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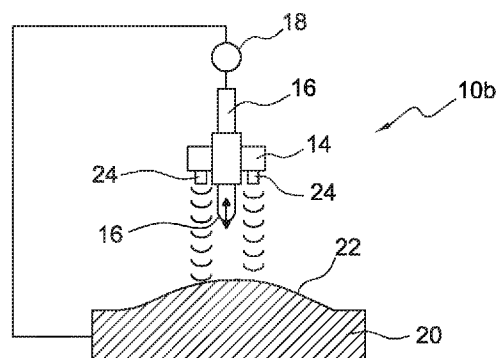
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FIG. 1B



(57) Abstract: Methods, systems and apparatuses for determining the surface potential distribution of treated composite material surfaces, and for non-destructively predicting the fracture toughness of a composite material are disclosed herein.

METHODS, SYSTEMS AND APPARATUSES FOR DETERMINING COMPOSITE MATERIAL CHARACTERISTICS

RELATED APPLICATIONS

5 This application claims the benefit of U.S. Provisional Application No. 62/621,513 filed January 24, 2018 and U.S. Provisional Application No. 62/621,520 filed January 24, 2018, the disclosures of which are incorporated by reference herein in their entireties.

TECHNOLOGICAL FIELD

10 The present disclosure relates generally to the field of non-destructive testing methods to determine if composite surface condition will result in adequate bond strength for composite components. More specifically, the present disclosure related to methods, systems and apparatuses to facilitate the non-destructive inspection of composite components by evaluating composite material surfaces prior to bonding.

BACKGROUND

15 Composite materials continue to attract attention as lightweight materials for structural applications, especially those having weight constraints. To fabricate composite assemblies, bonded joints offer advantages over bolted joints, and would therefore be preferable. These advantages include, without limitation, lighter weight, fewer parts, reduced inventory of parts, increased production rate, lower manufacturing cost, etc. If the surface of a composite material is adequately prepared prior to bonding, then adhesive joining of composite materials can produce bonded joints that are stronger than the composite material itself. However, surface preparation of composite parts (e.g., components, with the terms "parts" and "components" used
20 equivalently throughout the present disclosure) used for making bonded composite assemblies using, for example, structural adhesives, is challenging.

25 The surfaces of composite materials to be joined are often treated prior to bonding the composite materials with structural adhesives. The various pre-treatments used, generally facilitate a change in the surface characteristics of the composite materials. For example, a change in the characteristics of a material surface can change the bonding behavior of a composite material. However, little is known about the surface chemistry that results from treatment of composite surfaces. The lack of fundamental knowledge has become an impediment to the reliable manufacture of robust structural assemblies comprised of composite parts.

35 Many accepted protocols and inspection techniques exist for determining an adequate strength of, for example, metal joints having, for example, physical fasteners. Structures made from joined composite parts must also satisfy various safety and other industry and

governmental agency manufacturing and performance standards. At the present time, the testing, for example, of bond strength of joined composite parts made from composite materials, requires destructive testing of test coupons or alternative design means to assure adequate structural integrity of a component. That is, composite structures comprising bonded composite parts are often sacrificed and destroyed as force is applied to separate the bond. Such destructive testing and/or destructive inspecting results in the destruction of the parts and structures under investigation, and contributes to manufacturing material loss, added manufacturing time and delay, commensurate increases in manufacturing costs, etc. In addition, test coupons may not have the same properties as the actual composite parts (i.e., in-use/production composite parts may have varied properties from test coupons). Illustrative examples of industry standards for composite bonding that must be performed, for example, before joined (i.e. bonded) composite components are deemed acceptable can be found in ASTMs D-5528, D-3163, D-3165, etc. Alternative design architecture that requires alternative load path for the structure in case of the bonded joint failure may also be costly and less weight efficient.

SUMMARY

The present disclosure is directed to methods, systems and apparatuses for determining the adequacy of an activation state of a composite material surface to enable one to predictively determine, non-destructively, the suitability of a composite surface for a composite component for achieving a bond with a structural adhesive to another composite material that, after conducting a bonding or joining process, will have a bond strength that will equal or surpass desired bonding strength values that, until now, have only been determined (e.g., after the bonding process) by destructively testing a joined or bonded assembly that comprises composite material components.

An aspect of the present disclosure is directed to a method of determining the surface potential of a composite component surface, with the method including inspecting the surface of a composite component made from a composite material, with the composite component including a composite component surface and the composite component surface including a treated composite component surface. The surface potential distribution of the treated composite component surface is then determined.

Another aspect of the present disclosure is directed to a method of non-destructively inspecting a treated composite component surface including determining surface potential distribution of the treated composite component surface.

Another aspect of the present disclosure is directed to determining surface potential distribution of the treated composite component surface by measuring the treated composite

component surface with an atomic force microscope, with the atomic force microscope including at least one atomic force microscope probes.

Another aspect of the present disclosure is directed to determining surface potential distribution of the treated composite component surface by measuring the treated composite component surface with an atomic force microscope, with the atomic force microscope including at least one atomic force microscope probes, with the at least one atomic force microscope probe including a Kelvin force probe.

Another aspect of the present disclosure is directed to determining surface potential distribution of the treated composite component surface by measuring the treated composite component surface with an atomic force microscope, with the atomic force microscope including a plurality of atomic force microscope probes.

Another aspect of the present disclosure is directed to determining surface potential distribution of the treated composite component surface by measuring the treated composite component surface with an atomic force microscope, with the atomic force microscope including a plurality of atomic force microscope probes, with the plurality of atomic force microscope probes including Kelvin force probes.

In another aspect, the present disclosure is directed to a method of non-destructively inspecting a treated composite component surface, with the method including determining surface potential distribution of the treated composite component surface, wherein the surface potential distribution of the treated composite component surface is indicative of a fracture toughness ranging from about 1 lb./in.² to about 10 lbs./ in.².

The features, functions and advantages that have been discussed can be achieved independently in various aspects or may be combined in yet other aspects, further details of which can be seen with reference to the following description and the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Having thus described variations of the disclosure in general terms, reference will now be made to the accompanying drawings, which are not necessarily drawn to scale.

FIGs. 1A, 1B, and 1C are representative side views of an apparatus according to aspects of the present disclosure showing an individual atomic force microscope probe, more specifically, an individual Kelvin force probe.

FIGs. 1D, 1E, and 1F are representative side views of an apparatus according to aspects of the present disclosure showing a plurality of atomic force microscope probes, more specifically, a plurality of Kelvin force probes in an array.

FIG. 2A is a representative view of a CFRP composite sample.

FIG. 2B is a representative view of a CFRP composite sample shown with confirming scale.

FIG. 2C is a representative side view of a plasma pre-treatment arrangement according to aspect of the present disclosure.

FIG. 3A is a topographic map of the surface of a CFRP control sample.

FIG. 3B is a surface potential map of the surface of the CRFP sample shown in FIG. 3A.

