

5 METHOD OF PROMOTING ADHESION AND BONDING OF STRUCTURES AND
STRUCTURES PRODUCED THEREBY

BACKGROUND

Field of the Disclosure

The disclosure relates generally to methods for bonding of structures, and
10 more particularly, to methods for promoting adhesion and bonding of composite and
metal structures, and the bonded structures produced thereby, such as for use in
aircraft, spacecraft, and other vehicles and structures.

Description of Related Art

Composite and metal structures or component parts are used in a wide
15 variety of applications, including in the manufacture of aircraft, spacecraft, rotorcraft,
watercraft, automobiles, trucks, and other vehicles and structures. In particular, in
aircraft construction, structures or component parts, such as composite structures or
component parts, are used in increasing quantities to form the fuselage, wings, tail
section, and other component parts of the aircraft. Such large-sized structural aircraft
20 components may be manufactured by bonding together composites to composites,
composites to metals, and metals to metals.

Known methods and systems for bonding composite and metal component
parts together, such as aircraft component parts, typically involve using fastener
devices, such as bolts, screws, pins, or other fastener devices to secure the component
25 parts together. However, using such known fastener devices can add to the overall
weight of the aircraft, which can, in turn, increase fuel costs. Further, using such known
fastener devices can take time and labor to install and can require procurement and

5 storage of the fastener devices, which can, in turn, increase installation, labor, and manufacturing costs.

In addition, known methods and systems for bonding composite and metal component parts together, such as aircraft component parts, typically also involve using film adhesives to join or bond two composite materials together, two metal materials
10 together, or a composite material to a metal material. In order to form the large-sized structural component, the components are firstly positioned and aligned with respect to one another on a suitable supporting structure, in accordance with previously known methods. The adhesive films are typically applied in advance between the components which are to be adhesively bonded to one another. To improve structural bonding,
15 known methods exist for modifying the surface of the composite or metal structure or part prior to applying the adhesive. Known surface modification methods may require the roughening of the composite or metal surface via sanding or grit blasting. Such known procedures can create some active oxide functional groups on the surface. However, it is believed that no known methods or systems exist for durable surface
20 modification for improved structural bonding and for identifying functional groups which have an affinity to enhance durable and sustainable structural bonding and thereby improve secondary bonding forces (Van der Waals forces) and which can, in turn, increase the durable, long-term life of a composite bonded joint.

Accordingly, there is a need in the art for methods and systems for promoting
25 adhesion and bonding of composite and metal structures that provide advantages over known methods and systems.

SUMMARY

This need for methods and systems for promoting adhesion and bonding of composite and metal structures is satisfied. As discussed in the below detailed description, embodiments of the methods and systems may provide significant advantages over existing methods, systems, and devices.

In one aspect, there is provided a method of promoting adhesion on a composite surface, the method comprising: providing a composite structure having at least one composite surface to be bonded; preparing the at least one composite surface; providing a chemical derivatization compound containing active molecular functional groups that promote adhesion and detect adhesion mechanisms, wherein the chemical derivatization compound is selected from the group consisting of tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, and glycidyoctafluoropentyl ether; depositing the chemical derivatization compound on the prepared composite surface and activating the molecular functional groups through chemical derivatization reaction mechanisms to form a molecular functional group-adhesive promoter derivatized layer on the prepared composite surface as a bonding agent, the chemical derivatization reaction mechanisms creating reactive molecular functional groups on the prepared composite surface, and the chemical derivatization reaction mechanisms selected from the group consisting of bromination, silylation, and thionation; applying an adhesive layer to the derivatized layer; and, heat curing the adhesive layer to result in a bond with another structure made of a composite, a metal, or a combination thereof.

In another aspect, there is provided a method for structural bonding of structures comprising: providing a first structure made of a composite material and a second structure made of a composite material, a metal, or a combination thereof; preparing a surface to be bonded on each of the first and second structures to form a first prepared surface and a second prepared surface; providing a chemical derivatization compound containing active molecular functional groups that promote adhesion and detect adhesion mechanisms, wherein the chemical derivatization compound is selected from the group consisting of tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, and glycidyoctafluoropentyl ether; depositing the chemical derivatization compound on each of the first and second prepared surfaces and activating the molecular functional groups through chemical derivatization reaction mechanisms to form a first molecular functional group-adhesive promoter derivatized layer on the first prepared composite surface as a first bonding agent and a second molecular functional group-adhesive promoter derivatized layer on the second prepared composite surface as a second bonding agent, the chemical derivatization reaction mechanisms creating reactive molecular functional groups on the first and second prepared surfaces, and the chemical derivatization reaction mechanisms selected from the

group consisting of bromination, silination, and thionation; applying an adhesive layer to at least one of the derivatized layers of the first and second molecular functional group-adhesive promoter derivatized layers; joining the first and second structures together with the adhesive layer and the first and second molecular functional group-adhesive promoter derivatized layers therebetween; and, heat curing the adhesive layer to the joined first and second structures to form a structural bond between the first and second structures.

In yet another aspect, there is provided a method for structural bonding of polymeric composite structures of an aircraft, the method comprising: providing a first polymeric composite aircraft structure and a second polymeric composite aircraft structure; preparing a surface to be bonded on each of the first and second polymeric composite aircraft structures to form a first prepared surface and a second prepared surface; providing a chemical derivatization compound containing active molecular functional groups that promote adhesion and detect adhesion mechanisms, wherein the chemical derivatization compound is selected from the group consisting of tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, and glycidyoctafluoropentyl ether; depositing the chemical derivatization compound on each of the first and second prepared surfaces and activating the molecular functional groups through chemical derivatization reaction mechanisms to form a first molecular functional group-adhesive promoter derivatized layer on the first prepared composite surface as a first bonding agent and a second molecular functional group-adhesive promoter derivatized layer on the second prepared composite surface as a second bonding agent, the chemical derivatization reaction mechanisms creating reactive molecular functional groups on the first and second prepared surfaces, and the chemical derivatization reaction mechanisms selected from the group consisting of bromination, silination, and thionation; applying an adhesive layer to at least one of the first and second molecular functional group-adhesive promoter derivatized layers; joining the first and second polymeric composite aircraft structures together with the adhesive layer and the first and second molecular functional group-adhesive promoter derivatized layers therebetween; and, heat curing the adhesive to the joined first and second polymeric composite aircraft structures to form an aircraft structural bond between the first and second polymeric composite aircraft structures.

In an embodiment of the disclosure, there is provided a method of promoting adhesion on a composite surface. The method comprises providing a composite structure having at least one composite surface to be bonded. The method further comprises preparing the at least one composite surface, wherein the composite surface may be prepared with one or more surface preparation treatments selected from the group comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning, and chemical etching.. The method further comprises providing a chemical derivatization compound containing active functional groups that promote adhesion. The method further comprises depositing the chemical derivatization compound on the prepared composite surface to form a functional group-adhesive promoter derivatized layer, wherein the chemical derivatization compound is may be deposited via chemical vapor deposition or vacuum deposition.. The method further comprises applying an adhesive layer to the derivatized layer. The method further comprises heat curing the adhesive layer to result in a bond with another structure made of a composite, a metal, or a combination thereof. The method further comprises a method wherein the resulting bond may be selected from the group comprising a structural bond and a repair bond or wherein the composite structure and the other

5 structure made of the composite, the metal, or the combination thereof, may be aircraft structures.

