(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 June 2012 (21.06.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/082778 A2

(51) International Patent Classification:
B29C 70/50 (2006.01) *B29C 70/06* (2006.01)

(21) International Application Number:
PCT/US2011/064703

(22) International Filing Date:
13 December 2011 (13.12.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/424,158 17 December 2010 (17.12.2010) US

(71) Applicant *(for all designated States except US)*: **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **SADLO, James L.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **MROZINSKI, James S.** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US). **NICHUM, Kim L.** [DK/DK]; Fabriksparken 15, DK-2600 Glostrup (DK).

(74) Agents: **NOWAK, Sandra K.** et al.; 3M Center Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, Minnesota 55133-3427 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

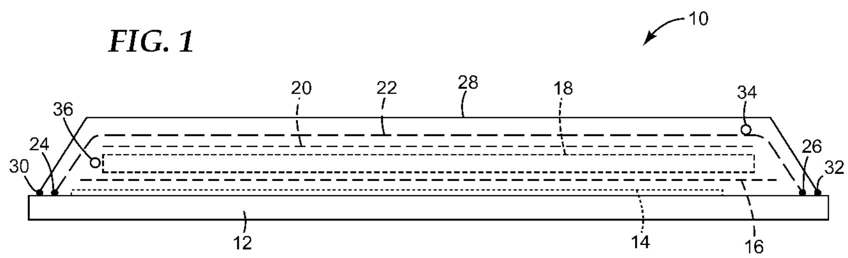
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:
— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: COMPOSITE ARTICLE AND METHOD OF MANUFACTURE

FIG. 1



(57) Abstract: The present application is directed to a method for producing a composite component. The method comprises providing a composite preform on a tool, providing a polymeric microporous membrane encapsulating the composite preform and providing a gas impermeable membrane encapsulating the microporous membrane. Air is removed from between the microporous membrane and the gas impermeable membrane. A matrix material is then introduced in contact with the composite preform and the mircoporous membrane and is infused into the pores of the microporous membrane. The application is additionally directed to a device for producing composite components. The device comprises a tool configured to hold a composite preform, a microporous membrane encapsulating the preform, and a gas impermeable membrane encapsulating the microporous membrane. The microporous membrane is permeable to a matrix material.

WO 2012/082778 A2

COMPOSITE ARTICLE AND METHOD OF MANUFACTURE

FIELD OF THE INVENTION

The present invention is directed to a composite article and the method of manufacturing the composite article.

BACKGROUND INFORMATION

Many methods to manufacture composite articles are known using composite preforms. The composite preform can be a woven fabric, a multi-axis interlaid scrim or a warp-thread reinforced unidirectional preform. The preforms are used in the production of components made of fiber-reinforced material, for example airplane wings, boat hulls and wind turbine blades. They represent an intermediate process step before infiltration by resin and curing.

The composite preform is then infused with a matrix resin material. This may be accomplished using vacuum infusion. Vacuum infusion, utilizes a vacuum to remove air from around a composite preform and a resin is allowed to be infused by the vacuum to completely wet-out all air voids in the composite preform. Typical resins used are polyester, vinyl ester, and epoxy. The resin is then generally cured.

The vacuum infusion process is limited by the length of the flow the resin must travel to completely wet all air voids. The vacuum infusion process is limited by the length of the flow the resin must travel to completely wet all air voids. During infusion a pressure gradient develops along the part length between the injection and the vacuum lines. Which in turn results in a thickness gradient along the length of the part, the thickness gradient directly creates a variation in the fiber volume fraction. Voids can occur in the final part due to entrapped air in the fiber-bundle, entrapped air during the resin mixing process and due to generation of volatiles during resin curing. Thickness gradient, fiber volume fraction variations and voids can result in significant variation in the mechanical properties of the composite. In some processes, a membrane is used as an aid to control such variations. The membranes used in these processes are generally semipermeable, or impermeable to resin while being permeable to a gas.