5 FIG. 3C is a topographic map of the surface of a plasma-treated CFRP sample.

FIG. 3D is a surface potential map of the surface of the CRFP sample shown in FIG. 3B.

FIG. 3E is a histogram showing the comparative surface potential distribution of the CFRP control sample shown in FIGs 3A and 3C and the plasma-treated CFRP sample shown in FIGs. 3B and 3D.

10 FIG. 3F is a histogram showing comparative normalized fracture toughness of the CFRP control sample and the plasma-treated CFRP sample.

FIG. 4A and 4B are graphs showing intensity plotted against and as a function of binding energy for the control and plasma-treated CFRP samples.

15 FIG. 5 is a graph illustrating comparative contact angle of plasma-treated samples versus control samples.

FIGs 6A, 6B, 6C, and 6D are plotted force-retract curves for equal but opposite magnetized probes (M+/M-) showing that plasma-treatment causes a magnetization of the plasma-treated sample surface (FIGs. 6A and 6B).

20 FIGs. 7A, 7B, 7C, and 7D are topography and phase shift maps of the same region of a plasma-treated CFRP sample for a M+ probe (FIGs. 7A and 7C) and an M- probe (FIGs 7B and 7D) the control sample (FIGs. 6C and 6D).

FIG. 7E is a phase shift difference map.

FIG. 7F is a graph showing the plots from the phase shift difference map shown in FIG. 7E.

25 FIGs. 8A, 8B, and 8C are graphs showing normalized fracture toughness correlated for low and medium intensity plasma-treatment of the CFRP sample surfaces.

FIG. 9 is a flowchart outlining methods according to aspects of the present disclosure.

FIG. 10 is a flowchart outlining methods according to aspects of the present disclosure.

30 FIG. 11 is a non-limiting illustration of an aircraft comprising a composite component assembly comprising a composite component non-destructively inspected according to aspects of the present disclosure.

DETAILED DESCRIPTION

35 According to aspects of the present disclosure, methods, systems and apparatuses are presented to predictively determine the adequacy of a resulting bonding condition strength by non-destructively evaluating the surface of a composite material, and more particularly evaluating the surface potential distribution of a pre-treated composite material surface prior to

application of a bonding adhesive to pretreated composite surfaces and in advance of the bonding protocols typically used to manufacture composite assemblies comprising composite components.

According to aspects of the present disclosure, changes in surface chemistry of a composite material surface are inspected before a bonding process. The surface activation state of a composite material surface is determined by investigating and correlating the activation state of the composite material surface to functionalities in bonding processes using structural adhesives to join (e.g. bond) composite material components together.

CFRP composites having a thermoplastic matrix, for example polyaryl ether ketones (PAEK), such as polyether ether ketone (PEEK) and polyether ketone ketones (PEKK), have begun attracting attention as potentially useful composite materials.

Thermoplastics offer a number of advantages over thermosets. From a mechanical perspective, thermoplastics have high fracture toughness among polymers. Fracture toughness is a measure of durability and strength. High fracture toughness is a function of the semi-crystalline structure of a material. Amorphous regions are thought to increase durability, while crystalline regions improve strength. Moreover, thermoplastics are more chemically inert than thermosets, contributing to heightened resistance to solvents and moisture, again improving long term durability in the wide variety of environments that a large structure made from composite components may encounter (e.g., buildings, bridges, vehicles such as aircraft or automobile, etc.).

For example, surface regions of components made from carbon fiber reinforced polymers (CFRPs) can an increase in surface activation by subjecting CFRP component surfaces to various plasma treatments.

According to present aspects, "pre-treatment" or simply "treatment" processes for activating a composite material surface into a non-equilibrium state are intended to affect the surface chemistry and thereby enable the surface to strongly interact with adhesives, thereby enabling a more robust bond between joined composite parts. Such activation of the surface prior to bonding (e.g., pre-treatment or treatment) can increase the fracture toughness of a final assembly by more than an order of magnitude.

Similarly, surface treatment designed to increase a surface activation can result from, for example, plasma surface treatments, physical surface treatments including abrasion, (e.g. physically abrading a surface, etc.), chemical surface treatments (e.g., including chemically abrading a surface), laser surface treatments, chemical etching treatments, surface coating treatments, (e.g. to produce a coated surface, etc.) plasma treatments, etc.

According to another aspect, in the case of plasma treatments to produce plasma treated surfaces, the plasma treatment includes at least one of a low intensity plasma treatment, or a medium intensity plasma treatment. The non-destructive surface inspection methods

disclosed herein contemplate the investigation of surfaces that are "treated" according to any of the aforementioned surface treatment methods to produce the treated surfaces.

In one aspect, plasma treatments are believed to change the electrochemical potential of electrons on a plasma-treated CFRP surface, thus changing an activation state of a CFRP at its surface. However, if a composite surface is not treated or activated adequately or uniformly, the bonding process may be negatively impacted such that the effected bond will fail to meet required or desired bond strengths. Further, insufficient surface preparation lowers the strength of composite material joints formed using adhesives. This observation has motivated investigations presently described herein into technologies for activating the surface into a non-equilibrium state that can react with adhesives to form a robust bond due to the relative chemical inertness of the constituent composite materials at the composite material surface.

While it is known that increased bonding potential of composite material surfaces facilitates bonding for the purpose of potentially satisfying various ASTM-related bonding standards, (e.g., ASTM D 3163; ASTM D 3165; ASTM D 5528, etc.), such bonded components must still be subjected to destructive testing to comply with manufacturing protocols and to otherwise assure that a desired level of bonding has been accomplished.

While being bound to no particular theory, it is now believed that non-thermal oxygen plasma reacts with the surface of an organic polymer in a composite material to functionalize it with charge-stabilized radicals. Organic ions combine with peroxy radicals on the surface of the composite material polymer and a mutual stabilization effect increases the lifetime of the complex. The lifetime of the ion-radical complex is believed to be significantly longer than a day, while ions, for example, decay in a few minutes in the absence of radicals.

While experiments were conducted on CFRP samples, aspects of the present disclosure contemplate measuring the surface activation of various composite materials having various resin systems impregnated by various reinforcing fiber materials. The resin system can be PAEK (e.g. PEEK, PEKK, etc.), epoxy-based, acrylate-based, fluoropolymer-based or silicone-based. The useful reinforcing fibers used with the resin systems include carbon fibers, boron fibers, aramid fibers, glass fibers, etc. Further, the composite materials may include thermoplastic materials or thermoset materials. A particular treated composite component comprising a composite material having a treated composite component surface, where the surface potential distribution is determined according to present aspects, includes a treated thermoplastic composite component including carbon fibers. According to further aspects, a treated composite component comprising a composite material having a treated composite component surface, where the surface potential distribution is determined according to present aspects, includes a carbon fiber reinforced polymer.

