Method embodiments for producing a fiber-reinforced epoxy composite comprise providing a mold defining a shape for a composite, applying a fiber reinforcement over the mold, covering the mold and fiber reinforcement thereon in a vacuum enclosure, performing a vacuum on the vacuum enclosure to produce a pressure gradient, insulating at least a portion of the vacuum enclosure with thermal insulation, infusing the fiber reinforcement with a reactive mixture of uncured epoxy resin and curing agent under vacuum conditions, wherein the reactive mixture of uncured epoxy resin and curing agent generates exothermic heat, and producing the fiber-reinforced epoxy composite having a glass transition temperature of at least about 100° C. by curing the fiber reinforcement infused with the reactive mixture of uncured epoxy resin and curing agent by utilizing the exothermically generated heat, wherein the curing is conducted inside the thermally insulated vacuum enclosure without utilization of an external heat source or an external radiation source.
References Cited

OTHER PUBLICATIONS

Partial translation of RU 2488612 C1, provided by USPTO translations branch (no date).*

Technical Data Sheet for Stretchlon 700, provided by Airetex International, Inc (2013).*

Technical Data Sheet for DER 330, provided by Dow (no date).*


* cited by examiner
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FIBER-REINFORCED EPoxy COMPOSITES
AND METHODS OF MAKING SAME
WITHOUT THE USE OF OVEN OR
AUToclAVE

STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support by The
National Aeronautics and Space Administration (NASA)
under Contract Numbers NNX11CE48P and
NNX13CA31C. The government has certain rights in this
application pursuant to the contract.

TECHNICAL FIELD

Embodiments of the present disclosure are generally
related to fiber-reinforced epoxy composites and methods of
making fiber-reinforced epoxy composites, and are specifi-
cally related to fiber-reinforced epoxy composites and
methods of making fiber-reinforced epoxy composites without
utilizing an external heat curing step.

SUMMARY

Composites are commonly used in structural applications
where weight savings, fatigue resistance, corrosion resis-
tance, and performance tailorability justify the replacement
of traditional metal parts. However, the widespread use of
composites, for example, fiber-reinforced epoxy composites,
is hindered by conventional manufacturing limitations. The
fabrication of most high-performance composite parts, which
may be conducted through processes such as Vacuum
Assisted Resin Transfer Molding (VARTM), Vacuum
Infusion Process (VIP), Resin Transfer Molding (RTM), requires
autoclaves and ovens of a size that can accommodate the parts
and their tooling. Often, large composite structures must be
made in smaller sections for assembly downstream in order to
employ the capital equipment available and avoid the capital
investments needed for large autoclaves or ovens; however,
the making and assembly of smaller parts into a large struc-
ture increases labor cost and production time and complicates
the design and analysis of the overall composite structure to
be fabricated. In addition, the joining and bonding of smaller
sections may lead to presence of weak points in the structure
that are more prone to mechanical failure. When using tooling
materials with coefficients of thermal expansion (CTEs) dif-
f erent from that of the composite part to be made, thermal
cycles in ovens or autoclaves can create issues with maintain-
ing dimensional tolerances i.e., the oven or autoclave curing
steps may cause significant and undesirable dimensional
differences during curing. When making composite tooling
which is subsequently used to shape and produce composite
parts, lack of dimensional control and tolerance are undesir-
able.

Low CTE Invar alloy (64 wt % Fe and 36 wt % Ni) metal
tooling can be used to obtain high precision composite parts,
but such a tool is expensive, heavy, difficult to handle, and
requires extensive effort to machine. Furthermore, Invar has
a high specific heat capacity which requires long cycle times
in an oven or autoclave to cure high Tg composites i.e.,
composites having a Tg of at least 100°C. Consequently,
the labor, time, material and energy cost for employing such
tooling are significantly higher compared with using polymer
tooling or other higher CTE metal tooling, such as aluminum.

Room temperature curing (i.e., no ovens, autoclaves or
external heat sources) processes avoid issues with CTE mis-
match in making composites with strict dimensional toler-
ance; however conventional room temperature cured epoxy
composites can typically only achieve glass transition (Tg)
temperatures of 60°C, which is indicative of a low perfor-
mance composite ineffective for various industrial applica-
tions, for example, aerospace applications.