In another embodiment of the disclosure, there is provided a method for structural bonding of structures. The method comprises providing a first structure made of a composite material and a second structure made of a composite material, a metal, 10 or a combination thereof. The method further comprises preparing a surface to be bonded on each of the first and second structures to form a first prepared surface and a second prepared surface, wherein the surfaces to be bonded may be prepared with one or more surface preparation treatments selected from the group comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning, and chemical 15 etching. The method further comprises providing a chemical derivatization compound containing active functional groups that promote adhesion. The method further comprises depositing the chemical derivatization compound on each of the first and second prepared surfaces to form a first functional group-adhesive promoter derivitized layer and a second functional group-adhesive promoter derivitized layer, wherein the 20 chemical derivatization compound may be deposited via chemical vapor deposition or vacuum deposition. The method further comprises applying an adhesive layer to at least one of the derivitized layer of the first and second functional group-adhesive promoter derivitized layer. The method further comprises joining the first and second structures together with the adhesive layer and the first and second functional group-adhesive promoter derivitized layer therebetween. The method further comprises heat 25 curing the adhesive to the joined first and second structures to form a structural bond between the first and second structures, wherein first and second structures may be aircraft structures.

5 In another embodiment of the disclosure, there is provided a method for structural bonding of polymeric composite structures of an aircraft. The method comprises providing a first polymeric composite aircraft structure and a second polymeric composite aircraft structure. The method further comprises preparing a surface to be bonded on each of the first and second polymeric composite aircraft
10 structures to form a first prepared surface and a second prepared surface, wherein the surface to be bonded may be prepared with one or more surface preparation treatments selected from the group comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning, and chemical etching.. The method further comprises providing a chemical derivatization compound containing active functional groups that
15 promote adhesion. The method further comprises depositing the chemical derivatization compound on each of the first and second prepared surfaces to form a first functional group-adhesive promoter derivitized layer and a second functional group-adhesive promoter derivitized layer. The method further comprises applying an adhesive layer to at least one of the first and second functional group-adhesive
20 promoter derivitized layers. The method further comprises joining the first and second polymeric composite aircraft structures together with the adhesive layer and the first and second functional group-adhesive promoter derivitized layers therebetween. The method further comprises heat curing the adhesive layer to the joined first and second polymeric composite aircraft structures to form a structural bond between the first and
25 second polymeric composite aircraft structures. The features, functions, and advantages that have been discussed can be achieved independently in various embodiments of the disclosure or may be combined in yet other embodiments further details of which can be seen with reference to the following description and drawings.

5 BRIEF DESCRIPTION OF THE DRAWINGS

The disclosure can be better understood with reference to the following detailed description taken in conjunction with the accompanying drawings which illustrate preferred and exemplary embodiments, but which are not necessarily drawn to scale, wherein:

10 FIG. 1 is an illustration of a perspective view of an exemplary aircraft for which embodiments of the methods and structures made with the methods may be used;

FIG. 2A is an illustration of a partial cross-sectional exploded view of an embodiment of a bonded structure made with one of the embodiments of the methods
15 disclosed herein;

FIG. 2B is an illustration of a partial cross-sectional view of the bonded structure of FIG. 2A;

FIG. 2C is an illustration of a partial cross-sectional exploded view of another embodiment of a bonded structure made with one of the embodiments of the methods
20 disclosed herein;

FIG. 2D is an illustration of a partial cross-sectional view of the bonded structure of FIG. 2C;

FIG. 2E is an illustration of a partial cross-sectional exploded view of a bonded aircraft structure that may be made with one of the embodiments of the
25 methods disclosed herein;

5 FIG. 2F is an illustration of a partial cross-sectional view of the bonded aircraft structure of FIG. 2E;

 FIG. 3A is an illustration of a partial cross-sectional exploded view of an embodiment of a repair bonded structure made with one of the embodiments of the methods disclosed herein;

10 FIG. 3B is an illustration of a partial cross-sectional view of the repair bonded structure of FIG. 3A;

 FIG. 4A is an illustration of the chemical structure of a bismaleimide prepolymer and its functional groups;

 FIG. 4B is an illustration of the chemical structure of a first R group for the
15 bismaleimide prepolymer of FIG. 4A;

 FIG. 4C is an illustration of the chemical structure of a second R group for the bismaleimide prepolymer of FIG. 4A;

 FIG. 4D is an illustration of a table listing the functional groups of the bismaleimide prepolymer of FIG. 3A and the reactions of the functional groups;

20 FIG. 5 is an illustration of a bromination derivatization reaction mechanism of the functional groups of the bismaleimide prepolymer before and after the bromination reaction;

 FIG. 6A is an illustration of the chemical structure of a chemical derivatization compound pentafluorophenol that may be used in embodiments of the methods
25 disclosed herein;

5 FIG. 6B is an illustration of the chemical structure of a chemical derivatization compound allyl pentafluorobenzene that may be used in embodiments of the methods disclosed herein;

 FIG. 6C is an illustration of the chemical structure of a chemical derivatization compound tridecafluorononyl maleimide that may be used in embodiments of the
10 methods disclosed herein;

 FIG. 6D is an illustration of the chemical structure of a chemical derivatization compound glycidyoctafluoropentyl ether that may be used in embodiments of the methods disclosed herein;

 FIG. 7 is an illustration of a silylation derivatization reaction mechanism that
15 may be used in embodiments of the methods disclosed herein;

 FIG. 8 is an illustration of a thionation derivatization reaction mechanism that may be used in embodiments of the methods disclosed herein;

 FIG. 9 is an illustration of a table listing the potential bismaleimide adhesion reactions;

20 FIG. 10 is an illustration of a graph comparing bismaleimide surface compositions after various surface preparation treatments;

 FIG. 11 is an illustration of a graph comparing bismaleimide surface compositions before and after tetrafluoroaceticanhydride (TFAA) exposure;

5 FIG. 12 is an illustration of a graph comparing derivatized bismaleimide surface compositions after exposure to various fluorinated chemical derivatization compounds;

 FIG. 13 is an illustration of a graph comparing the results of bromine and tetrafluoroacetic anhydride (TFAA) derivatization on shear strength of bismaleimide-
10 adhesive joints;

 FIG. 14 is an illustration of a graph showing the results of the binding energy of fluorine of pentafluorophenol to resin and fibers of a derivatized bismaleimide surface;

 FIG. 15 is an illustration of a graph showing the results of the binding energy
15 of fluorine of allyl pentafluorobenzene to resin and fibers of a derivatized bismaleimide surface;

 FIG. 16 is an illustration of a graph showing the results of the binding energy of fluorine of tridecafluorononyl maleimide to resin and fibers of a derivatized bismaleimide surface;

20 FIG. 17 is an illustration of a graph showing the results of the binding energy of fluorine of glycidyoctafluoropentyl ether to resin and fibers of a derivatized bismaleimide surface;

 FIG. 18 is an illustration of a flow diagram of one of the embodiments of a method of the disclosure;

5 FIG. 19 is an illustration of a flow diagram of another one of the embodiments of a method of the disclosure;

 FIG. 20 is an illustration of a flow diagram of another one of the embodiments of a method of the disclosure; and,

 FIG. 21 is an illustration of a partial cross-sectional view of an exemplary
10 chemical vapor deposition in a vacuum bag set-up that may be used with embodiments of the methods of the disclosure.

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DETAILED DESCRIPTION

Disclosed embodiments will now be described more fully hereinafter with reference to the accompanying drawings, in which some, but not all of the disclosed embodiments are shown. Indeed, several different embodiments may be provided and should not be construed as limited to the embodiments set forth herein. Rather, these
10 embodiments are provided so that this disclosure will be thorough and complete and will fully convey the scope of the disclosure to those skilled in the art.