Summary

The present application is directed to a method for producing a composite component. The method comprises providing a composite preform on a tool, providing a polymeric microporous membrane encapsulating the composite preform and providing a gas impermeable membrane encapsulating the microporous membrane. Air is removed from between the microporous membrane and the gas impermeable membrane. A matrix material is then introduced in contact with the composite preform and the mircoporous membrane and is infused into the pores of the microporous membrane.

In certain embodiments, the matrix material renders the microporous membrane translucent.

In some embodiments, a breather layer is between the microporous membrane and the gas impermeable membrane

The application is additionally directed to a device for producing composite components. The device comprises a tool configured to hold a composite preform, a microporous membrane encapsulating the preform, and a gas impermeable membrane encapsulating the microporous membrane. The microporous membrane is permeable to a matrix material.

Brief Description of the Drawings

The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings, in which:

Figure 1 is a side view of the apparatus used in the method of the present application.

Detailed Description

The present application is directed to a composite article and its method of manufacture. In specific embodiments, the composite article is a multilayer composite.

The composite preform (generally, a preform is used for reinforcement layers such as glass fibers, etc.) may be any reinforcement material such as glass fiber, carbon, etc. useful for a desired end application. The composite may be a reinforced plastic component including carbon fibers, glass fibers, aramid fibers, boron fibers or hybrid materials, the geometric shape of which maybe any desired shape. In some embodiments, the material is a combination of multiple homogeneous systems. Such embodiments are intended to be described as a composite. The composite may be suitable for the production of wind turbine blades, aircraft components and boat hulls.

The composite preform is mounted on a tool. The tool may be made from various suitable materials, e.g., wood, steel, sheet metal, glass, etc. In some embodiments, the composite preform is separated from the tool for ease of final separation, for example with a peel-ply and/or a release layer. In embodiments, where the permeability of the preform is low a flow media is used to facilitate uniform resin flow across the surface of the composite. For example, netted mesh with high permeability available under the name Green Flow 75 at www.airtechonline.com.

The resin may be any resin material useful in the desired application. For example, in wind blade manufacture, a useful resin is epoxy resin, for example, one commercially available under the trade designation "EPIKOTE RESIN MGS RIMR 135" from Hexion Specialty Chemicals, Columbus, Ohio. The resin is fed to the composite material using an infusion line. A vacuum is created around the composite and the resin flows into the lower pressure void from an attached reservoir.

A microporous membrane encapsulates the composite preform. Encapsulation means, for the purpose of the present application, that the membrane is sealed around the composite, for example sealed to the tool with any method known (e.g. vacuum tape). There may be layers between the membrane and the composite, for example a peel-ply to facilitate removal after the process is complete and a flow media to produce a channel for uniform distribution of the resin. The presence of membrane equalizes vacuum pressure throughout the length of the part reducing the thickness gradient. It also reduces the void content in the final composite thus improving its physical properties. The use of membrane also reduces the overall fill time of a given part geometry.

The microporous membrane is made as shown in U.S. Patent numbers 5,238,623; 5,120,594; and 4,726,989, the teaching of which are incorporated by reference herein.

These microporous membranes contain actual microporous holes. For the purpose of the present application the term microporous is defined as having an open morphology of a controlled pore size typically ranging from about 0.01 μm to about 10 μm. In certain embodiments, the microporous membrane has an open morphology of a controlled pore size typically ranging from about 0.1 μm to 1 μm.

The micropores may be formulated with a tortuous path through the membrane. Generally, the tortuous path provides a slow path through the microporous membrane. The membrane is therefore permeable to both gas and fluid. It is therefore surprising that such a membrane can be used in this process, as it has the ability to still contain the resin. Its permeability to the resin allows for the membrane to become transparent/translucent when the resin begins to permeate. Therefore, the operator can see the resin location and note when the part have been completely filled, this helps the operator from over filling the part with excess resin. Excess resin reduces the fiber weight fraction of the composite part which can result in significant loss of its mechanical properties. Therefore the transparency/translucency property of this membrane plays an important to obtain control and repeatability in the current process. Such a process allows for the resin flow to move without inhibition and the resin is still contained so as to not enter the vacuum lines. The use of a transparent or translucent membrane will increase process robustness, which will reduce the risk of dry spot formation in complex part shapes.