As a result, current fabrication processes have been inef-
fective at obtaining low cost, high performance composites
which maintain suitable dimensional control, consequently,
there is a need for improved processes of producing high
performance (i.e. high Tg) fiber-reinforced epoxy compos-
tes, e.g., composites having a Tg of at least 100°C.

Accordingly, embodiments of the present disclosure are
directed to fiber-reinforced epoxy composites having a glass
transition temperature of at least 100°C, by utilizing a pro-
cess which does not use any external heating sources or
radiation sources. The present embodiments remove design
restrictions imposed by autoclaves and ovens and offers sig-
nificant cost and time saving over current composite tooling
methods. Due to the efficiency of the manufacturing method
and robust properties of the present composites, the present
fiber-reinforced epoxy composites are suitable for various
industrial applications. For example, and not by way of limi-
tation, these industrial applications may include Heavy Lift
Launch Vehicles, military and commercial aircraft, wind
blades and towers, civil and automotive infrastructure, and
marine vessels, and especially in the composite tooling indus-
try.

In accordance with another embodiment of the present
disclosure, a method for producing a fiber-reinforced epoxy
composite is provided. The method comprises providing a
mold defining a shape for a composite, applying a fiber rein-
forcement over the mold, covering the mold and fiber rein-
forcement therein in a vacuum enclosure, creating a vacuum
on the vacuum enclosure to produce a pressure gradient,
insulating at least a portion of the vacuum enclosure with
thermal insulation, infusing the fiber reinforcement with a
reactive mixture of uncured epoxy resin and curing agent
under vacuum conditions, wherein the reactive mixture of
uncured epoxy resin and curing agent generates exothermic
heat, and producing the fiber-reinforced epoxy composite
having a glass transition temperature of at least about 100°C
by curing the fiber reinforcement infused with the reactive
mixture of uncured epoxy resin and curing agent by utilizing
the exothermically generated heat, wherein the curing is con-
ducted inside the thermally insulated vacuum enclosure with-
out utilization of an external heat source or an external radia-
tion source.

Additionally, it is contemplated that the utilization of exo-
thermic heat instead of external heat and radiation sources
could also be incorporated into other composite fabrication
techniques such as prepregging, hand lay-up technique, and
the like. Without being bound by theory, the present process
of utilizing this exothermic heat in composite fabrication
techniques advantageously achieves high performance com-
posites with stricter dimensional tolerance, while minimizing
capital investment and cost.

In accordance with another embodiment of the present
disclosure, a fiber-reinforced epoxy composite is provided.
The fiber-reinforced epoxy composite defines a glass transi-
tion temperature of at least 100°C and a dimensional change
value of less than 2500 µm/m during the cure process.

BRIEF DESCRIPTION OF THE DRAWINGS

The following detailed description of the preferred
embodiments of the present disclosure can best be understood
when read in conjunction with the following drawings:
DETAILED DESCRIPTION

Embodiments of the present disclosure are directed to methods for producing fiber-reinforced epoxy composites without utilizing external or separate heating elements. As used herein, “external heating element” or “external heating source” includes ovens, autoclaves, hot air heating sources, heat blankets, resistive heaters, or the like that are conventionally used during curing steps, but are eliminated in the embodiments of the present disclosure. As further used herein, “external radiation element” or “external radiation source” includes infra-red lamps or heaters, ultra-violet (UV) light devices, electron beam (e-beam) curing devices, or the like that are also conventionally used during curing steps, but are eliminated in the embodiments of the present disclosure.

Referring to FIG. 1, the process for forming the fiber-reinforced epoxy composites comprises providing a mold 10 defining a shape for a composite. As shown in FIG. 3, the mold 10 may have one or more recessed regions 12 which are used to define the desired shape of the composite to be produced. As shown in the embodiments depicted in FIG. 3, the fiber-reinforced epoxy composites 100 by the mold 10 produced may be used composite tooling, which itself may be used as a mold for another composite part 200. However, for clarity in this application, “mold” is being used to define the frame used to shape the fiber-reinforced epoxy composites, which may in some embodiments be used as a composite tool.

Various materials are considered suitable for the mold 10. For example, the mold 10 may comprise at least one component selected from the group consisting of polymer, glass, ceramic, carbon-carbon composite, fiber-reinforced polymer composite, metal, wood, polymeric foam, ceramic foam, glass foam, syntactic foam, carbon foam, metal foam, a honeycomb structure, a sandwiched structure, and combinations thereof.