According to aspects of the present disclosure, the methods, systems and apparatuses disclosed herein non-destructively test, assess, and successfully predict the strength of bonds

of joined composite assemblies made from joined composite components by determining the state of the surface of composite material components before they are joined. This is in strong contrast to the destructive, wasteful, time-consuming, and costly testing of joined composite assemblies that can only have their bond strength assessed after the curing of the composite assembly, by destroying the coupons, and inferring that the observed properties of the test coupon are representative of in-use/in-production parts..

According to aspects of the present disclosure, it has now been determined that predetermined levels of bonding and bond strength of composite materials can be non-destructively determined by evaluating the surface activation of composite surfaces of composite components to be joined and bonded together before such component surfaces are bonded together. The activation state of the surface of the composite is assessed by determining the width of a surface potential distribution at a composite material surface. It has been determined that the surface potential distribution is inversely related to the density of active species on the composite material surface. The width of the surface potential distribution is determined by calculating the area of the distribution after it has been normalized to have a maximum value of 1.

According to aspects of the present disclosure, the surface activation of composite materials is achieved by surface treatment methods including at least low intensity plasma treatment and medium intensity plasma treatment. While the described experimentation has been conducted for plasma-treated samples, other surface-activation methods and processes that or enhance the activation of a composite surface (prior to bonding) are also contemplated.

FIGs 1A, 1B, and 1C illustrate but one method for investigating the surface activation and surface activation distribution of a composite material surface using atomic force microscopy techniques. FIG. 1A shows a system 10a including an atomic force probe 12 (e.g., a Kelvin force probe). The atomic force probe 12 is in communication with a stationary head 14 in communication with means (not shown) for controlling the position of the stationary head. The atomic force probe 12 vibrates in the direction of the arrow shown in the atomic force probe tip 16. A current is directed to the probe through controller 18. The atomic force probe tip 16 is maintained an average lift height d' distance from composite component surface 22 of composite component 20. According to certain aspects of the present disclosure, the stationary head 14 maintains the probe at an orientation substantially perpendicular to the composite component surface 22. The head height d'' represents the distance from the composite component surface 22 to the stationary head 14. As shown in FIG. 1A, the composite component surface 22 is substantially flat across the area of the surface to be scanned by atomic force probe 12.

FIG. 1B shows a further system 10b where the stationary head 14 further comprises distance detectors 24. The stationary head may comprise any number of distance detectors 24

as desired. The distance detectors 24 sense the surface characteristics from the composite component surface 22 of composite component 20 by emitting and receiving signals from the composite component surface 22. The signals received by the distance detectors 24 are relayed to a data collection means (not shown) where the signals are converted to various functions. The remainder of the features shown in FIG. 1B are as described above and present in system 10a (e.g. as illustrated in FIG. 1A). As shown in FIG. 1B, the composite component surface 22 is irregularly shaped (i.e. not flat) across the area of the surface to be scanned by atomic force probe 12.

FIG. 1C shows a system 10c where the stationary head 14 is pivoted to an orientation such that the atomic force probe 12 is oriented substantially perpendicular to the composite component surface 22 of composite component 20 during a scan of the atomic force probe 12 across the area of the composite component surface 22 to be scanned by the atomic force probe 12. The remainder of the features shown in FIG. 1C are as described above and present in system 10a shown in FIGs. 1A and/or 1B. As shown in FIG. 1C, the composite component surface 22 is irregularly shaped (i.e. not flat) across the area of the surface to be scanned by atomic force probe 12.

FIGs. 1D, 1E, and 1F illustrate a further method for investigating the surface activation and surface activation distribution of a composite material surface using atomic force microscopy techniques. FIG. 1D shows a system 10d including a plurality (e.g. five) of atomic force probes 12 (e.g., Kelvin force probes). The atomic force probes are in communication with a stationary head 14 in communication with means (not shown) for controlling the position of the stationary head 14. The atomic force probes 12 vibrate in the direction of the arrow shown in the atomic force probe tips 16. A current is directed to the probes through controllers 18. The atomic force probe tips 16 are maintained an average lift height d' distance from composite component surface 22 of composite component 20. According to certain aspects of the present disclosure, the stationary head 14 maintains the probes at an orientation substantially perpendicular to the composite component surface 22. The head height d'' represents the distance from the composite component surface 22 to the stationary head 14. As shown in FIG. 1D, the composite component surface 22 is substantially flat across the area of the surface to be scanned by atomic force probes 12.

FIG. 1E shows a further system 10e where the stationary head 14 further comprises distance detectors 24. The stationary head 14 may comprise any number of distance detectors 24 as desired. The distance detectors 24 sense the surface characteristics from the composite component surface 22 of composite component 20 by emitting and receiving signals from the composite component surface 22. Such signals are shown in FIGs 1E and 1F as curved lines extending between the composite component surface 22 and the distance detectors 24. The signals received by the distance detectors 24 are relayed to a data collection means (not

shown) where the signals are converted to various functions. The remainder of the features shown in FIG. 1D are as described above, and present in system 10e shown in FIG. 1E. As shown in FIG. 1E, the composite component surface 22 is irregularly shaped (i.e., not flat) across the area of the surface to be scanned by atomic force probes 12.

FIG. 1F shows a system 10f where the stationary head 14 is pivoted to an orientation such that the atomic force probes 12 are oriented substantially perpendicular to the composite sample surface 22 of composite component 20 during a scan of the probe across the area of the composite component surface 22 to be scanned by the probes 12. The remainder of the features shown in FIG. 1F are as described above and present in system 10d and 10e shown in FIGs. 1D and E, respectively. As shown in FIG. 1F, the composite component surface 22 is irregularly shaped (i.e., not flat) across the area of the surface to be scanned by atomic force probes 12.

While five atomic force probes 12 are shown in FIGs 1D, 1E and 1F, aspects of the present disclosure contemplate any practical number of atomic force probes (e.g., based on sample size) in communication with stationary head 14 as desired.

EXPERIMENTAL

Three types of composite material samples (equivalently referred to herein as “composite components”, “composite component samples” or “samples”) were prepared. The treated composite material samples tested herein are of the type and represent the type of treated composite component materials referred to herein, and comprise treated composite component surfaces. All of the composite material samples consisted of 7 μm diameter carbon fibers embedded in a PAEK matrix (e.g., PEKK), which were cut from the same large panel. Therefore the composite materials used include unidirectional standard modulus carbon fiber PEKK matrix composite materials. Composite material samples for material characterization were nominally 10 mm $\times$ 10 mm, while coupons for mechanical measurements were larger (e.g., 250 mm long $\times$ 25 mm wide). Control and non-control composite material samples were solvent cleaned using ketones. The control samples were not processed any further.