Now referring to the Figures, FIG. 1 is an illustration of a perspective view of an exemplary prior art aircraft 10 for which embodiments of methods 150 (see FIG. 18), 200 (see FIG. 19), 300 (see FIG. 20), and structurally bonded structures 30 (see FIGS.
15 2A, 2B), 50 (see FIGS. 2C, 2D), and 170 (see FIGS. 2E, 2F), and repair bonded structure 60 (see FIGS. 3A, 3B) made from such methods 150, 200, 300, may be used. As shown in FIG. 1, the aircraft 10 comprises a fuselage 12, a nose 14, a cockpit 16, wings 18 operatively coupled to the fuselage 12, one or more propulsion units 20, a tail vertical stabilizer 22, and one or more tail horizontal stabilizers 24. Although the aircraft
20 10 shown in FIG. 1 is generally representative of a commercial passenger aircraft, the methods 150, 200, 300, and structurally bonded structures 30 (see FIGS. 2A, 2B), 50 (see FIGS. 2C, 2D), and repair bonded structure 60 (see FIGS. 3A, 3B) made from such methods 150, 200, 300, as disclosed herein, may also be employed in other types of aircraft. More specifically, the teachings of the disclosed embodiments may be applied
25 to other passenger aircraft, cargo aircraft, military aircraft, rotorcraft, and other types of aircraft or aerial vehicles, as well as aerospace vehicles, satellites, space launch vehicles, rockets, and other aerospace vehicles. It may also be appreciated that embodiments of methods, systems, and apparatuses in accordance with the disclosure

5 may be utilized in other vehicles, such as boats and other watercraft, trains, automobiles, trucks, and buses, as well as buildings and other architectural structures that use composite and metal structural components.

In one of the embodiments there is provided a bonded structure 30 (see FIGS. 2A, 2B) that may be formed or made with embodiments of the methods 150, 200, 10 300 disclosed herein. FIG. 2A is an illustration of a partial cross-sectional exploded view of an exemplary embodiment of a bonded structure 30 that may be made with embodiments of the methods 150, 200, 300 disclosed herein. FIG. 2B is an illustration of a partial cross-sectional view of the bonded structure 30 of FIG. 2A. Preferably, the bonded structure 30 is a composite bonded structure comprising a first composite 15 structure or substrate 32 having a first composite surface 34 to be bonded and a second composite structure or substrate 36 having a second composite surface 38 to be bonded. As discussed in detail below, the first composite surface 34 and/or the second composite surface 38 are prepared or treated with a surface preparation treatment or process prior to structural bonding. The first and second composite structures 32, 36 20 are made of a polymeric composite material comprising preferably, one or more of bismaleimides (BMI), epoxies, or another suitable polymeric composite material; more preferably, graphite (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, graphite (Gr)/bismaleimide (BMI).

In another one of the embodiments there is provided a bonded structure 50 25 (see FIGS. 2C, 2D) that may be formed or made with embodiments of the methods 150, 200, 300 disclosed herein. FIG. 2C is an illustration of a partial cross-sectional exploded view of the bonded structure 50 that may be made with one of the

5 embodiments of the methods 150, 200, 300 disclosed herein. FIG. 2D is an illustration of a partial cross-sectional view of the bonded structure 50 of FIG. 2C. The bonded structure 50 may comprise the first composite structure or substrate 32 having the first composite surface 34 to be bonded and may comprise a metal structure or substrate 52 having a metal surface 54 to be bonded. The metal structure or substrate 52 may
10 preferably be made of a metal material, such as aluminum, titanium, steel, alloys thereof, or another suitable metal material. As discussed in detail below, the first composite surface 34 and/or the second metal surface 34 are prepared or treated with a surface preparation treatment or process prior to structural bonding. Alternatively, the bonded structure may comprise a first metal structure or substrate bonded to a second
15 metal structure or substrate without a primer layer.

 In another one of the embodiments there is provided a bonded polymeric composite aircraft structure 170 (see FIGS. 2E, 2F) for an aircraft 10 (see FIGS. 1, 2E, 2F) that may be formed or made with embodiments of the methods 150, 200, 300 disclosed herein. FIG. 2E is an illustration of a partial cross-sectional exploded view of
20 the bonded aircraft structure 170 that may be made with one of the embodiments of the methods 150, 200, 300 disclosed herein. FIG. 2F is an illustration of a partial cross-sectional view of the bonded aircraft structure 170 of FIG. 2E. The bonded polymeric composite aircraft structure 170 may comprise a first polymeric composite aircraft structure 172 and a second polymeric composite aircraft structure 176 in an aircraft 10.
25 Preferably, the bonded aircraft structure has a first prepared surface 174 and a second prepared surface 178 that has been prepared or treated with a surface preparation treatment or process, discussed in detail below, prior to structural bonding. The first and second polymeric composite aircraft structures 172, 176 are made of a polymeric

5 composite material comprising preferably, one or more of bismaleimides (BMI), epoxies, polyimides, or another suitable polymeric composite material; more preferably, graphite (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, graphite (Gr)/bismaleimide (BMI).

10 In another one of the embodiments there is provided a repair bonded structure 60 that may be formed or made with embodiments of the methods 150, 200, 300 is disclosed. FIG. 3A is an illustration of a partial cross-sectional exploded view of an embodiment of the repair bonded structure 60 that may be made with embodiments of the methods 150, 200, 300 disclosed herein. FIG. 3B is an illustration of a partial cross-sectional view of the repair bonded structure 60 of FIG. 3A. As shown in FIGS.
15 3A and 3B, the repair bonded structure 60 is preferably a composite structure comprising a first composite structural portion 62 having a first composite surface 64 to be repair bonded and a second composite structural portion 66 having a second composite surface 68 to be repaired. The first and second composite structural portions 62, 66 may be made of a polymeric composite material comprising preferably,
20 one or more of bismaleimides (BMI), epoxies, polyimides, or another suitable polymeric composite material; more preferably, graphite (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, bismaleimide (BMI). As discussed in detail below, the first composite surface 64 and/or the second composite surface 68 are prepared or treated with a surface preparation treatment or process prior to repair
25 bonding.

As further shown in FIGS. 2A-2F and 3A, 3B, the bonded structures 30, 50, 170 and the repair bonded structure 60 further comprise at least one functional group-

5 adhesive promoter derivatized layer 40 that is deposited on the prepared composite or metal surface to be bonded. The functional group-adhesive promoter derivatized layer 40 has a surface 42 and functional groups 44 which are discussed in detail below. As shown in FIGS. 2A, 2C, 2E, 3A, the bonded structures 30, 50, 170 and the repair bonded structure 60 may comprise a first functional group-adhesive promoter derivitized layer 40a and a second functional group-adhesive promoter derivitized layer 40b. As shown in FIGS. 2A-2F and 3A, 3B, the bonded structures 30, 50, 170 and the repair bonded structure 60 each further comprise an adhesive layer 46, discussed in detail below, that is applied to the surface 42 of at least one of the functional group-adhesive promoter derivatized layers 40, so as to form a structural bond 48 (see FIG. 2B), structural bond 56 (see FIG. 2D), an aircraft structural bond 180 (see FIG. 2F), or a repair bond 70 (see FIG. 3B).

In another one of the embodiments of the disclosure, there is provided a method 150, as shown in FIG. 18, of promoting adhesion on a composite surface prior to bonding, such as structural bonding or repair bonding. FIG. 18 is an illustration of a flow diagram of one of the embodiments of the method 150 of the disclosure. The method 150 comprises step 152 of providing a composite structure or substrate 32 (see FIGS. 2A-2B) having at least one composite surface 34 (see FIGS. 2A-2B) to be bonded or repaired. The composite structure or substrate 32 is made of a polymeric composite material comprising preferably, one or more of bismaleimides (BMI), epoxies, polyimides, or another suitable polymeric composite material; more preferably, graphite (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, graphite (Gr)/bismaleimide (BMI). Bismaleimides are particularly preferred for use in high performance structural composites requiring higher temperature use and increased

5 toughness and durability. The double bond of the maleimide is very reactive and can undergo chain extension reactions. Epoxy blends of bismaleimide have exhibited use temperatures of 205°C (degrees Celsius) to 245°C and increased toughness and durability.