In one embodiment, the mold 10 comprises polymeric foam. For the polymeric foam material, it is contemplated that at least one component of the foam is selected from the group consisting of polyurethane, epoxy, phenyl maleimide (PMI), polyetherimide (PEI), polyurethane, nylon, acrylic, and combinations thereof. In an exemplary embodiment, a polyurethane foam mold is utilized.

Various properties may also be used to define the mold 10 of the present disclosure. For example, the mold may have a specific heat capacity from 0.1 to 3.0 J/g.K. Polymeric molds may have a specific heat capacity of from about 1.0 to about 3.0 J/g.K, or from about 1.2 to about 2 J/g.K. Metal molds may have a specific heat capacity of from about 0.1 to about 1.2, or between about 0.2 to about 0.9 J/g.K.

Further, the mold may have a thermal conductivity from about 0.01 to about 0.2 W/m.K, or a thermal conductivity from about 0.01 to about 0.10 W/m.K, or from about 0.03 to about 0.07 W/m.K. Additionally, the mold may have a coefficient of thermal expansion from about 2 to about 80 ppm/° C., or from about 40 to about 60 ppm/° C. Further, the mold, for example, the polymeric foam mold, may have a density of from about 0.05 to about 0.5 g/cc, or from about 0.2 to about 0.35 g/cc. Moreover, the mold may have a glass transition temperature of from about 100 to about 500 °C, or from about 120 to about 300 °C, or from about 200 to about 250 °C.

Optionally, it may be desirable to apply one or more coatings or layers (not shown) over the mold 10 prior to applying the fiber reinforcement 30 as shown in FIG. 1. As used herein, the terms “over” or “on” may mean directly adjacent or contacting another layer, but also contemplates that intervening layers may be disposed therebetween. In one or more embodiments, the mold 10 may include thereon a release layer 40, a face-sheet, a sealing coating, a non-stick coating, or combinations thereof. Generally, a release layer is applied over the mold 10 and generally attached to the mold 10. The release layer 40 may be used to seal the mold before the infusion. If the mold includes a sealing coating, an additional face-sheet or release layer may not be needed. After the infusion and curing process is conducted, the release layer may be used to separate the resulting cured fiber reinforcement composite from the mold. Various components are contemplated for the face-sheet, for example, carbon fiber-epoxy composite, metal, and combinations thereof. Generally, the face-sheet is applied over the mold using a suitable adhesive and/or tape.

Similarly, various compositions are contemplated for the sealing coating. In one embodiment, the sealing component comprises vinyl ester, and is applied via any suitable coating or deposition technique. Optionally, the sealing coating may also perform a non-stick function, which prevents the fiber reinforcement from sticking to the mold 10 during demolding. Further as stated above, it is contemplated to use a non-stick or release coating which may comprise various suitable components. For example, the non-stick or mold release coating may be selected from the group consisting of silane, siloxane, polytetrafluoroethylene, hydrocarbon, and mixtures and combinations thereof. A suitable seal coating commercial embodiment in accordance with the present disclosure is Frekote® 55-NCT™ produced by Henkel International.

Additionally, it is contemplated to use a combination of coatings or layers prior to the addition of the fiber reinforcement. In one embodiment, a seal coating and a mold release agent may be used together. For example, a suitable surface primer for sealing a mold surface, such as the Duratec Vinyl Ester Primer® from Hawkeye Industries, may be applied to seal the porous polymeric foam mold surface as an alternative to an adhesive release film, facesheet, or other sealing material. Then a mold release agent, such as Frekote 55-NC is applied thereon.