A breather layer is generally between the microporous membrane and the gas impermeable membrane. The breather layer facilitates the air flow during the vacuum process. It separates the gas impermeable membrane from the microporous membrane, and allows for tangential air flow, which creates the vacuum as air flows out of the area between the microporous membrane and the gas impermeable membrane. Air is further removed from the area between the microporous membrane and the composite preform as the air flows through the microporous membrane to the breather layer. In some embodiments, the breather material is a nonwoven material. It may also be laminated to the microporous membrane. In other embodiments, the breather layer is a structured surface on the microporous membrane.

The breather layer is encapsulated by a gas impermeable membrane. The gas impermeable membrane is any material known to be effective as a vacuum bag or bladder.

In some embodiments, the resin flows over the top of the composite preform, between the composite preform and the microporous membrane. In other embodiments, the resin flows over side of the composite facing the tool. The present application is directed to a process that will limit flow time. For example, the resin will flow over the entire surface of the composite and will flow through the thickness. In embodiments where the resin flow from the tool side to the microporous membrane side, the completion of the flow will be marked by the change of the microporous membrane from opaque to transparent/translucent and indicated above.

The present application may allow for faster infusion times. It may also allow for more complex geometries to be filled. Additionally, resin systems with nano-particles may be used, allowing for a higher compression strength without the loss of productivity.

One embodiment of the present application can be seen in Figure 1. The device 10 comprises a tool 12. In the embodiment of Figure 1, a flow media 14 and a peel-ply 16 are on the tool. The composite preform 18 is on the tool 12. An additional peel-ply 20 sits over the preform 18. A microporous membrane 22 encapsulates the preform 18 and is attached to the tool 12 around the perimeter of the composite preform. In the cross section of Figure 1, the perimeter is represented by points 24 and 26. A gas impermeable membrane 28 encapsulates the microporous membrane, and is attached to the tool round the perimeter of the microporous membrane, represented by points 30 and 32. A vacuum line 34 is used to pull the vacuum from the space between the gas impermeable membrane 28 and the microporous membrane 22. A resin infusion line 36 delivers resin to the composite preform 18.

Embodiments and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

EXAMPLES

All patents and publications referred to herein are hereby incorporated by reference in their entirety. Various modifications and alterations of this disclosure may be made by those skilled in the art without departing from the scope and spirit of this disclosure, and it should be understood that this disclosure is not to be unduly limited to the illustrative embodiments set forth herein.

A Seeman Composites Resin Infusion Molding Process (SCRIMP) system was set up as shown in Figure 1. Two embodiments of the microporous membrane were introduced into the system. The first embodiment was a single layer 5 mil/127 microns (μm) thick membrane with average pore size of 0.5 μm , 40 % porosity and a Gurley value of 50 second/50 cc. The second embodiment was 2 layer laminate with a 38.1 μm thick membrane and average pore size of 0.20 μm thermal bonded to a spun bond polypropylene backing of about 40 grams per square meter (gsm), ~180 μm thick from BBA Nonwovens South Carolina, identified as 1.25 oz PP spunbond. The microporous membranes were made accordingly:

A sheet of microporous membrane material, as taught in U.S. Patent numbers 5,238,623; 5,120,594; and 4,726,989US, was prepared using a thermally induced phase separation technique combining about 59.9 parts by weight polypropylene (PP) having a melt flow index of 0.8 dg/min ASTM 1238 (available from Sunoco Inc., Philadelphia Penn), about 0.10 parts Millad 3988 nucleating agent (NA) from Milliken Chemical, and about 40 parts mineral oil (MO), (available as #31 USP Grade). The PP/NA/MO composition was melt extruded on a twin screw extruder operated at a decreasing temperature profile of 260° to 193° C. through a slip gap sheeting die having an orifice of 35.6 cm × 0.05 cm and quenched on a patterned casting wheel maintained at 49° C. The mineral oil containing film was continuously length stretched 1.8:1 at 110 ° C and width stretched or oriented (cross direction) in a tenter oven to a 1.8:1 stretch ratio at 120° C. and heat annealed at 130° C resulting in a membrane that was 127 μm thick, had a pore size of 0.50 μm, a 40 % porosity, and a 50 seconds/50cc Gurley value.