FIG. 4A is an illustration of the chemical structure of a bismaleimide prepolymer 72 and shows the functional groups of allyl 74 and hydroxyl 76 and "R" group 78. FIG. 4B is an illustration of the chemical structure where the "R" group 78 is propenyl 80 for the bismaleimide prepolymer 72 of FIG. 4A. FIG. 4C is an illustration of the chemical structure where the "R" group 78 is maleimide 82 for the bismaleimide prepolymer 72 of FIG. 4A. FIG. 4D is an illustration of a table 84 listing the functional groups allyl 74, hydroxyl 76, propenyl 80, and maleimide 82 of the bismaleimide prepolymer 72 of FIG. 3A and the reactions of the functional groups. As shown in the table 84 of FIG. 4D, the reaction of allyl 74 is an addition reaction to maleimide, the reaction of hydroxyl 76 is a condensation reaction to ether, and the reactions of propenyl 80 and maleimide 82 are crosslinking via homopolymerization. For purpose of this disclosure, "functional groups" mean specific groups of atoms within molecules that are responsible for the characteristic chemical reactions of those molecules. The atoms of functional groups are linked to each other and to the rest of the molecule by covalent bonds. Organic reactions are facilitated and controlled by the functional groups of the reactants.

25 The method 150 further comprises step 154 of preparing or treating with one or more surface preparation treatments the at least one composite surface 34 (see FIGS. 2A, 2C) prior to structural bonding or composite surface 64 (see FIG. 3A) prior to

5 repair bonding. In addition, the preparing or treating step 154 with one or more surface preparation treatments may comprise preparing or treating composite surface 38 (see FIG. 2A) or metal surface 54 (see FIG. 2C) prior to structural bonding or composite surface 68 (see FIG. 3A) prior to repair bonding. The composite, metal or combination composite/metal surfaces may be prepared with one or more surface preparation
10 treatments comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning, chemical etching, or another suitable surface preparation treatment.

In particular, structural bonding processes rely on sanding to remove contaminants, and increase the surface energy on a limited basis on the composite surface. Preparing or treating the composite surface, such as sanding the composite
15 surface, unexpectedly exposed unique and additional secondary functional groups on the composite surface that have positive durable adhesive promoter effects by increasing adhesive wettability tension and long-term bonding joint durability between composite structures, for example, an aircraft skin and an aircraft stringer. Increased surface energy due to these unique and additional secondary functional groups
20 improves the wettability tension of the adhesive that results in mechanical lock between composite structures. For purposes of this disclosure, "wettability tension" means the ability of a solid surface to reduce the surface tension of a liquid in contact with it such that it spreads over the surface and wets it. Fluids with low surface tension have high wettability, and fluids with high surface tension have low wettability.

25 The method 150 further comprises step 156 of providing a chemical derivatization compound, such as for example, a fluorinated compound, tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene,

5 tridecafluorononyl maleimide, glycidyl octafluoropentyl ether, or another fluorinated compound or another suitable chemical derivatization compound. FIG. 6A is an illustration of the chemical structure of chemical derivatization compound pentafluorophenol 90 that may be used in method 150, as well as methods 200, 300 disclosed herein. FIG. 6B is an illustration of the chemical structure of chemical
10 derivatization compound allyl pentafluorobenzene 92 that may be used in method 150, as well as methods 200, 300 disclosed herein. FIG. 6C is an illustration of the chemical structure of chemical derivatization compound tridecafluorononyl maleimide 94 that may be used in method 150, as well as methods 200, 300 disclosed herein. FIG. 6D is an illustration of the chemical structure of chemical derivatization compound
15 glycidyl octafluoropentyl ether 96 that may be used in method 150, as well as methods 200, 300 disclosed herein. The chemical derivatization compounds contain active functional groups that promote adhesion and detect adhesion mechanisms. For example, as shown in FIGS. 6A-6D, pentafluorophenol 90 contains hydroxyl, allyl pentafluorobenzene 92 contains allyl, tridecafluorononyl maleimide 94 contains
20 maleimide, and glycidyl octafluoropentyl ether 96 contains epoxy.

The method 150 further comprises step 158 of depositing or applying the chemical derivatization compound on the composite surface 34 or 64, for example, that has been prepared in order to form a functional group-adhesive promoter derivatized layer 40 (see FIGS. 2A-2D and 3A-3B) via a derivatization reaction. For purposes of
25 this disclosure, the term "derivatization" means a technique or reaction used in chemistry which transforms a chemical compound into a product (a reaction's derivate) of similar chemical structure called a derivative. A specific functional group of the compound participates in the derivatization reaction and transforms the educt to a

5 derivate of deviating reactivity, solubility, boiling point, melting point, aggregate state, or chemical composition. The derivatization reactions used in the methods 150, 200, 300 disclosed herein transform the composite surface 34 or 64, for example, by covalently bonding chemicals or molecules to the composite surface 34 or 64.

10 The chemical derivatization compound 90, 92, 94, 96, may be deposited on the prepared composite surface 34 or 64, for example, via chemical vapor deposition, such as chemical vapor deposition in a vacuum bag set-up, vacuum deposition, or another suitable deposition or application process. FIG. 21 is an illustration of a partial cross-sectional view of an exemplary chemical vapor deposition in a vacuum bag set-up 250 that may be used with embodiments of the methods 150, 200, 300 of the disclosure. As shown in FIG. 21, the chemical vapor deposition in a vacuum bag set-up 250 comprises a vacuum bag 256 coupled with seals 258 to a top surface 252 of a flat table 254 or other flat surface. A separator element 260, such as for example, a mesh wire screen, may be placed between the vacuum bag 256 and the first composite structure or substrate 32. A liquid phase chemical derivatization compound 264 is 20 poured into a container 262, such as a glass vial, and is heated with a heat source 266. With heat, the liquid phase chemical derivatization compound 264 vaporizes to become a vapor phase chemical derivatization compound 268. The vapor phase chemical derivatization compound 268 travels along a path 270 and over the substrate 32 to react and deposit to form the functional group-adhesive promoter derivatized layer 40 on the 25 substrate 32. Any vapor phase chemical derivatization compound 268 that is unreacted travels along the path 270 and through a vacuum port 272 and an opening 274 in the vacuum bag 256. The vacuum port 272 comprises a first portion 276 attached above the vacuum bag 256 and a second portion 278 attached below the vacuum bag 256.

5 Any unreacted vapor phase chemical derivatization compound 280 escapes out of the vacuum port 272 and out of the vacuum bag set-up 250. Preferably, the prepared composite surface or substrate 34 or 64, for example, may be exposed to the vapor phase chemical derivatization compound 268 containing selected functional groups. The selection of the functional groups is preferably based on a resin formulation of the
10 composite structure, for example. In particular, for composite structures made of bismaleimide, it has been unexpectedly found that the chemical derivatization compounds 90, 92, 94, 96 form carbon-carbon double bond functional groups on a derivatized surface of the bismaleimide.

Derivatization reaction mechanisms capable of creating reactive useful
15 functional groups on a composite structure include such derivatization reaction mechanisms as bromination, silination, and thionation. FIG. 5 is an illustration of a bromination derivatization reaction mechanism 86 in which the functional groups allyl 74, propenyl 80, and maleimide 82 of the bismaleimide prepolymer 72 (see FIG. 4A) react with bromine 88 to obtain a bromination reaction product 89. The bromination
20 derivatization reaction attacks double bonds exposed on the composite surface. Double bonds are electron rich environments that promote secondary bonding forces between the adhesive and the composite structural surface.

FIG. 7 is an illustration of a silination derivatization reaction mechanism 98 in which a silane solution or gel 100 reacts with carbon-carbon double bond 102 to obtain
25 a silination reaction product 104. The silination derivatization reaction is capable of reaction with units of unsaturation on the composite surface and introduces entire organic functional groups onto the composite surface.

5 FIG. 8 is an illustration of a thionation derivatization reaction mechanism 106 in which a thiol solution or gel 108 reacts with carbon-carbon double bond 102 to obtain a thionation reaction product 110. The thionation derivatization reaction reacts with units of unsaturation introducing organic containing sulfur functional groups onto the composite surface.