EXAMPLE 1

Composite Component Treatment

Composite material samples were treated with low, medium, or high intensity plasma. The plasma was generated using air as the process gas in a commercial unit. The plasma source parameters were held constant, but the translation velocity of the composite material sample under the beam (i.e., treatment time) was varied. Low intensity corresponded to a plasma beam translational velocity of 13 mm s^{-1} , while medium corresponded to a translational velocity of 6.4 mm s^{-1} . The area of plasma treatment was approximately 10 mm diameter, and

thus, the treatment time was approximately 0.8 seconds for low intensity and 1.6 seconds for medium intensity. The high intensity plasma treatment caused mechanical deformation of the composite material sample. Characterization of the samples was then performed as a function of time after plasma treatment. For select experiments, samples were treated with a modified
5 plasma unit that consisted of a 16 mm diameter plasma jet that was generated using radiofrequency at a nominal power of 50 W at 13.56 MHz, which was coupled to the reactor through an impedance matching network. The plasma was generated in a gas mixture that was 9% O₂ (with the balance being Ar) at a pressure of 89 Pa. FIG. 2A is a representative view of a CFRP composite sample.

10 FIG. 2B is a representative view of a CFRP composite sample shown with confirming scale.

FIG. 2C illustrates the custom plasma system during operation. The samples were affixed to the holder using double-sided vacuum-compatible carbon tape. Experiments comparing the commercial plasma unit to the custom unit showed that the plasma treatment
15 provided a similar effect on the (PEKK) CFRP composite material samples.

Exposure of the thermoplastic (PEKK) CFRP composite material to low temperature oxygen plasma produced a uniform surface with a well-defined electrochemical potential of electrons. The well-defined surface state produced by plasma exposure was effective for bonding thermoplastic composite parts into assemblies using structural adhesives. The
20 presently described experimentation considered the interaction between electrostatic charges on the surface, which originate in the plasma and radicals on the surface. The interaction of charges and radicals was determined to impact the lifetime of the activated surface.

One type of plasma generator contemplated according to aspects of the present disclosure includes, for example, a Plasmatreat FG5001 generator having an input voltage
25 range of 100-260 V, 50-60 Hz (+/- 5%) with a supply protection of 18A at 230 V/25 A at 100V, and having a total output of 1 KVA. The power supply is continuous (0.4 – 1.0kVA), with a maximum output voltage of 1kVss, and an output frequency of 19-23 kHz. Permissible operating ambient temperature is 0°C to 40°C with standard switch cabinet housing side housing and optional front-side operation. The overall dimensions are 540 x 519 x 277 mm (W
30 x H x D), and having an approximate weight of 35 kg. Exemplary plasma jets include 2 pcs: PFW10, PFW20, RD1004, RD2004 and 1 pc RD2005, RD1010. According to further aspects the plasma treatment comprises at least one of a plurality of plasma processing parameters, said plasma processing parameters comprising at least one of: a translation speed ranging from about 5 in./min. to about 300 in./min.; a working height ranging from about 0.1 in. to about 1.0
35 in.; or an overlap ranging from about 0% to about 50%.

While the investigated composite resin was a thermoplastic (PEKK) CFRP system, aspects of the present disclosure contemplate the useful non-destructive testing methods

described herein with composite resin systems that include: 1) thermoplastic materials including polyether ether ketone (PEEK), polyphenylene sulfide (PPS), polycarbonate (PC), polyetherimide (PEI), etc.; 2) thermoset materials including polyester (PE), epoxy (Ep), bismaleimide (BMI), polyimide (PI), phenolic (Ph), vinylester (VE), etc.; 3) fluoropolymers including polyvinyl fluoride (PVF), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) etc.; 4) silicone-containing polymer materials including polysiloxanes and other composite systems. Further, the fiber reinforcements that can be used with the various resins to make composite materials that can be non-destructively assessed according to aspects of the present disclosure include, in addition to CFRPs, boron fibers, glass fibers, aramid fibers, etc.

EXAMPLE 2

A study of the changes in surface chemistry that result from exposure of thermoplastic CFRP composites to non-thermal plasmas containing oxygen was conducted. Solvent-cleaned control samples were determined to have a surface with a highly poly-dispersed surface potential distribution (See the "Control" peaks shown in FIG. 3E) indicating a wide distribution of electrochemical potential values for electrons. After plasma treatment, the surface potential distribution became very narrow (See the "Plasma" peak shown in FIG. 3E), suggesting that plasma exposure produced a well-defined, and substantially uniform surface state on the plasma-treated surface.

EXAMPLE 3

Without being bound to any particular theory, the chemical functionality that underlies that narrow surface potential distribution was believed to result from the presence of charge-stabilized peroxy radicals. A correlation was derived between the width of the surface potential distribution and the fracture toughness of bonded CFRP assemblies as measured by double cantilever beam (DCB) experiments. For DCB experiments, two 152 mm × 381 mm CFRP composite material sample coupons were bonded using structural adhesive that was cured in an autoclave. A 350°F cure adhesive film processed at 350°F for a 2 hour dwell period. The pressure was held constant within a range of 30 to 100 psi, and the pressure was selected based on the composite process requirements. Prior to bonding the composite samples together, the to-be-opposed surfaces of each of the two sample coupons were prepared using the same procedure and conditions described in Example 1 (*i.e.* control, low intensity or medium intensity plasma). While both of the opposed surfaces were treated, aspects of the present disclosure further contemplate treating one or the other of the surfaces to be bonded, as well as treating both surfaces. The DCB experimentation consisted of determining the fracture toughness of the two bonded coupons by prying them apart under controlled conditions. Each data point is the average of three different measurements at the same nominal combination of

the two independent variables (plasma intensity and time after plasma treatment). The reported values are the average of those three measurements performed on different samples that were nominally the same, and the error bars are the standard deviations. Fracture toughness of the CFRP composite samples were registered ranging from about 4 to about 10.

5 Aspects of the present disclosure contemplate a wide variety of useful composite materials that can be non-destructively assessed for strength. Therefore aspects of the present disclosure further contemplate a wide range of adhesives that would be selected to adequately bond particular composite materials. That is, thermoset materials such as epoxies; composite adhesives such as 350°F film adhesive and 250°F film adhesive, elevated temperature cure
10 paste adhesives, and room temperature cure paste adhesives are contemplated. Once a composite material is selected for a component, the surface of the composite material is treated to achieve a particular activation state that is then assessed according to the present disclosure. It is understood that a composite surface having a particular activation state will interact with adhesive materials, and the adhesive will join the activated surfaces of the composite
15 components together to form a bonded composite assembly having a bond strength and fracture toughness that was determined non-destructively (by determining the composite component surface potential distribution) before the components are joined, and before adhesive is applied.

20 EXAMPLES 4 and 5

X-ray photoelectron spectroscopy (XPS) – (Example 4) was carried out in a Physical Electronics 5000 VersaProbe II Scanning ESCA using Al $K\alpha$ radiation. Contact angle measurements (Example 5) were used to assess the components of the surface energy using the sessile drop method and a Kyowa DME-211 contact angle meter. The probe liquids were
25 pure deionized water, diiodomethane, and ethylene glycol.