A second microporous material was made except the PP/NA/MO ratio was 64.9/0.1/35.0 and the molten blend was extruded through twin screw system equipped with a film die having an orifice of 130 cm x 0.05 cm. The resulting film became porous after stretching and was 38.1 μm thick, with a pore size of 0.20 μm, 35 % porosity, and 120 seconds/50 cc Gurley value. This membrane was thermal point bonded (18 % point bond pattern) to a 40 gsm PP spunbond web that was about 180 μm thick to create a durable laminate.

Test Method – Thickness: The thickness of a material was measured to the thousandths of an inch using a TMI caliper gauge (Testing Machines Inc., Amityville New York). The measurement was converted into microns.

Test Method - Bubble Point: The Bubble Point pore size is the bubble point value representing the largest effective pore size in a sample, measured in microns, according to ASTM-F-316-80.

Test Method - Porosity: Porosity was calculated from the measured bulk density of the membrane and known pure polyproylene density using the following equation:

Porosity = (1 – membrane bulk density/PP density) x 100

Bulk density was determined by multiplying the weight of a 47 mm diameter disc of material times by a conversion factor of 22.69 and dividing the result by the thickness of the material in inches, as follows:

Bulk density = (weight of 47 mm disc) x (conversion factor 22.69)/thickness (inches).

Test Method – Gurley: The Gurley resistance to air flow value is the time in seconds for 50 cubic centimeters (cc) of air, or another specified volume, to pass through 6.35 cm^2 (one square inch) of the porous membrane at a pressure of 124 mm of water as specified in ASTM D726-58, Method A, also referred to herein as “the Gurley porosity” or “the Gurley resistance to air flow.”

Epoxy resin, commercially available under the trade designation "EPIKOTE RESIN MGS RIMR 135" from Hexion Specialty Chemicals, Columbus, Ohio, was used as the matrix system along with 4 layers of biaxial 800 g/m^2 E-Glass fabric as the reinforcement.

The infusion line, flow media and the peel-ply layers were sealed inside the microporous membrane along with the composite preform. The backing of the entire microporous membrane acted as the breather which ensured uniform vacuum distribution on the part. The vent was placed directly on top of the microporous membrane. Finally, the vacuum bag (gas impermeable membrane) sealed all these materials. The peel-ply layers separates the reinforcements from the distribution medium and the membrane respectively. The distribution medium has a much higher in-plane permeability compared to the fabric stack allowing fast surface resin wet-out of the part ensuing resin penetration through the thickness of the fiber reinforcements under vacuum (100 mbar).

During infusion it was observed that the microporous membrane turned translucent instantaneously as the resin came in contact after penetrating through the reinforcements. This helped to identify the flow front of the resin throughout the infusion process. The first embodiment turned more transparent than the second as it did not have the addition of the nonwoven layer.

What is claimed is:

1. A method for producing a composite component comprising:
providing a composite preform on a tool;
providing a polymeric microporous membrane encapsulating the composite preform;
providing a gas impermeable membrane encapsulating the microporous membrane; and
removing air from between the microporous membrane and the gas impermeable membrane, wherein a matrix material is then introduced in contact with the composite preform and the mircoporous membrane,
wherein the matrix material is infused into the pores of the microporous membrane.

2. The method of claim 1, wherein the matrix material renders the microporous membrane translucent.

3. The method of claim 1 wherein the polymeric microporous membrane is a polyolefin.

4. The method of claim 1 wherein the matrix material is introduced between the composite preform and the microporous membrane.

5. The method of claim 1 wherein the matrix material is introduced between the composite preform and the tool.

6. The method of claim 1 wherein the matrix material is introduced into the composite.

7. The method of claim 1 comprising a breather layer between the microporous membrane and the gas impermeable membrane

8. The method of claim 7 wherein the breather layer is a breather material between the microporous membrane and the gas impermeable membrane.