10 X-ray photoelectron spectroscopy techniques can be used to identify specific functional groups that influence a composite to composite bond or joint when one or both composites are made from a bismaleimide matrix material. FIG. 9 is an illustration of a table 112 listing the potential bismaleimide adhesion reactions, including the functional group types, the possible reactions with bismaleimide/epoxy adhesive, and
15 the temperature range. For the functional group allyl 74, the possible reaction with bismaleimide/epoxy adhesive is "ene" addition to maleimide at a temperature in the range of 200°C (degrees Celsius) to 300°C. For the functional group hydroxyl 76, the possible reaction with bismaleimide/epoxy adhesive is etherification at a temperature of greater than 240°C. For the functional group hydroxyl-epoxide, the possible reaction
20 with bismaleimide/epoxy adhesive is epoxy addition at a temperature of greater than 100°C. For the functional group maleimide 82, the possible reaction with bismaleimide/epoxy adhesive is maleimide addition to maleimide at a temperature of greater than 100°C.

 The method 150, as well as methods 200, 300, discussed below, introduce
25 unique functional groups as a structural adhesive promoter on composite surfaces made of a polymeric composite material comprising preferably, one or more of bismaleimides (BMI), epoxies, polyimides, or another suitable polymeric composite

5 material; more preferably, graphite (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, bismaleimide (BMI). This is achieved by introducing functional groups through derivatization reaction mechanisms on the composite surface to be bonded such as for structural bonding or repair bonding. These functional groups accelerate the secondary interaction between the adhesive and
10 the composite surface thereby increasing the repair design long life and durability of the composite bonded joint under hostile operating environments. The method 150, as well as methods 200, 300, discussed below, transform the composite surface of the composite structure from a limited active surface to a highly activated adhesive promoter of durable-bonding surface characteristics. A variety of forces are presumed
15 to be responsible for a successful and effective composite bonded joint or repair bond. Primary bonding forces include the covalent bonds created between the composite surface and the adhesive material, as well as Van der Waals forces that are also created at the composite-adhesive interface. For purposes of this disclosure, "Van der Waals forces" mean the sum of the attractive or repulsive forces between molecules or
20 between parts of the same molecule other than those due to covalent bonds or to electrostatic interaction of ions with one another or with neutral molecules. For purposes of this disclosure, "covalent bonds" means a chemical bond that is characterized by the sharing of pairs of electrons between atoms, and other covalent bonds.

25 The method 150, as well as methods 200, 300, discussed below, use chemical derivatization to create a functional group-adhesive promoter type layer on the structural composite surface as a bonding agent. Moreover, on bismaleimide composite surfaces, the formation of carbon-carbon double bond (C=C) (unsaturation) functional

5 groups on such surfaces through derivatization reactions was unexpectedly found, which results in a structurally sound and durable composite bond that can be used in various structures, for example, aircraft structures. A mono layer of derivatizing chemicals at otherwise inactive sites on the composite surface creates a thin film adhesive promoter that promotes adhesion. For purposes of this disclosure, “adhesive
10 promoter” means a material that helps an adhesive bond to a surface and that is applied to the surface before the adhesive is applied.

The method 150 further comprises step 160 of applying an adhesive layer 46 (see FIGS. 2A-2F and 3A, 3B) to the surface 42 of the functional group-adhesive promoter derivatized layer 40 of at least, for example, the composite structure 32 (see
15 FIGS. 2A, 2C), the first polymeric composite aircraft structure 172 (see FIG. 2E), or the first composite structural portion 62 (see FIG. 3A). In addition, the adhesive layer 46 may also be applied to the surface 42 of the functional group-adhesive promoter derivatized layer 40 of the composite structure 36 (see FIG. 2A) or the second polymeric composite aircraft structure 176 (see FIG. 2E) or the metal structure 52 (see
20 FIG. 2C) or the second composite structural portion 66 (see FIG. 3A). The adhesive layer 46 may preferably comprise film adhesives, such as epoxies, bismaleimides, or another suitable adhesive.

The method 150 further comprises step 162 of heat curing the adhesive layer 46 to result in a bond with another structure made of a composite, a metal, or a
25 combination thereof. The bond may comprise, for example, a structural bond 48 (see FIG. 2B), 56 (see FIG. 2D), or 180 (see FIG. 2F), or a repair bond 70 (see FIG. 3B). As shown in the drawings, heat curing the adhesive layer 46 can result in the structural

5 bond 48 (see FIG. 2B) with another structure, such as between first composite structure 32 and second composite structure, or can result in the structural bond 56 (see FIG. 2D) with another structure, such as between first composite structure 32 and metal structure 52, or can result in the aircraft structural bond 180 (see FIG. 2F) with another structure, such as between first polymeric composite aircraft 172 and second polymeric composite
10 aircraft structure 174, or can result in the repair bond 70 (see FIG. 3B), such as between first composite structural portion 62 and second composite structural portion 66. The other structure may comprise, for example, a composite structure 36 (see FIGS. 2A-2B) that is comprised of the same composite material as the composite structure 32 or a different composite material than the composite structure 32. In
15 another embodiment, the other structure may comprise a metal structure 52 (see FIGS. 2C-2D) that may preferably be made of a metal material such as aluminum, titanium, steel, alloys thereof, or another suitable metal material. In another embodiment, the other structure may comprise a structure made of a combination of a composite material and a metal material. The composite structure 32 and the other structure made of the
20 composite, the metal, or the combination thereof, are preferably aircraft structures for manufacturing an aircraft 10 (see FIG. 1), for example, polymeric aircraft structures 172, 176 (see FIG. 2E) may be used to form the wings 18 or fuselage 12 or aircraft 10.

FIG. 19 is an illustration of a flow diagram of another one of the embodiments of a method 200 for structural bonding of structures. The method 200 comprises step
25 202 of providing a first structure 32 (see FIGS. 2A-2D) made of a composite material and a second structure 36 (see FIG. 2A) made of a composite material, a second structure 52 made of a metal material, or a second structure made of a combination of a composite material and a metal material. The first composite structure 32 and the

5 second structure, if made of a composite material or a combination of composite material, are made of a polymeric composite material comprising preferably, one or more of bismaleimides (BMI), epoxies, polyimides, or another suitable polymeric composite material; more preferably, graphite (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, bismaleimide (BMI). If the second
10 structure is made of metal material or a combination of metal material and composite material, preferably the metal material comprise such as aluminum, titanium, steel, alloys thereof, or another suitable metal material. Preferably, the first and second structures are aircraft structures.

The method 200 further comprises step 204 of preparing a surface to be
15 bonded, such as composite surfaces 34, 38 (see FIG. 2A) or a metal surface 54 (see FIG. 2C) on each of the first and second structures 32, 36 (see FIG. 2A) or 32, 52 (see FIG. 2C) to obtain a first surface 34 that has been prepared and a second surface 38 or 54 that has been prepared. As discussed above, the surface to be bonded is preferably prepared with one or more surface preparation treatments comprising solvent wiping,
20 abrading, grit blasting, sanding, sandblasting, chemical etching, or another suitable surface preparation treatment.

The method 200 further comprises step 206 of providing a chemical derivatization compound (90, 92, 94, 96 (see FIGS. 6A-6D)) containing active functional groups that promote adhesion. As discussed above, the chemical derivatization
25 compound preferably comprises fluorinated compounds, tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, glycidyoctafluoropentyl ether, or another fluorinated compound, or another suitable

5 chemical derivatization compound. The method 200 further comprises step 208 of depositing the chemical derivatization compound (90, 92, 94, 96 (see FIGS. 6A-6D)) on each of the first and second surfaces 34, 38 (see FIG. 2A) or 34, 54 (see FIG. 2C) that have been prepared in order to form a first functional group-adhesive promoter derivitized layer 40a (see FIGS. 2A, 2C) and a second functional group-adhesive promoter derivitized layer 40b (see FIGS. 2A, 2C). The chemical derivatization compound may be deposited on the prepared composite surface via chemical vapor deposition, such as chemical vapor deposition in a vacuum bag set-up; vacuum deposition; or another suitable deposition or application process. The chemical vapor deposition in a vacuum bag set-up 250 is shown in FIG. 21 and is discussed in detail above. The method 200 further comprises step 210 of applying an adhesive layer 46 to at least one of the first and second functional group-adhesive promoter derivitized layers 40a, 40b. As discussed above, the adhesive layer 46 may preferably comprise film adhesives, such as epoxies, bismaleimides, or another suitable adhesive.