EXAMPLE 6

The electrochemical potential of electrons on the surface of a solid, which is also known as the work function, was measured by Kelvin probe force microscopy (KPFM). The experiment
30 was executed as follows. A sharp nanoscopic probe, with a tip radius of approximately 25 nm, was used to first acquire the topography of the composite surface. The probe was then lifted off the surface at a well-defined distance, which was 125 nm in our experiments. At that distance, dispersion forces are negligible. The probe was electrically conducting and connected to the conducting CFRP composite. In general, the electrochemical potential of electrons in the
35 sample was different from the probe, and therefore charge flowed between the sample and probe to equilibrate the Fermi levels. The result of this current flow is that a difference in static charge develops between the sample and probe, which causes an attractive force to develop.

That force can be measured from its effect on the vibrations of the probe. A DC bias is then applied between the probe and sample to cancel the force. The DC bias required to cancel the force was recorded as a function of position of the probe.

Surface potential measurements were performed by Kelvin probe force microscopy (KPFM) using the frequency modulated approach in a Bruker Dimensions Icon Atomic Force Microscope. Measurements were performed on 3 nominally identical CFRP composite material samples and the reported numerical values were the average of those measurements and the error bars are the standard deviation. The conductive, nonmagnetic probes were Bruker SCM-PIT-V2 probes that were not modified. The probes were coated at the manufacturer with a Pt-Ir alloy and a nominal tip radius of 25 nm. The resonance frequency was 75 kHz and the spring constant 2.80 N/m. All scans were performed at a rate of 0.595 lines per second over a 10×10 μm area, which was divided up into 512×512 pixels. For Peak Force KPFM, the topography was first acquired in peak force tapping mode, and then an interleave scan was performed wherein the probe was lifted 125 nm off the surface. While the probe was lifted off the surface, an AC voltage bias was applied, which causes the appearance of side bands on either side of the probe resonance frequency. A DC bias was applied to the probe to minimize the side bands. The DC bias at which the side bands are minimized is the surface potential, which was mapped as a function of position, and used to construct the surface potential distributions.

Magnetic force microscopy (MFM) experiments were carried out at a lift-off height of 125 nm also in interleave mode. The probes for MFM experiments were Bruker MESP-V2, which consisted of a silicon probe coated with a conductive CoCr film and a nominal tip radius of 35 to 50 nm. The probes were magnetized by placing them on a strong permanent magnet at a controlled distance. The direction of magnetization was controlled by placing the probes at the same distance from the permanent magnet such that the magnetic moment induced in the probe pointed either towards the cantilever (M+) or towards the tip (M-). The directions of the magnetic moments of the tip for the M+ and M- configurations are thus taken to be equal but opposite.

The electrochemical potential of a species is the sum of the chemical potential and the electrostatic potential. The electrochemical potential of electrons is therefore influenced by the chemical functional group on the surface and the local electrostatic environment (e.g., static charge and dipoles). In our experiments, the potential of the surface was reported with respect to the probe, which was comprised of silicon coated with a platinum alloy. If the probe is assumed to have the work function of platinum (5.32 eV), then to a first order approximation, the reported surface potential values are with respect to -5.32 V vs. the vacuum level. In other words, if desired, one could make the following estimate of the potential of electrons on the surface: $E_{surf} = E_p - E_{SP}$, where E_{surf} is the electrochemical potential of electrons on the

surface with respect to the vacuum level, E_p is the probe potential of -5.32 V vs. vacuum level, and E_{SP} is the measured surface potential.

Exposure of the CFRP thermoplastic composite samples to the low temperature oxygen plasma produced a surface with a well-defined electrochemical potential of electrons.

5 Topographical maps of a control sample (only solvent cleaning) and sample treated with low temperature oxygen plasma at medium intensity are presented in FIGs. 3A and 3C respectively. The corresponding surface potential maps are presented in FIGs. 3B and 3D. Plasma treatment had very little effect on topography of the CFRP composite samples, which can be seen by comparing FIG. 3A to FIG. 3C. The measured surface area increased by
10 approximately 6%; from $103 \pm 0.6 \mu\text{m}^2$ for the control samples to about $109 \pm 4.9 \mu\text{m}^2$ for the CFRP composite samples "treated" with medium intensity plasma treatment. In other words, negligible changes in surface roughness and surface area were observed due to plasma treatment. However, there were significant changes in the surface potential maps. The control sample exhibited rather large features in the surface potential maps; some being as large as 8
15 V. Interestingly, after plasma treatment, the surface potential map was featureless on the same scale (See FIG. 3D). The effect of the plasma on the surface potential is shown in the histogram FIG. 3E. The surface potential distribution in the control sample was very polydispersed, with peak width on the order of 5 V, indicating a wide variety of different surface states. After plasma treatment, however, the surface potential distribution became very narrow,
20 with a full peak width at half maximum of 0.09 mV (See FIG. 3E). Full width at half maximum (FWHM) is an expression of the extent of a function given by the difference between the two extreme values of the independent variable at which the dependent variable is equal to half of its maximum value. Thus, the surface produced by exposure to low temperature oxygen plasma was uniform and had a well-defined electrochemical potential of electrons.

25 According to the present disclosure, a peak width is not limited by the peak position. The surface potential distribution signal width or peak width is a measurement of the difference between where the signal begins and where it ends, and not a measurement of where the peak resides on the peak resides, as shown in FIG. 3E, on the x-axis of the graph. According to an aspect of the present disclosure the surface potential distribution of a treated composite
30 component surface comprises a peak width ranging from about 0.01 mV to about 4 V, more preferably 0.01 mV to 1V, and even more preferably 0.01 mV to 0.1V.

Additional signal widths contemplated by the present disclosure include for example 0.01 mV to 4.0 V; 0.01 mV to 3.0 V; 0.01 mV to 2 V or 0.01 mV to 1 V (most preferred).. Similarly, additional signal widths according to the present disclosure include, for example, 0.05 mV to 4,
35 3, 2 or 1 V (0.01 mV to 1 V being most preferred). Similarly, additional signal widths include, for example, 0.1 V to 4, 3, 2, or 1 V. (0.01 mV to 1 V being most preferred). Signal width (also termed "peak width") is determined by/same as, the full width at half maximum (FWHM).

According to aspects of the present disclosure, the peak position is the surface potential value at which the surface potential distribution reaches its maximum value.

The fracture toughness of bonded composite parts prepared by the two different methods was different. Plotted in FIG. 3F is the normalized fracture toughness for a composite material control sample (solvent cleaned) and plasma treatment at medium intensity. All other parameters were the same. The fracture toughness values represented in FIG. 3E are the averages of three measurements on different composite control samples, and the error bars are the standard deviations of those measurements. The assemblies made from the composite samples that were bonded using plasma-prepared (plasma "treated") surfaces had, on average, 15 times higher fracture toughness than solvent-cleaned controls. Moreover, failure occurred at the adhesive-composite interface for solvent-cleaned controls, but in the adhesive itself for plasma-treated samples; clearly demonstrating that the plasma-activated surface produced a stronger bond with the adhesive. Without being bound to a particular theory, two intermediate conclusions can be made: 1) plasma activates the composite to produce a uniform surface in a state with a well-defined electrochemical potential of electrons, and 2) the plasma-activated surface state results in a bond with high fracture toughness, presumably a result of a change in the way the surface reacts with the adhesive during bonding.