9. The method of claim 8 wherein the breather material is a nonwoven.

10. The method of claim 8 wherein the breather material is laminated to the microporous membrane.

11. The method of claim 7 wherein the breather layer comprises a structured surface on the surface of microporous film facing the gas impermeable membrane.

12. The method of claim 1 wherein the air is removed by suction.

13. The method of claim 1 wherein the matrix material is introduced as a result of flowing to lower pressure surrounding the composite preform from a reservoir.

14. The method of claim 1 wherein the microporous membrane has an open morphology of a controlled pore size typically ranging from about 0.01 to 10 μm.

15. The method of claim 14 wherein the microporous membrane has an open morphology of a controlled pore size typically ranging from about 0.1 μm to about 1 μm.

16. A device for producing composite components comprising:
a tool configured to hold a composite preform;
a microporous membrane encapsulating the preform;
a gas impermeable membrane encapsulating the microporous membrane,
wherein the microporous membrane is permeable to a matrix material.

17. The device of claim 16 wherein the polymeric microporous membrane is a polyolefin.

18. The device of claim 16 comprising a breather layer between the microporous membrane and the gas impermeable membrane

19. The device of claim 18 wherein the breather layer is a breather material between the microporous membrane and the gas impermeable membrane.

20. The device of claim 19 wherein the breather material is a nonwoven.

21. The device of claim 19 wherein the breather material is laminated to the microporous membrane.

22. The device of claim 18 wherein the breather layer comprises a structured surface on the surface of microporous film facing the gas impermeable membrane.

23. The device of claim 16 wherein the microporous membrane has an open morphology of a controlled pore size typically ranging from about 0.01 to 10 μm.

24. The device of claim 23 wherein the microporous membrane has an open morphology of a controlled pore size typically ranging from about 0.1 μm to about 1 μm.

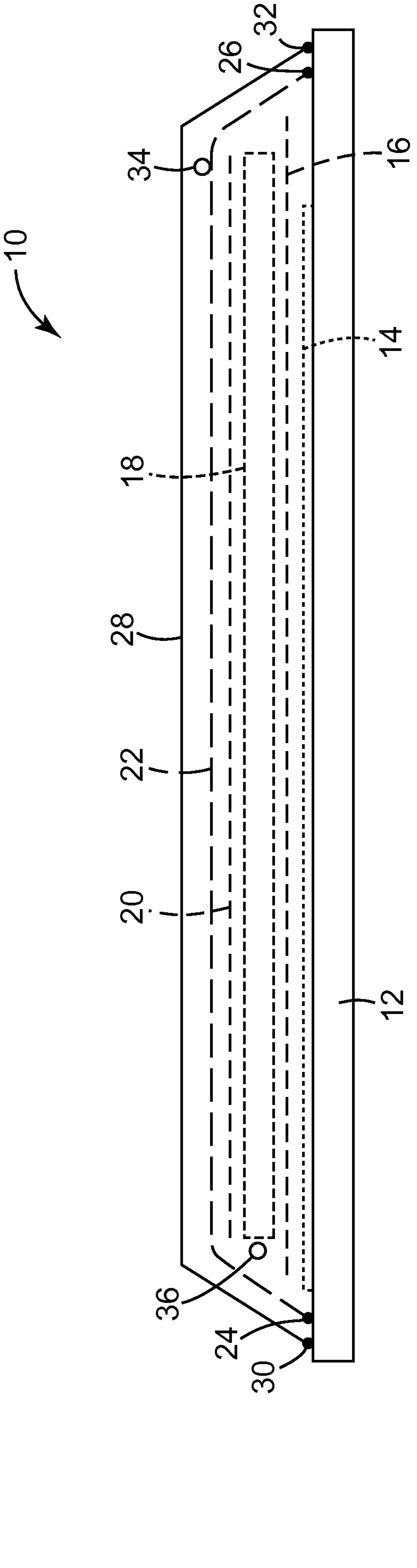


FIG. 1