The method 200 further comprises step 212 of joining the first and second structures 32, 36 (see FIG. 2A) or 32, 52 (see FIG. 2C) together with the adhesive layer 46 and the first and second functional group-adhesive promoter derivitized layers 40a, 40b therebetween. The method 200 further comprises step 214 of heat curing the adhesive layer 46 to the joined first and second structures 32, 36 (see FIG. 2A) or 32, 52 (see FIG. 2C) to form a structural bond 48 (see FIG. 2B) or 56 (FIG. 2D) between the first and second structures 32, 36 (see FIG. 2A) or 32, 52 (see FIG. 2C), respectively. The first structure 32 made of a composite material is preferably an aircraft structure. The other second structure 36 (see FIG. 2A) made of the composite, the other second

5 structure 52 made of the metal, or the other second structure made of a combination of composite and metal, are also preferably aircraft structures.

FIG. 20 is an illustration of a flow diagram of another one of the embodiments of a method 300 for structural bonding of polymeric composite structures of an aircraft 10 (see FIGS. 1, 2E, 2F). The method 300 comprises step 302 of providing a first polymeric composite aircraft structure 172 and a second polymeric composite aircraft structure 176 (see FIG. 2E). The first polymeric composite aircraft structure 172 and the second polymeric composite aircraft structure 176 are made of a polymeric composite material comprising preferably, one or more of bismaleimides (BMI), epoxies, polyimides, or another suitable polymeric composite material; more preferably, graphite 15 (Gr)/bismaleimide, graphite (Gr)/epoxy, or graphite (Gr)/polyimide; and most preferably, bismaleimide (BMI).

The method 300 further comprises step 304 of preparing a surface to be bonded on each of the first and second polymeric composite aircraft structures 172, 176 in order to form a first prepared surface 174 and a second prepared surface 178 (see 20 FIG. 2E), respectively. The first prepared surface 174 and the second prepared surface 178 are preferably prepared with one or more surface preparation treatments comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical etching, or another suitable surface preparation treatment.

The method 300 further comprises step 306 of providing a chemical 25 derivatization compound (90, 92, 94, 96 (see FIGS. 6A-6D)) containing active functional groups that promote adhesion. As discussed above, the chemical derivatization compound preferably comprises fluorinated compounds, tetrafluoroaceticanhydride

5 (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, glycidyoctafluoropentyl ether, or another fluorinated compound, or another suitable chemical derivatization compound. The method 300 further comprises step 308 of depositing the chemical derivatization compound (90, 92, 94, 96 (see FIGS. 6A-6D)) on each of the first and second prepared surfaces 174, 178, to form a first functional group-
10 adhesive promoter derivitized layer 40a and a second functional group-adhesive promoter derivitized layer 40b (see FIG. 2E). The chemical derivatization compound may be deposited on the first and second prepared surfaces 174, 178 via chemical vapor deposition, such as chemical vapor deposition in a vacuum bag set-up; vacuum deposition; or another suitable deposition or application process. The chemical vapor
15 deposition in a vacuum bag set-up 250 is shown in FIG. 21 and is discussed in detail above. For first and second polymeric composite aircraft structures 172, 176 made of bismaleimide, chemical derivatization compounds can form carbon-carbon double bond functional groups on the derivitized layer or surface of the bismaleimide.

The method 300 further comprises step 310 of applying an adhesive layer 46
20 to at least one of the first and second functional group-adhesive promoter derivitized layers 40a, 40b. As discussed above, the adhesive layer 46 may preferably comprise film adhesives, such as epoxies, bismaleimides, or another suitable adhesive. The method 300 further comprises step 312 of joining the first and second polymeric composite aircraft structures 172, 176 together with the adhesive layer 46 and the first
25 and second functional group-adhesive promoter derivitized layers 40a, 40b therebetween. The method 300 further comprises step 314 of heat curing the adhesive layer 46 to the joined first and second polymeric composite aircraft structures 172, 176

- 5 to form an aircraft structural bond 180 (see FIG. 2F) between the first and second polymeric composite aircraft structures 172, 176.

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EXAMPLES

Tests were conducted with various derivatization compounds or agents on bismaleimide (BMI) composite surface substrates as follows:

Example 1

Comparative Surface Preparation Tests of Bismaleimide (BMI) Samples. Four (4)

10 samples of bismaleimide (BMI) composite surface substrates were prepared, tested and evaluated using various surface preparation treatments, including: (1) "As received" which means the BMI composite surface had no surface preparation and the BMI composite surface had no exposure; (2) "Extracted" which means the BMI composite surface was washed with acetone solvent and then dried; (3) "Wiped" which means the
15 BMI composite surface was hand wiped with an acetone silk cloth; and, (4) "Hand sanded" which means the BMI composite surface was hand sanded with 60 grit aluminum oxide sandpaper until black dust has been produced and a top layer of the BMI composite matrix material was removed with the hand sanding. An X-ray photoelectron spectroscopy (XPS) machine (Model SSX-100) obtained from Surface
20 Sciences Inc. of Brea, California, was used to measure the concentrations of carbon (C), oxygen (O), nitrogen (N), silicon (Si), and fluorine (F) present after each of the surface preparations was conducted. FIG. 10 is an illustration of a graph 114 comparing bismaleimide surface compositions after the various surface preparation treatments, "As received", "Extracted", "Wiped", and "Hand sanded". The results of this
25 test showed that hand sanding of a BMI composite surface alone removed contaminants and also introduced carbon species on the surface of the BMI composite.

- 5 This was likely due to the exposure of carbon fibers that are typical of carbon-epoxy composites.

Example 2

Comparative Surface Preparation Tests of Bismaleimide (BMI) Samples With Addition of TFAA (Tetrafluoroaceticanhydride). Four (4) samples of bismaleimide (BMI) composite surface substrates were prepared, tested and evaluated using wiped and hand sanded surface preparation treatments before and after exposure to TFAA, including: (1) "Wiped" with isopropyl alcohol (IPA) which means the BMI composite surface was hand wiped with an isopropyl alcohol (IPA) soaked silk cloth; (2) "Wiped, TFAA exposure" which means the BMI composite surface was hand wiped with an isopropyl alcohol (IPA) soaked silk cloth and then the wiped BMI composite surface was treated with chemical derivatization compound TFAA; (3) "Hand sanded" which means the BMI composite surface was hand sanded with 60 grit aluminum oxide sandpaper until black dust has been produced and a top layer of the BMI composite matrix material was removed with the hand sanding; and (4) "Hand sanded, TFAA exposure" which means the BMI composite surface was hand sanded with a 60 grit aluminum oxide sandpaper until black dust has been produced and a top layer of the BMI composite matrix material was removed with the hand sanding, and then the exposed BMI composite surface was treated with chemical derivatization compound TFAA. An X-ray photoelectron spectroscopy (XPS) machine (Model SSX-100) obtained from Surface Sciences Inc. of Brea, California, was used to measure the concentrations of carbon (C), oxygen (O), nitrogen (N), silicon (Si), and fluorine (F) present after each of the surface preparations was conducted. FIG. 11 is an illustration of a graph

5 comparing BMI composite surface compositions before and after TFAA exposure for BMI surface compositions with surface preparation treatments, "Wiped", "Wiped, TFAA exposure", "Hand sanded", and "Hand sanded, TFAA exposure". The results of this test showed that hand sanding activated the BMI composite surface toward TFAA grafting. After treatment with TFAA, the results showed some carbon was consumed and oxygen
10 and fluorine concentrations increased. The results of increased oxygen during the TFAA derivatization process demonstrated improved availability of reactive species on the BMI composite surface and improved covalent and Van der Waals forces during the composite-to-composite bonding process.