While being bound by no particular theory, it is believed that the surface state produced by plasma activation consists of ion-radical complexes. More specifically, the ions on the surface are expected to be negative, and the radicals are expected to be peroxy species. Floating surfaces in contact with low temperature plasma acquire a negative charge to balance the fluxes of electrons and gaseous positive ions to maintain overall charge neutrality. In low temperature plasma, the electrons have a much higher temperature (c.a. 20,000 °K) than the neutral species and gaseous ions, which are typically assumed to be near ambient temperature. Since the electrons have lower mass and higher temperature compared to the gaseous ions, they move in the plasma bulk with a much higher velocity. However, the plasma, overall, is charge neutral, requiring the losses of electrons and gaseous ions to floating surfaces to be equal ($J_i = J_e$). Thus, floating surfaces in contact with the plasma adopt a negative charge to decelerate electrons and accelerate ions to balance fluxes. If the surface is poorly connected to ground, then it is expected that ions present on the surface of the composite after exposure to the plasma would be negative. Peroxy radicals $\text{ROO}^{\bullet}$ have relatively high stability due to resonance stabilization and have been experimentally observed on polymer surfaces exposed to low temperature oxygen plasmas. It has now been determined that the surface state produced by oxygen plasma activation consists of negative ion – peroxy radical complexes.

X-ray photoelectron spectroscopy (XPS) revealed a significant increase in the amount of oxygen present on the surface after plasma treatment and a redistribution of the carbon speciation. XPS spectra of the O1s and C1s peaks are presented in FIG. 4A and 4B

respectively. Exposure of the composite to the low temperature plasma increased the amount of oxygen on the surface by a factor of 2.21 (FIG. 4A). However, the amount of carbon on the surface did not change significantly (FIG. 4B). The speciation of carbon did change somewhat, with fraction of carbon participating in C-O and C=O bonds increasing after plasma exposure.

- 5 The observation of an increase in oxygen on the surface of the composite after exposure to the low temperature plasma is consistent with the formation of peroxy radicals.

EXAMPLE 7

- 10 Contact angle experiments were consistent with the idea that the surface becomes negatively charged during plasma exposure, and that negative charge persists. Contact angles were measured using water, diiodomethane (DIM) and ethylene glycol (EG) and are shown in Table 1.

Table 1

Sample	Water	DIM	EG
Control	64.8 +/- 2.2°	55.2 +/- 0.56°	50.4 +/- 1.6°
Plasma	2.5 +/- 2.5°	20.1 +/- 0.42°	8.0 +/- 1.0°

- 15 The acid/base model for determining surface energy from contact angle measurements allows the net charge on the surface to be assessed. The acid/base model considers three components of the surface energy: dispersive (γ_d), electron acceptor (γ^+) and electron donor (γ^-). An increase in negative charge on the surface is expected to manifest as an increase in the electron donor component γ^- .

- 20 Contact angle measurements were performed using the sessile drop method with water, diiodomethane and ethylene glycol. The measured contact angles and resulting components of the surface energy calculated using acid/base theory are presented in FIG. 5. After plasma treatment, the electron donor component of the surface energy increased considerably. This finding was determined to be consistent with negative charging. Evidence consistent with
25 negative charging can also be seen in FIG. 3E where, after plasma treatment, the average value of the surface potential decreases compared to the control. The direction of the shift in surface potential builds is consistent with the data shown regarding the interpretation of the surface energy data in FIG. 5.

- 30 A surface functionalized with unpaired electrons interacts with magnetic fields. That interaction can be detected by performing scanning probe experiments with a magnetized tip. A KPFM probes was magnetized such that the magnetic field pointed from the sample to the probe (M+), or from the probe to the sample (M-). If the probe can overcome the coercivity of

the radicals on the sample surface, then the force will be uniformly attractive, by analogy to a hard magnet (e.g., SmCo) being attracted to a soft magnet (e.g. Fe). On the other hand, if the probe cannot overcome the coercivity of the sample surface, then in one direction (e.g. M+) the force will be attractive, while in the other direction (e.g. M-) the force will be repulsive. Two different experiments were conducted.

EXAMPLE 8

In the first experiment, a magnetized force microscopy (MFM) probe was brought into contact with the sample surface, and then the force required to pull it off was measured. In such an experiment, the force required to lift the probe off the surface is the sum of dispersion, electrostatic, and magnetic components. The magnetic component can be isolated by comparing probes that are magnetized equal but opposite, but are otherwise identical (i.e. M+ vs. M-).

EXAMPLE 9

The second experiment was conducted using magnetic force microscopy (MFM). For MFM experiments, the magnetized MFM probe was held at a constant distance above the surface of the sample, specifically 125 nm, and allowed to oscillate. At such long distances, dispersion forces are negligible. Forces acting on the tip produce a phase shift between the probe oscillation and the driving signal. Assuming the phase shift is relatively small, it is proportional to the spatial gradient of the force in the direction of the macroscopic surface normal ($\Delta\phi \propto dF/dz$). In general, the force gradient has components due to the electrostatic force and the magnetic force. If both the probe and sample are magnetically hard, then the magnetic component of the phase shift can be isolated from the electrostatic component by subtracting, at the same point in space, the phase shift for an M+ probe from the phase shift for an M- probe that are otherwise identical. In other words, for a sample that the probe cannot magnetically coerce, $\Delta\phi(x, y, M+) - \Delta\phi(x, y, M-) = 2\Delta\phi_M(x, y)$; and $\Delta\phi_M \propto dF_M/dz$, where $\Delta\phi_M$ is the phase shift due only to the magnetic component of the force (F_M). Experiments were performed with silicon probes that were coated with CoCr and prepared to have equal but opposite magnetization (i.e. M+ and M-).

The thermoplastic composite sample surface after plasma treatment was magnetized and was not coerced by the probe. In other words, both the probe and plasma-treated samples were magnetically hard. The experiments were conducted as follows. The probe was brought into contact with the surface and then lifted off. While retracting the probe from the sample surface, the force acting on the tip was recorded as a function of vertical position of the piezo stage to which the probe was secured. The results are presented in FIGs. 6A-6D for both M+ and M- probes and both plasma-treated and control samples. The force-retract curves

presented as FIGs. 6A-6D measured equal but oppositely magnetized probes (M+/M-) on plasma-treated (FIG. 6A, 6B) samples and solvent-cleaned control (FIG. 6C, 6D) samples. The vertical position in FIGs. 6A-6D is defined such that increasing z values correspond to moving the piezo stage closer to the sample. At large values of z , the probe was pressed onto the sample surface. As z decreased, the force passed through 0 when the probe was simply resting on the surface of the sample, and then passed through a well and a minimum value that was caused by an attractive force between the probe and sample. Eventually, the probe was lifted to a sufficiently small z value that the attraction decreased and the force oscillated about 0 pN for small z values. The minimum value of the curve is a measure of the attractive force. In other words, a deeper well on the force-retract curve corresponds to a stronger attractive force. A total of 500 curves were measured for each of the 4 cases at different locations on the sample surface. The plots in FIGs. 6A-6D are two-dimensional histograms of those 500 measurements for each case. The attractive force for the plasma-treated sample measured using an M+ probe was approximately double the attractive force using an M- probe on the same sample. For the control samples, the depth of the well was approximately the same for both M+ and M- probes, and both were shallower than the plasma-treated sample with M+ probe. Therefore, it may be concluded that plasma treatment causes the surface to become magnetized, and the magnetization of the surface cannot be coerced by the probe. The result is consistent with the presence of unpaired electrons on the plasma-treated sample surface, which in turn, is consistent with the formation of peroxy radicals during plasma treatment.