Subsequently, a fiber reinforcement 30 is applied over the mold. As used herein, the “fiber reinforcement” means one layer or multiple stacked fiber layers used as the substrate material for the epoxy resin infusion. The fiber layers may have various structures. For example and not by way of limitation, these structures may include random mats, scrim, chopped fibers, knits, unidirectional plies, three-dimensional weaves (3D weaves), three-dimensional fiber preforms (3D fiber preforms), and fabrics, such as plain weave, twill, harness satin. It is further contemplated to use combinations of the above structures. Depending on the industrial application and the part thickness desired, it may be desirable to use one layer or multiple layers for the fiber reinforcement 30. While the majority of the contemplated embodiments utilize up to 300 layers, the present process is suitable for greater than 300 fiber layers as well. In specific embodiments, the fiber rein-
The fiber reinforcement 30 may include from 1 to 100 fiber layers, or from 1 to 30 fiber layers. For the fiber reinforcement 30 as shown in FIG. 1, various compositions are contemplated. For example, the fiber reinforcement 30 may comprise one or more components such as carbon fiber, glass fiber, aramid fiber, boron fiber, basalt fiber, polymer fiber, or combinations thereof. In a specific embodiment, the fiber reinforcement 30 may comprise one or more carbon fiber layers. While various commercial carbon fiber layers are considered suitable, one such suitable commercial carbon fiber layer is the Toho Tenax® HTS40 3K carbon fiber having a 2/2 twill fabric weaving construction.

Optionally, the present method may utilize the step of adding at least one mesh flow media 20 over the fiber reinforcement 30 to facilitate distribution and flow of the resin through the thickness of the fiber reinforcement 30. As would be familiar to one of ordinary skill in the art, flow media layer options are vast in design, material, and dimension. The defined channels of the flow media are generally uniform; however, it is contemplated to have differing channel diameters within the same flow media layer. In specific embodiments, the flow media layers may be layers comprised of woven material such as Style 6781 S2-Glass fabric from Fibre Glast, or non-woven materials. Examples of non-woven materials that can be used as flow media layers are knit material e.g. Breathercell 60 from Airtech, pressed directional materials, such as Resinflow 60 from Airtech, random mats, such as Continuous Strand Mat from Fibre Glast, as well as other mesh or scrim material, or combinations thereof. Another commercially suitable embodiment is the GREENFLOW 75 produced by Airtech Advanced Materials Group. Various compositions are contemplated for use in the woven or non-woven structures. For example, the flow media may comprise nylon, polypropylene, propylene ethylene copolymer, aluminum screen material or combinations thereof. In a further optional embodiment, it is contemplated to use a peel-ply layer between the fiber reinforcement and the flow media.

Whether using flow media 20 or not, vacuum conduits and resin conduits are then applied and affixed over the fiber reinforcement 30, and the flow media 20. Referring to FIG. 1 as used herein, “vacuum conduits” are tubing 71, tubing connectors 72, or other suitable components applied on the periphery of the mold 10 or fiber reinforcement 30, across the surface of the fiber reinforcement 30, or both, wherein the tubing 71 is connected to the vacuum 70 and is utilized to create a vacuum underneath the vacuum enclosure 50. Similarly as used herein, “resin conduits” are tubing 61, tubing connectors 62, or other suitable components applied on the periphery of the mold 10 or fiber reinforcement 30, across the surface of the fiber reinforcement 30, or both, wherein the tubing 61 is connected to the resin infusion device 60, which may be any suitable vessel. In a specific embodiment, the resin conduit delivers resin material across the thickness of the fiber reinforcement 30 via the flow media 20. Various materials are contemplated for the vacuum conduits and resin conduits. For example, flexible tubing such as a polyethylene tube may be utilized. In a further optional embodiment, it is contemplated to use multiple resin conduits for production of large composite part to shorten the time required for resin infusion.

Referring again to FIG. 1, the mold 10 and fiber reinforcement 30 are then covered in a vacuum enclosure 50. The vacuum enclosure 50 may encompass various components suitable for achieving a sealed environment, for example, a container or a polymer vacuum bagging film. The vacuum enclosure 50 is generally affixed to the periphery of the mold 10 via adhesive, tape, putty, etc.

After the vacuum enclosure 50 is applied over the mold, the vacuum pump 70 is applied to remove air beneath the vacuum enclosure 50. Creating a vacuum on the vacuum enclosure 50 produces a pressure gradient. For example and not by way of limitation, the pressure gradient is from about 760 torr to about 1 torr. In addition to the use of a vacuum pump to generate the pressure gradient, it is further contemplated to use a pressurized system to generate the necessary pressure difference to infuse resin into the fiber reinforcement.