Example 3

15 Derivatization of Sanded Bismaleimide (BMI) Samples with Fluorinated Derivatization Compounds. Five (5) samples of bismaleimide (BMI) composite surface substrates were prepared, tested and evaluated using hand sanding surface preparation treatment and exposure to various fluorinated derivatization compounds. Each of the BMI substrate samples was prepared by first solvent wiping with acetone to remove handling
20 contamination. Each of the BMI substrate samples was then hand sanded with 60 grit aluminum oxide sandpaper until black dust was produced. Each of the BMI substrate samples was then wiped with acetone and KIMWIPES (KIMWIPES is a registered trademark of Kimberly-Clark Corporation of Neenah, Wisconsin) followed by wiping with dry KIMWIPES until all of the sanding debris was removed. Each of four (4) BMI
25 substrate samples was exposed to a different fluorinated derivatization compound vapor by suspending each of the four (4) BMI samples over a different fluorinated derivatization compound sealed in glass vials. The four (4) fluorinated derivatization

5 compounds included: (1) pentafluorophenol; (2) allyl pentafluorobenzene; (3) tridecafluorononyl maleimide; and (4) glycidyl octafluoropentyl ether. The fifth BMI substrate sample was a control and was only hand sanded and was not exposed to a fluorinated derivatization compound. The four (4) BMI samples exposed to the fluorinated derivatization compounds and the one control BMI sample were exposed to
10 the same cure cycle as adhesive, that is, the temperature was ramped up from room temperature to 177° C (degrees Celsius) over 100 minutes, held at 177° C for 240 minutes, and cooled down at room temperature. The BMI samples were post-cured using the following schedule: ramped up to 227° C over 100 minutes, held 360 minutes, and cooled down. X-ray photoelectron spectroscopy (XPS) was performed to determine
15 whether any bonding took place. The samples were removed from the glass vials, immediately placed in an X-ray photoelectron spectroscopy (XPS) sample introduction chamber (~ (approximately) 10⁻⁶ torr), and allowed to outgas overnight. The samples were then gently heated for 20 (twenty) minutes with an ultraviolet (UV) heat lamp in the introduction chamber to drive off any physisorbed (physically adsorbed) fluorinated
20 derivatization compounds. The samples were grounded with carbon tape to allow resin and fiber signals to be resolved. Flooding the sample surfaces with low energy electrons allowed for data from conductive fibers to be separated from nonconductive resin.

FIG. 12 is an illustration of a graph 118 comparing the following: (1) BMI
25 surface compositions of carbon, oxygen, and nitrogen for a "Sanded Control" BMI sample; (2) BMI surface compositions of carbon, oxygen, nitrogen, and fluorine for a sanded BMI sample exposed to fluorinated derivatization compound pentafluorophenol; (3) BMI surface compositions of carbon, oxygen, fluorine, and silicon for a sanded BMI

5 sample exposed to fluorinated derivatization compound allyl pentafluorobenzene (there was an unknown source of silicon in the spectra of the allyl pentafluorobenzene-exposed surfaces); (4) BMI surface compositions of carbon, oxygen, nitrogen, and fluorine for a sanded BMI sample exposed to fluorinated derivatization compound tridecafluorononylmaleimide; and (5) BMI surface compositions of carbon, oxygen,
10 nitrogen, and fluorine for a sanded BMI sample exposed to fluorinated derivatization compound glycidyoctafluoropentyl ether. The tests results showed evidence of all of the fluorinated derivatization compounds or derivatizing agents on the BMI surface after exposure and cure cycle. The allyl pentafluorobenzene-exposed sample showed significant silicon (Si) which was evidence of possible contamination. The allyl
15 pentafluorobenzene-exposed sample and the glycidyoctafluoropentyl ether-exposed sample showed no nitrogen in the sampling depth which suggests that the derivatizing agent itself polymerized on the BMI surface to the extent that it covered or masked the nitrogen on the surface and nitrogen could not be detected via XPS. XPS typically only penetrates the first monolayer of the surface. The test results indicated that each of
20 the fluorinated derivatization compounds was chemically bonded to its respective sanded BMI surface sample. Exposed fibers and exposed resin surfaces appeared equally reactive toward all of the fluorinated derivatization compounds. The test results seemed to further indicate that exposed fiber surfaces played an important role in adhesion.

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Example 4

Comparative Shear Strength Tests of Bismaleimide (BMI) Samples With Addition of Bromine and TFAA (Tetrafluoroaceticanhydride). Four (4) samples of bismaleimide

5 (BMI) composite surface substrates were prepared, tested and evaluated for shear strength, including: (1) a BMI sample substrate that was a "Control abraded surface" with no exposure to a derivatization compound; (2) a BMI sample substrate that was first sanded and then exposed to bromine derivatization; (3) a BMI sample substrate that was first sanded and then exposed to TFAA derivatization; and (4) a BMI sample
10 substrate that was first sanded and then exposed to bromine and TFAA derivatization. FIG. 13 is an illustration of a graph 120 comparing the results of the lap joint strength or shear strength in pounds per square inch (psi) for BMI samples for "Control abraded surface", "Br (Bromine) derivatization", "TFAA derivatization", and "Br plus TFAA derivatization". This test showed the impact of consuming functional groups on the
15 bonding surface of a BMI composite surface. The test results showed that the consumption of units of unsaturation (double bonds) by bromination derivatization had direct impact on the shear strength of the resulting composite joint, that consumption of hydroxyl groups through TFAA derivatization had no appreciable effect, and that a combination of bromination and TFAA treatment had an appreciably negative effect on
20 the joint's ultimate shear strength. This suggested that promotion of carbon-carbon double bonds through derivatization increased the performance of the bonded joint.

Example 5

Binding Energy Tests for BMI Samples Exposed to Fluorinated Derivatization Compounds. Binding energy tests were performed on the BMI samples of Example 3
25 above that were exposed to various fluorinated derivatization compounds. The binding energy tests were measured by X-ray photoelectron spectroscopy (XPS). XPS measures the energy of electrons displaced from the sample surface via X-ray

5 impingement. The energy of the displaced electrons is measured as they come off the surface. This energy represents the binding energy of the electrons on the surface, approximately: X-ray energy in minus electron energy out plus binding energy equals zero (0).

FIG. 14 is an illustration of a graph 122 showing the results of the binding
10 energy test for F (fluorine) (1s) of the pentafluorophenol-exposed BMI sample. The test results showed fluorine from the pentafluorophenol derivatization compound bonded to fibers and bonded to resin of the derivatized bismaleimide surface. There was evidence of hydroxyl grafting to both resin and fiber surfaces of the BMI sample. BMI adhesive appeared to adhere covalently to both resin and fiber surfaces of the BMI sample.

15 FIG. 15 is an illustration of a graph 124 showing the results of the binding energy test for F (fluorine) (1s) of the allyl pentafluorobenzene-exposed BMI sample. The test results showed fluorine from the allyl pentafluorobenzene derivatization compound bonded to fibers and bonded to resin of the derivatized bismaleimide surface. There was evidence of allyl grafting to both resin and fiber surfaces of the BMI
20 sample. BMI adhesive appeared to adhere covalently to both resin and fiber surfaces of the BMI sample.

FIG. 16 is an illustration of a graph 126 showing the results of the binding energy test for F (fluorine) (1s) of the tridecafluorononyl maleimide-exposed BMI sample. The test results showed fluorine from the tridecafluorononyl maleimide
25 derivatization compound bonded to fibers and bonded to resin of the derivatized bismaleimide surface. There was evidence of maleimide grafting to both resin and fiber

5 surfaces of the BMI sample. BMI adhesive appeared to adhere covalently to both resin and fiber surfaces of the BMI sample.

FIG. 17 is an illustration of a graph 128 showing the results of the binding energy test for F (fluorine) (1s) of the glycidyloctafluoropentyl ether-exposed BMI sample. The test results showed no polymerization reaction. The
10 glycidyloctafluoropentyl ether derivatization compound is bonded to the functional group on the bismaleimide substrate surface. There was evidence of active BMI surface initiated polymerization of the epoxide group. A thick layer of polymer was chemically bonded to the BMI surface.