The uniformity of spins created by plasma treatment was characterized by MFM. Since both the probe and sample were magnetically hard (FIGs. 6A and 6B), the magnetic component of the force gradient was isolated by subtracting the phase shift map for an M- probe from the phase shift map for an M+ probe. The resulting phase shift difference map does not contain electrostatic contributions and is therefore proportional to the magnetic force gradient, which in turn, is proportional to the spin density on the surface. Topography and phase shift maps for an M+ probe (FIGs. 7A and 7C), and an M- probe (FIGs. 6B and 6D) were recorded at the same location on a plasma-treated sample. The phase shift maps were acquired using an interleave liftoff scan at 125 nm. Issues with imaging topography in peak force tapping mode on plasma-treated samples using magnetized probes were observed. Such issues were not observed using nonmagnetic probes (e.g., for KPFM). Though bound to no particular theory, those occurrences that were only encountered with magnetized probes, are believed to reinforce the present findings that there were spins present on the surface of plasma-treated samples. The phase shift difference map, $2\Delta\phi_M(x, y) = \Delta\phi(x, y, M+) - \Delta\phi(x, y, M-)$ is plotted in FIG. 7E and the histogram of values is presented in FIG. 7F. The phase shift difference map in FIG. 7E is fairly uniform at positive values, revealing a relatively uniform spin density. Only a small fraction of the image lies at values less than or equal to zero (FIG. 7F). The full width at half-maximum of

the histogram in FIG. 7F is approximately the same as the mean value, which indicates that the spin density on the surface varies by approximately $\pm 50\%$ of the mean value from location to location. The methodology developed and disclosed herein can be used to characterize the ability of low temperature oxygen plasma to impart radical chemical functionality to other polymer surfaces.

As time passes, the plasma-activated surface relaxes. Though not bound to any particular theory, we believe that the negative charge stabilizes the peroxy radicals, but not indefinitely.

EXAMPLE 10A

An experiment was conducted wherein a set of CFRP composite material samples were prepared either by solvent cleaning, low intensity plasma, or medium intensity plasma. These samples were then characterized as a function of time. Time in this case refers to the number of days that elapsed after surface preparation before bonding and characterization. On day 0, 1, 3 and 7, two experiments were performed. First, the surface potential distribution was measured. Second, composite material samples were bonded using a structural adhesive and then the fracture toughness was characterized by double cantilever beam experiments. Thus, the activation state of the composite and the bond strength were measured as a function of time after treatment. The activation state was assessed from the width of the surface potential distribution. The idea is that as the ion-radical complex decays, the surface potential distribution widens. Thus, the width of the surface potential distribution is inversely related to the density of active species on the surface. The width of the surface potential distribution can be assessed by calculating the area of the distribution after it has been normalized to have a maximum value of 1. Since the distribution width is inversely related to the areal density of active species, we have derived and otherwise defined the following surface potential signal that is expected to increase with increasing areal density of ion-peroxy complexes on the surface according to formula (1):

$$SP_Signal = \left[\int_{-\infty}^{\infty} \hat{\mu}(\phi) d\phi \right]^{-1}, \quad (1)$$

wherein: $\hat{\mu}$ is the normalized surface potential distribution, which is a function of the surface potential ϕ , and has a maximum value of 1. Using this definition, we then proceeded to measure the surface potential distribution and calculated. SP_Signal as a function of time after treatment to correlate to fracture toughness.

The surface potential signal and fracture toughness were found to increase with increasing plasma intensity from control, to low intensity, to medium intensity. Furthermore, the surface potential signal and fracture toughness were found to generally decrease with

increasing time after treatment. Normalized fracture toughness and the surface potential signal shown in FIGs. 8A and 8B are plotted as a function of time after treatment. Each point represents the average of three samples that were nominally the same and the error bars are the standard deviation. With the exception of the point at $t=0$ for the medium intensity case, the surface potential signal were found to correspond to the normalized fracture toughness very well as a function of both treatment type and time after treatment. The correlation between the normalized fracture toughness and the surface potential signal is presented in FIG. 8C. FIG. 8C was generated by plotting the normalized fracture toughness (FIG. 8A) as a function of the surface potential signal (FIG. 8B) for the same combination of independent variables. Generally, the fracture toughness was found to increase with increases in the surface potential signal. .

EXAMPLE 10B

A set of epoxy composite material samples are prepared either by solvent cleaning, low intensity plasma, or medium intensity plasma. These samples are then characterized as a function of time. Time in this case refers to the number of days that elapsed after surface preparation before bonding and characterization. On day 0, 1, 3 and 7, two experiments were performed. First, the surface potential distribution is measured. Second, composite material samples are bonded using a structural adhesive and then the fracture toughness was characterized by double cantilever beam experiments. Thus, the activation state of the composite and the bond strength are measured as a function of time after treatment. The activation state is assessed from the width of the surface potential distribution. The idea is that as the ion-radical complex decays, the surface potential distribution widens. Thus, the width of the surface potential distribution is inversely related to the density of active species on the surface. The width of the surface potential distribution can be assessed by calculating the area of the distribution after it has been normalized to have a maximum value of 1. Since the distribution width is inversely related to the areal density of active species, the following surface potential signal that is expected to increase with increasing areal density of ion-peroxy complexes on the surface is derived or otherwise defined according to formula (1):

$$SP_Signal = \left[\int_{-\infty}^{\infty} \hat{\mu}(\phi) d\phi \right]^{-1}, \quad (1)$$

wherein: $\hat{\mu}$ is the normalized surface potential distribution, which is a function of the surface potential ϕ , and has a maximum value of 1. Using this definition, the surface potential distribution is measured and calculated. SP_Signal is calculated as a function of time after treatment to correlate to fracture toughness.

The surface potential signal and fracture toughness increase with increasing plasma intensity from control, to low intensity, to medium intensity. Furthermore, the surface potential signal and fracture toughness generally decrease with increasing time after treatment.