Additionally as shown in FIG. 2, the thermal insulation 90 may be applied over at least a portion of the vacuum enclosure 50. In the specific embodiment shown in FIG. 2, the thermal insulation 90 may be applied over the top of the vacuum enclosure 50 and may be positioned to cover the fiber reinforcement 30. For example and not by way of limitation, the thermal insulation 90 may include fiberglass, cellulose, polymer foam, earth materials, and combinations thereof. Various polymer foams are considered suitable for thermal insulation. In one embodiment, the polymer foam comprises polyurethane foam. As would be familiar to the skilled person, earth materials may include pumice, vermiculite, asbestos, and the like. As will be described in greater detail below, the use of insulation in the present process reduces exothermic heat loss and thereby eliminates the need for the above-defined external heating elements utilized in the curing process. In one embodiment, the insulation may have a thermal conductivity from about 0.01 to about 0.2 W/m/K, or a thermal conductivity from about 0.01 to about 0.10 W/m/K, or from about 0.03 to about 0.07 W/m/K, or about 0.04 W/m.K.

After vacuum conditions have been achieved, a reactive mixture of uncured epoxy resin and curing agent may be infused into the fiber reinforcement 30. In specific embodiments, the reactive mixture of uncured epoxy resin and curing agent may be delivered from a resin infusion device 60 or vessel into the fiber reinforcement 30 via the resin conduit described above. For the infusion process, the uncured epoxy resin and curing agents may be mixed in a vessel prior to infusion. Generally, the uncured epoxy resin and curing agents are mixed two hours or less prior to infusion, but modifications to the procedure are contemplated. The uncured epoxy resin and curing agent are maintained at a temperature from about 10 to about 50 °C, or from about 10 to about 35 °C prior to infusion. It is further contemplated to use separate uncured epoxy resin and curing agent feeds which react upon delivery to the fiber reinforcement. Alternatively, it is contemplated that the uncured epoxy resin and curing agent may be kept separate until mixed in the tubing 61 (i.e., static mixing) of the resin conduit.

The mixing of uncured epoxy resin and curing agent generates exothermic heat. In specific embodiments, the uncured epoxy resin has a high enthalpy of reaction as measured by differential scanning calorimetry (DSC), specifically, an enthalpy of reaction in the range of about 300 to about 1000 J/g, or about 500 to about 1000 J/g, or about 500 to about 800 J/g. In light of these higher enthalpies of reaction, there are present high enthalpy uncured epoxy resins are traditionally viewed as difficult to handle because they are highly exothermic upon mixing with the curing agent, which may potentially lead to matrix degradation of the part. Further without being bound by theory, the present high enthalpy uncured epoxy resins are traditionally viewed as difficult to handle because they are highly exothermic upon mixing with the curing agent, which may potentially lead to matrix degradation of the part. Further without being bound by theory, the enthalpy of the resin is matched with an appropriate thermal conductivity of the mold and overall insulation so that only a desirable amount of heat is generated to sufficiently heat the part to the target temperature.
for curing. If additional heat is supplied via conventional oven or autoclave processes, excessive exothermic heat may be generated thereby leading to undesirable matrix degradation of the part. In addition, the uncured epoxy resin may have a viscosity range of about 100 to about 1000 centipoise at 20°C, or about 200 to about 600 centipoise at 20°C.

Various compositions are contemplated for the uncured epoxy resin. For example and not by way of limitation, the uncured epoxy resin may comprise Diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol F, resorcino1 diglycidyl ether, N,N-Diglycidyl-4-glycidoxyaniline, brominated diglycidyl ether of bisphenol A, novolac epoxy, tetraglycidyl meta-xlylenediamine, 1,4-butanediol diglycidyl ether, 4,4'-Methylenebis(N,N-diglycidylaniline), tris(4-hydroxyphenyl)methylylgycidyl ether, tris(2,3-epoxypropyl)isocyanurate, or combinations thereof.

The curing agent, also called a hardener, may include various suitable components. In one embodiment, the curing agent may comprise amine curing agents. In specific embodiments, these amine curing agents may comprise 4,4'-Methylenebis(2-chloroaniline), 4,4'-diaminodiphenyl sulfone, isophorone diisocyanate, Diethyltoluenediamine, Diaminodiphenylmethane, 1,3-phenylenediamine, piperezine, Triethylentetramine, 5-Amino-1,3,3-trimethylcyclohexanemethylamine, m-Xylylenediamine, bis-p-aminocyclohexylmethane, 2,4-Diaminotoluene, N,N-dimethylthiodiisocyanurate, or combinations thereof. One suitable resin system is the epoxy-based resin system, NONA-001 produced by Cornerstone Research Group, specifically for NONA infusion processing.

