymer film thickness. Well before the film thickness is reduced to zero and the fibres touch the tool surface, polymer is added to the film by another slot in the tool, etc., until the fibre bundle is fully impregnated. With relatively low viscosity polymers, 50 Pa.s and below (at 10^3 - 10^4 Pa.s shear stress and operating temperature), the travelling speed of the polymer through the fibre bundle may be so high that one slot and a small contact area on the tool is sufficient. But with relatively high viscosity polymers, 100 Pa.s and higher (at 10^3 - 10^4 Pa.s shear and operating temperature), the pultrusion speed would need to be reduced to an extent that the process is no longer economically attractive. The process of this invention is particularly suitable for thermoplastic polymers having a relative viscosity (measured according to the appropriate ASTM method) below 50.

- 4 -

The spacings between the slots do not have to be equal. Initial impregnation occurs much faster than impregnation at the end of the process. Slots that are reached first by the fibre have to be relatively close, gradually increasing the space between two slots.

5 The degree of impregnation also depends on the ratio of arcuate surface area: area of slots. The ratio is typically in the range 5 to 20. The length of each slot, in the direction transverse to the bundle, is chosen according to the width of the bundle passing over the arcuate surface; clearly it is unsatisfactory to impregnate only
10 part, for example the middle, of the bundle.

The width of each slot, in the direction along the bundle, is dependent mostly on the viscosity of the polymer. For instance, the slots should not be made too narrow as to cause blocking thereof; however at the same time thin slots allow shear thinning of certain
15 polymers, such as polypropylene. In general more but thinner slots are preferred over less but wider slots. Typical widths of slots are in the range 0.2 to 1.5 mm and preferably 0.2 to 0.5 mm for high viscosity polymers.

20 The slots are typically fed with polymer by, for instance, an extruder which may be heated if a thermoplastic polymer is being used. The extruder communicates with the plurality of slots through, for example, a bore in the support.

25 The supply of polymer through the slots in the arcuate surface tends to create a film of polymer under the fibre bundle to be impregnated, which extends over the entire contact area. This film practically eliminates the frictional forces between the fibre bundle and the arcuate surface. Therefore, there is no build-up of tension within the bundle, which normally causes damage to the fibres and which limits the speed of the process.

30 The degree of impregnation is improved by spreading the fibre bundle over the arcuate surface, thereby reducing the thickness of the fibre bundle on the surface. Reducing the thickness of the fibre bundle reduces the length through which the polymer has to travel, i.e. the impregnation path. Preferred bundle thicknesses are in the
35 range 5 to 25 filaments.

Apparatus suitable for use in the process of the invention can be designed suitably small for use in inline impregnation processes, such as pultrusion of profiles or filament winding.

5 Examples of suitable reinforcing fibres are glass, carbon and aramide fibres. Examples of suitable thermoplastic polymers, with which to impregnate these fibres, include polyolefin, such as polyethylene and polypropylene, polyesters such as polyethylene terephthalate (PET), and polyketones. Thermosetting polymers may also be used, such as phenolic and epoxy resins.

10 The invention will now be described in more detail by way of example only with reference to the accompanying drawings, in which:

Fig. 1 is a perspective view of part of apparatus suitable for use in the process of the invention; and

15 Fig. 2 is a part cross-section of the apparatus of Fig. 1 in use, with a fibre bundle passing over its surface.

Referring to Fig. 1, a support 1 has an arcuate surface 2 having side walls 3, i.e. in the form of trench in the support. A plurality of slots 4 is provided in the arcuate surface, through which polymer is injected into the fibre bundle. The support is typically connected to an extruder (not shown) which supplies polymer to a central bore 5 in the support, the bore being in connection with the slots 4.

25 Referring to Fig. 2, a fibre bundle 6 is passed over the arcuate surface 2 in a direction 7. Polymer is injected into the fibre bundle through channels 8, which are in turn supplied with polymer through central bore 5 connected to an extruder. The polymer that exits from channels 8 tends to create a film 9 of polymer over the contact area between the fibre bundle 6 and the arcuate surface 2, and this acts to reduce the friction between them.

30 The following example illustrates the invention:

Example

35 A 2400 tex glass fibre, with an appropriate sizing, is impregnated with a polypropylene matrix according to the process. The polypropylene has a melt flow index (MFI) of 25 gr/10 min and a relative viscosity of 2.1 (measured according to ASTM D 1601-86 in



- 6 -

decalin solution at 0.3 %wt concentration). The glass fibre is pulled over an extruder die as shown in Figure 1. The width of the arcuate surface, transverse to the direction of the fibre, is 14 mm. The fibre bundle is spread over the entire width of the surface, reducing the thickness of the fibre bundle to approximately 7 filaments. The radius of the arcuate surface is 25 mm and the contact angle of the fibre over the surface is 100°. In the surface there are 11 slots, with increasing spacing between them along the fibre direction; the width of each slot is 0.35 mm. The axial tension in the fibre bundle is approximately 80N. The extruder die is mounted on an extruder which heats the polypropylene to 250 °C and supplies it to the tool with a pressure of 2 bar. The impregnated fibre is then led through a heated circular die to produce rods that can be chopped into pellets for injection moulding. The pultrusion speed is 20 m/min.

Test specimens are injection moulded from the pellets and their tensile and flexural properties are measured. The tensile strength measured was 105 MPa, the flexural strength was 195 MPa, and the flexural modulus was 9.3 GPa.

Various modifications of the present invention will become apparent to those skilled in the art from the foregoing description and accompanying drawings. Such modifications are intended to fall within the scope of the appended claims.



This Sheet Has Been Replaced

C L A I M S

1. A process of making a fibre-reinforced polymeric material, comprising the steps of sliding a fibre bundle over an extruder die having an arcuate support surface (2) in the line of the arc, and injecting into the bundle a molten or liquid polymer, characterized in that the polymer is injected through a plurality of slots (4) in the arcuate surface, each slot being substantially transverse to the bundle.
2. The process as claimed in claim 1 wherein at least 8 transverse slots (4) are present in the arcuate support surface (2).
3. The process as claimed as claim 1 or 2 wherein the spacing between successive slots increases in the direction of bundle movement.
4. The process as claimed in any one of claims 1-3, wherein the width of each slot, in the direction along the fibre bundle, is in the range 0.2 to 1.5 mm.
5. The process as claimed in any one of claims 1-4, wherein the relative viscosity of the polymer is less than 50.
6. The process as claimed in any one of claims 1-5, wherein the polymer is a thermoplastic polymer selected from polyolefins, polyesters and polyketones.
7. Fibre-reinforced polymeric material whenever produced by a process as claimed in any one of claims 1-6.
8. Extruder die suitable for use in the process of any one of claims 1-7 which comprises an axial bore (5), communicating through radial channels (8) with slots (4) on an arcuate external surface, characterized in that there are a plurality of said slots.