Conclusions: Embodiments of the methods 150, 200, 300 and the bonded
15 structures produced thereby and disclosed herein provide for durable surface modification of the composite surface or metal surface which may result in improved structural bonding and repair as compared to existing methods. Further, embodiments of the methods 150, 200, 300 and the bonded structures produced thereby and disclosed herein eliminate the use of fastener devices to secure the composite structure
20 to the other structure made of the composite, the metal, or the combination thereof, or to repair the portions of the composite structure. In turn, this may reduce overall manufacturing costs and weight of the bonded composite or composite/metal structure by not having to use the fastener devices. Additionally, embodiments of the methods 150, 200, 300 and the bonded structures produced thereby and disclosed herein may
25 enable completely bonded joints for aircraft production and repair which can provide significant weight reduction and structural efficiency by distributing the load to larger surface areas by eliminating the need for fasteners. Cost savings may also be achieved

5 by the reduction of reworking of composite bonded or bolted structural components. Further, embodiments of the methods 150, 200, 300 and the bonded structures produced thereby and disclosed herein produce derivatized composite surfaces as an adhesive promoter for bonded composite and composite/metal joints and repair. Moreover, embodiments of the methods 150, 200, 300 and the bonded structures
10 produced thereby and disclosed herein use molecular functional groups as a durable adhesive promoter that may be grown or activated on the composite or metal surface to assist composite or metal adhesion during structural bonding or repair. Environmentally durable functional groups on the composite structural surface can act as a potential molecular layer-adhesive promoter and thus can improve the adhesion, which accounts
15 for increased structural bonding and repair performance. The resulting bond is intended to have a long durability without degradation and is intended to endure for the design life of an aircraft.

Many modifications and other embodiments of the disclosure will come to mind to one skilled in the art to which this disclosure pertains having the benefit of the
20 teachings presented in the foregoing descriptions and the associated drawings. The embodiments described herein are meant to be illustrative and are not intended to be limiting or exhaustive. Although specific terms are employed herein, they are used in a generic and descriptive sense only and not for purposes of limitation

CLAIMS

What is claimed is:

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1. A method of promoting adhesion on a composite surface, the method comprising:

providing a composite structure having at least one composite surface to be bonded;

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preparing the at least one composite surface;

providing a chemical derivatization compound containing active molecular functional groups that promote adhesion and detect adhesion mechanisms, wherein the chemical derivatization compound is selected from the group consisting of tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, and glycidyoctafluoropentyl ether;

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depositing the chemical derivatization compound on the prepared composite surface and activating the molecular functional groups through chemical derivatization reaction mechanisms to form a molecular functional group-adhesive promoter derivatized layer on the prepared composite surface as a bonding agent, the chemical derivatization reaction mechanisms creating reactive molecular functional groups on the prepared composite surface, and the chemical derivatization reaction mechanisms selected from the group consisting of bromination, silylation, and thionation;

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applying an adhesive layer to the derivatized layer; and,

heat curing the adhesive layer to result in a bond with another structure made of a composite, a metal, or a combination thereof.

2. The method of claim 1, wherein the composite structure is made of a polymeric composite material selected from the group comprising bismaleimides (BMI), epoxies, and polyimides.
3. The method of claim 1, wherein the composite structure comprises bismaleimide (BMI), and the chemical derivatization compound activates carbon-carbon double bond molecular functional groups on the composite surface of the bismaleimide.
4. The method of claim 1, wherein the composite surface is prepared with one or more surface preparation treatments selected from the group comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning, and chemical etching.
5. The method of claim 1, wherein the chemical derivatization compound is deposited via chemical vapor deposition or vacuum deposition.
6. The method of claim 1, wherein the prepared composite surface is exposed to a vapor phase chemical derivatization compound containing selected molecular functional groups, wherein selection of the molecular functional groups is based on a resin formulation of the composite structure.
7. The method of claim 1, wherein the resulting bond is selected from the group comprising a structural bond and a repair bond.
8. The method of claim 1, wherein the composite structure and the other structure made of the composite, the metal, or the combination thereof, are aircraft structures.
9. A method for structural bonding of structures comprising:
- providing a first structure made of a composite material and a second structure made of a composite material, a metal, or a combination thereof;
- preparing a surface to be bonded on each of the first and second structures to form a first prepared surface and a second prepared surface;

providing a chemical derivatization compound containing active molecular functional groups that promote adhesion and detect adhesion mechanisms, wherein the chemical derivatization compound is selected from the group consisting of tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, and glycidyoctafluoropentyl ether;

depositing the chemical derivatization compound on each of the first and second prepared surfaces and activating the molecular functional groups through chemical derivatization reaction mechanisms to form a first molecular functional group-adhesive promoter derivatized layer on the first prepared composite surface as a first bonding agent and a second molecular functional group-adhesive promoter derivatized layer on the second prepared composite surface as a second bonding agent, the chemical derivatization reaction mechanisms creating reactive molecular functional groups on the first and second prepared surfaces, and the chemical derivatization reaction mechanisms selected from the group consisting of bromination, silylation, and thionation;

applying an adhesive layer to at least one of the derivatized layers of the first and second molecular functional group-adhesive promoter derivatized layers;

joining the first and second structures together with the adhesive layer and the first and second molecular functional group-adhesive promoter derivatized layers therebetween; and,

heat curing the adhesive layer to the joined first and second structures to form a structural bond between the first and second structures.

10. The method of claim 9, wherein the composite material is selected from the group comprising bismaleimides (BMI), epoxies, and polyimides.

11. The method of claim 9, wherein the surface to be bonded is prepared with one or more surface preparation treatments selected from the group comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning, and chemical etching.

12. The method of claim 9, wherein the chemical derivatization compound is deposited via chemical vapor deposition or vacuum deposition.

13. The method of claim 9, wherein the first and second structures are aircraft structures.

5 14. A method for structural bonding of polymeric composite structures of an aircraft, the method comprising:

providing a first polymeric composite aircraft structure and a second polymeric composite aircraft structure;

10 preparing a surface to be bonded on each of the first and second polymeric composite aircraft structures to form a first prepared surface and a second prepared surface;

providing a chemical derivatization compound containing active molecular functional groups that promote adhesion and detect adhesion mechanisms, wherein the chemical derivatization compound is selected from the group
15 consisting of tetrafluoroacetic anhydride (TFAA), pentafluorophenol, allyl pentafluorobenzene, tridecafluorononyl maleimide, and glycidyoctafluoropentyl ether;

depositing the chemical derivatization compound on each of the first and second prepared surfaces and activating the molecular functional groups through
20 chemical derivatization reaction mechanisms to form a first molecular functional group-adhesive promoter derivatized layer on the first prepared composite surface as a first bonding agent and a second molecular functional group-adhesive promoter derivatized layer on the second prepared composite surface as a second bonding agent, the chemical derivatization reaction mechanisms
25 creating reactive molecular functional groups on the first and second prepared surfaces, and the chemical derivatization reaction mechanisms selected from the group consisting of bromination, silination, and thionation;

applying an adhesive layer to at least one of the first and second molecular functional group-adhesive promoter derivatized layers;

joining the first and second polymeric composite aircraft structures together with the adhesive layer and the first and second molecular functional group-adhesive promoter derivatized layers therebetween; and,
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heat curing the adhesive to the joined first and second polymeric composite aircraft structures to form an aircraft structural bond between the first and second polymeric composite aircraft structures.

15. The method of claim 14, wherein the first and second polymeric composite structures are made of a material selected from the group comprising
10 bismaleimides (BMI), epoxies, and polyimides.

16. The method of claim 14, wherein the surface to be bonded is prepared with one or more surface preparation treatments selected from the group comprising solvent wiping, abrading, grit blasting, sanding, sandblasting, chemical cleaning,
15 and chemical etching.