While the present disclosure primarily describes epoxy infused carbon composites, the present process is also applicable to various other high performance resins. For example, and not by way of limitation, these high performance resins may include bismaleimide, cyanate ester, polyimide, etc.

After infusion, the curing step is conducted to achieve the fiber-reinforced epoxy composite product, specifically an epoxy composite having a glass transition temperature of at least 100°C. Here, the curing step utilizes the exothermic heat generated by the reaction of uncured epoxy resin and curing agent to drive the curing process. Moreover, the thermal insulation ensures that the exothermic heat is maintained, and thereby eliminates the need for an alternative heating source such as an oven or autoclave.

Optionally, it is contemplated to include a radiative insulation sheet (not shown) over the vacuum enclosure and thermal insulation. The radiative insulation sheet minimizes heat loss caused by radiation. In that way, the insulation sheet may work synergistically with the thermal insulation that reduces conductive heat loss while the radiative insulation sheet reduces heat loss via radiation. Various materials are contemplated for use in the radiative insulation sheet. In one embodiment, the radiative insulation sheet is aluminum foil.

The curing step may be controlled and optimized so that the curing may occur over a period from about 1 minute to about 8 hours, or from about 30 minutes to about 6 hours, or from about 1 hour to about 4 hours. After curing, the resultant composite is a fiber-reinforced epoxy composite having a glass transition temperature of at least about 100°C, or from about 100°C to about 300°C, or from about 120 to about 210°C, or from about 150 to about 210°C, or at least about 180°C. Moreover, the cured fiber-reinforced epoxy composite defines a curing dimensional change value (i.e. deviation in dimensions of cured composite from the original dimensions of the tool surface at ambient temperature) of less than about 2500 µm/m, or less than about 2000 µm/m, or less than about 1500 µm/m. Without being bound by theory, the present curing process yields a more uniform curing profile, which provides advantages to the final product such as improved dimensional tolerance. Furthermore, the uniformity of internal heating by the resin exothermic heat also provides advantages in reducing residual stress within the composite and improving in-plane shear properties.

EXAMPLES

The following examples describe the curing profile of the present process and depict the reduction in residual stresses and improved dimensional tolerance of composite tooling produced by the present processes.

Such improvement in in-plane shear testing results are shown in Table 1 by comparison of the fiber reinforced composite fabricated in accordance with the present disclosure employing NONA-001 resin and fiber reinforcement (8 ply +/-45° IM7 carbon fiber in a plain weave) with a composite fabricated with commercial Cycom 5215 prepreg produced by Cytec Engineered Materials and the same fiber reinforcement cured according to conventional oven cured process at 127°C and postured at 177°C. In the NONA-001 composite, the mold used was polyurethane foam tooling board sealed with adhesive Teflon, wherein the tooling board has a thermal conductivity of 0.06 W/mK and a CTE of 49 ppm/°C.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Material</th>
<th>Mean Modulus (GPa)</th>
<th>COV</th>
<th>Mean Shear strength at 5% strain (MPa)</th>
<th>COV</th>
<th>Mean Shear strength at 5% strain (MPa)</th>
<th>COV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTD NONA-001</td>
<td>6.42</td>
<td>5.72</td>
<td>98.1</td>
<td>6.00</td>
<td>70.3</td>
<td>3.71</td>
<td></td>
</tr>
<tr>
<td>Cycom 5215</td>
<td>4.69</td>
<td>1.71</td>
<td>87.8</td>
<td>1.90</td>
<td>59.4</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>RTD NONA-001</td>
<td>4.78</td>
<td>2.86</td>
<td>73.0</td>
<td>7.40</td>
<td>42.6</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>Cycom 5215</td>
<td>3.93</td>
<td>1.58</td>
<td>N/A</td>
<td>N/A</td>
<td>42.3</td>
<td>1.48</td>
<td></td>
</tr>
<tr>
<td>ETW NONA-001</td>
<td>3.12</td>
<td>5.90</td>
<td>47.0</td>
<td>5.76</td>
<td>22.2</td>
<td>5.56</td>
<td></td>
</tr>
<tr>
<td>Cycom 5215</td>
<td>2.69</td>
<td>4.10</td>
<td>41.4</td>
<td>4.07</td>
<td>24.9</td>
<td>4.37</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 below lists the temperatures taken from the rheology experiment associated with gelation, vitrification, and maximum temperature reached, when producing a composite tool using the NONA-001 resin system produced by Cornerstone Research Group.

<table>
<thead>
<tr>
<th>Event</th>
<th>Time after Infusion (min)</th>
<th>Temperature of fiber-reinforced epoxy composite (°C)</th>
<th>Temperature of Foam Mold (bottom surface) (°C)</th>
<th>Temperature of Foam Mold (average across the thickness) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gellation</td>
<td>114</td>
<td>69</td>
<td>33</td>
<td>51</td>
</tr>
<tr>
<td>Vitrification</td>
<td>118</td>
<td>92</td>
<td>35.5</td>
<td>63.8</td>
</tr>
<tr>
<td>Max.</td>
<td>128</td>
<td>164</td>
<td>46</td>
<td>105</td>
</tr>
</tbody>
</table>
According to the data in Table 2, the bottom of the tool temperature is 35.5°C at the time of part vitrification. At this point it can be assumed that the part has locked in its final dimensions. For simplicity, one could assume that the average temperature of the foam tool is 63.8°C, which is 2.5 times the dimensional change of the comparative example (Cycom 5215). Assuming the current polyurethane temperature of the foam tool is 63.8°C, the dimensional change would be 1938 µm/m. In comparison, conventional tooling materials require slow temperature ramps to encourage consistent curing throughout the laminate and avoid potentially trapped volatiles. For example, the Cycom™ 5215 Out-of-Autoclave (OoA) tooling prepreg system has a two hour cure (not including time to heat and cool the tooling) at 127°C, giving a total change in temperature of 102°C (127-25). Referring to Table 3 below, the comparative example (Cycom 5215) is performed on the same tooling board as the inventive example (NONA-001); however, the comparative Cycom example has a dimensional change of 5100 µm/m, which is 2.5 times the dimensional change of the inventive example. Specifically, the inventive example undergoes significantly less dimensional change than the high temperature curing of the comparative example, thus producing part with greater precision in replicating the desired part geometry.

<table>
<thead>
<tr>
<th>Example</th>
<th>Density (kg/m³)</th>
<th>CTE (ppm/°C)</th>
<th>Temperature of Foam Tool (°C)</th>
<th>Dimensional Change (µm/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventive Example (NONA-001 resin)</td>
<td>&lt;500</td>
<td>50.0</td>
<td>25.0</td>
<td>63.8</td>
</tr>
<tr>
<td>Comparative Example (Cycom 5215)</td>
<td>&lt;500</td>
<td>50.0</td>
<td>25.0</td>
<td>127.0</td>
</tr>
</tbody>
</table>

While particular embodiments have been illustrated and described herein, it should be understood that various other changes and modifications may be made without departing from the spirit and scope of the claimed subject matter. Moreover, although various aspects of the claimed subject matter have been described herein, such aspects need not be utilized in combination. It is therefore intended that the appended claims cover all such changes and modifications that are within the scope of the claimed subject matter.

What is claimed is:
1. A method for producing a fiber-reinforced epoxy composite comprising:
   providing a mold defining a shape for a composite;
   applying a fiber reinforcement over the mold;
   covering the mold and fiber reinforcement thereon in a vacuum enclosure;
   performing a vacuum on the vacuum enclosure to produce a pressure gradient;
   insulating at least a portion of the vacuum enclosure with thermal insulation;
   infusing the fiber reinforcement with a reactive mixture of uncured epoxy resin and an amine curing agent under vacuum conditions, wherein the reactive mixture of uncured epoxy resin and curing agent generates exothermic heat; and
   producing the fiber-reinforced epoxy composite having a glass transition temperature of at least about 100°C by curing the fiber reinforcement infused with the reactive mixture of uncured epoxy resin and curing agent by utilizing the exothermically generated heat, wherein the curing is conducted inside the thermally insulated vacuum enclosure without utilization of an external heat source or an external radiation source.

2. The method of claim 1 wherein the mold comprises at least one component selected from the group consisting of polymer, glass, ceramic, carbon-carbon composite, fiber-reinforced polymer composite, metal, wood, polymeric foam, ceramic foam, glass foam, syntactic foam, carbon foam, metal foam, a honeycomb structure, a sandwiched structure, and combinations thereof.

3. The method of claim 1 wherein the mold comprises polymeric foam.

4. The method of claim 1 wherein the mold has a specific heat capacity from 0.1 to 3.0 J/g·K, and a thermal conductivity from 0.01 to 0.2 W/m·K.

5. The method of claim 1 wherein the mold further comprises a face-sheet, a sealing coating, a release coating, a non-stick coating, or combinations thereof.

6. The method of claim 1 wherein the fiber reinforcement comprises one or more components selected from the group consisting of carbon fiber, glass fiber, aramid fiber, boron fiber, basalt fiber, polymer fiber, and combinations thereof.

7. The method of claim 1 wherein the fiber reinforcement comprises random mats, scrim, chopped fibers, knits, unidirectional plies, three-dimensional weaves, three-dimensional fiber preforms, plain weave fabrics, twill fabrics, harness satin fabrics, or combinations thereof.

8. The method of claim 1 wherein the fiber reinforcement comprises prepreg material.

9. The method of claim 1 wherein the vacuum enclosure is a container or a polymer vacuum bagging film.

10. The method of claim 1 wherein the thermal insulation is selected from the group consisting of fiberglass, cellulose, polymer foams, earth materials and combinations thereof.

11. The method of claim 1 wherein the uncured epoxy resin has an enthalpy of reaction range of about 500 to about 800 J/g, and a viscosity range of from about 100 to about 600 centipoise at 20°C.
12. The method of claim 1 wherein the uncured epoxy resin comprises at least one component selected from the group consisting of Diglycidyl ether of bisphenol A, diglycidyl ether of bisphenol F, resorcinol diglycidyl ether, N,N-Diglycidyl-4-glycidoxyaniline, brominated diglycidyl ether of bisphenol A, novolac epoxy, tetraglycidyl meta-xylenediamine, 1,4-butanediol diglycidyl ether, 4,4'-Methylenebis(N,N-diglycidylaniline), tris(4-hydroxyphenyl)methane triglycidyl ether, tris(2,3-epoxypropyl)isocyanurate, and combinations thereof.

13. The method of claim 1 wherein the amine curing agents comprise one or more components selected from the group consisting of 4,4'-Methylene-bis(2-chloroaniline), 4,4'-diaminodiphenyl sulfone, isophorone diamine, Diethyltoluenediamine, Dimethylthiotoluenediamine, 4,4'-diaminodiphenylmethane, 1,3'-phenylenediamine, piperazine, Triethylenetetramine, 5-Amino-1,3,3-trimethylcyclohexanemethylamine, m-Xylylenediamine, bis(p-aminocyclohexylmethane), 2,4-Diaminotoluene, N,N-dimethylethylenediamine, and combinations thereof.

14. The method of claim 1 wherein the uncured epoxy resin and curing agent are maintained at a temperature between 10 to 50° C. prior to infusion.

15. The method of claim 1 further comprising adding at least one mesh flow media over the fiber reinforcement.

16. The method of claim 1 further comprising applying a radiative insulation sheet over the vacuum enclosure.

17. The method of claim 1 wherein the curing occurs over a period from 1 minute to 8 hours.

18. The method of claim 1 wherein the fiber-reinforced epoxy composite is composite tooling.

19. A fiber-reinforced epoxy composite produced by the method of claim 1, wherein the fiber-reinforced epoxy composite experiences a curing dimensional change value of less than 2500 µm/m.

20. The fiber-reinforced epoxy composite of claim 19 wherein the curing dimensional change value is less than 2000 µm/m.

21. The fiber-reinforced epoxy composite of claim 19 wherein the fiber-reinforced epoxy composite has a glass transition temperature of from about 120 to about 210° C.

22. The fiber-reinforced epoxy composite of claim 19 wherein the fiber reinforcement comprises prepreg material.

23. The fiber-reinforced epoxy composite of claim 19 wherein the fiber-reinforced epoxy composite is composite tooling.