5

EXAMPLE 10C

A set of polytertrafluoroethylene (PTFE) composite material samples are prepared either by solvent cleaning, low intensity plasma, or medium intensity plasma. These samples are then characterized as a function of time. Time in this case refers to the number of days that elapsed after surface preparation before bonding and characterization. On day 0, 1, 3 and 7, two
 10 experiments were performed. First, the surface potential distribution is measured. Second, composite material samples are bonded using a structural adhesive and then the fracture toughness was characterized by double cantilever beam experiments. Thus, the activation state of the composite and the bond strength are measured as a function of time after treatment. The activation state is assessed from the width of the surface potential distribution. The idea is
 15 that as the ion-radical complex decays, the surface potential distribution widens. Thus, the width of the surface potential distribution is inversely related to the density of active species on the surface. The width of the surface potential distribution can be assessed by calculating the area of the distribution after it has been normalized to have a maximum value of 1. Since the distribution width is inversely related to the areal density of active species, the following surface
 20 potential signal that is expected to increase with increasing areal density of ion-peroxy complexes on the surface is derived or otherwise defined according to formula (1):

$$SP_Signal = \left[\int_{-\infty}^{\infty} \hat{\mu}(\phi) d\phi \right]^{-1}, \quad (1)$$

wherein: $\hat{\mu}$ is the normalized surface potential distribution, which is a function of the surface potential ϕ , and has a maximum value of 1. Using this definition, the surface potential
 25 distribution is measured and calculated. SP_Signal is calculated as a function of time after treatment to correlate to fracture toughness.

The surface potential signal and fracture toughness increase with increasing plasma intensity from control, to low intensity, to medium intensity. Furthermore, the surface potential signal and fracture toughness generally decrease with increasing time after treatment.

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EXAMPLE 10D

A set of polydimethylsiloxane composite material samples are prepared either by solvent cleaning, low intensity plasma, or medium intensity plasma. These samples are then characterized as a function of time. Time in this case refers to the number of days that elapsed

after surface preparation before bonding and characterization. On day 0, 1, 3 and 7, two experiments were performed. First, the surface potential distribution is measured. Second, composite material samples are bonded using a structural adhesive and then the fracture toughness was characterized by double cantilever beam experiments. Thus, the activation state of the composite and the bond strength are measured as a function of time after treatment. The activation state is assessed from the width of the surface potential distribution. The idea is that as the ion-radical complex decays, the surface potential distribution widens. Thus, the width of the surface potential distribution is inversely related to the density of active species on the surface. The width of the surface potential distribution can be assessed by calculating the area of the distribution after it has been normalized to have a maximum value of 1. Since the distribution width is inversely related to the areal density of active species, the following surface potential signal that is expected to increase with increasing areal density of ion-peroxy complexes on the surface is derived or otherwise defined according to formula (1):

$$SP_Signal = \left[\int_{-\infty}^{\infty} \hat{\mu}(\phi) d\phi \right]^{-1}, \quad (1)$$

wherein: $\hat{\mu}$ is the normalized surface potential distribution, which is a function of the surface potential ϕ , and has a maximum value of 1. Using this definition, the surface potential distribution is measured and calculated. SP_Signal is calculated as a function of time after treatment to correlate to fracture toughness.

The surface potential signal and fracture toughness increase with increasing plasma intensity from control, to low intensity, to medium intensity. Furthermore, the surface potential signal and fracture toughness generally decrease with increasing time after treatment.

According to aspects of the present disclosure, the surface potential signal has been shown to closely predict the fracture toughness that would result from bonding a given part that has been prepared in a particular way. Further, the surface potential signal derived according to aspects present disclosure has now been shown to be a proxy for the areal density of ion-radical complexes as well as a reliable predictor for a desired and predetermined composite bonding strength.

In another aspect, the present disclosure is directed to a method of non-destructively inspecting a treated composite component surface, with the method including determining surface potential distribution of the treated composite component surface, wherein the surface potential distribution of the treated composite component surface is indicative of a fracture toughness ranging from about 1 lb./in.² to about 10 lbs./ in.².

FIG. 9 is a flowchart outlining a method according to aspects of the present disclosure. As shown in FIG. 9, a method 90 comprises determining 92 surface potential of a treated

composite component surface, and measuring 94 the treated composite component surface with an atomic force microscope.

FIG. 10 is a flowchart outlining a method according to aspects of the present disclosure. As shown in FIG. 11, a method 100 comprises determining 102 surface potential of a treated
5 composite component surface, and measuring 104 the treated composite component surface with an atomic force microscope.

FIG. 11 is a non-limiting illustration showing an aircraft 120 as one type of object that can comprise a composite component having a composite component surface that can be non-destructively tested according to aspects of the present disclosure. As shown in FIG. 11,
10 aircraft 120 includes a fuselage 122 with the aircraft 120 and fuselage 122 further including a composite component assembly 124. While an aircraft has been shown as including composite component assemblies having composite components made from composite materials with composite material surfaces can be non-destructively inspected and tested according to methods set forth and described according to present aspects, other objects, including vehicles
15 of all forms, as well as any non-vehicular objects that include composite components and/or composite assemblies.

Further, the disclosure comprises aspects according to the following clauses:

Clause 1. A method (90) of non-destructively inspecting a treated composite component surface, said method comprising determining (92) surface potential distribution of
20 the treated composite component surface.

Clause 2. The method of Clause 1, wherein determining (92) surface potential distribution of the treated composite component surface comprises measuring (94) the treated composite component surface with an atomic force microscope, said atomic force microscope comprising an atomic force microscope probe (12).

25 Clause 3. The method of any one of Clauses 1 through 2, wherein determining (92) surface potential distribution of the treated composite component surface comprises measuring the treated composite component surface with a Kelvin force probe.

Clause 4. The method of any one of Clauses 1 through 3, wherein the treated composite component surface comprises at least one of: a physically abraded surface; a chemically abraded surface; a laser treated surface; a chemically etched surface; or a coated
30 surface.

Clause 5. The method of any one of Clauses 1 through 4, wherein the treated composite component surface comprises a plasma-treated surface.

Clause 6. The method of any one of Clauses 1 through 5, wherein the
35 treated composite component surface is plasma treated by a plasma treatment, said plasma treatment comprising at least one of: a low intensity plasma treatment; or a medium intensity plasma treatment.

Clause 7. The method of Clause 6, wherein the plasma treatment comprises at least one of a plurality of plasma processing parameters, said plasma processing parameters comprising at least one of: a translation speed ranging from about 5 in./min. to about 300 in./min.; a working height ranging from about 0.1 in. to about 1.0 in.; or an overlap ranging from about 0% to about 50%.

Clause 8. The method of any one of Clauses 1 through 7, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of at least one of: a treated thermoplastic composite component; a treated thermoset composite component, a treated fluoropolymer composite component; or a treated silicone composite component.

Clause 9. The method of any one of Clauses 1 through 8, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated composite component comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

Clause 10. The method of any one of Clauses 1 through 9, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component.

Clause 11. The method of any one of Clauses 1 through 10, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising PEKK.

Clause 12. The method of any one of Clauses 1 through 11, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising carbon fiber.

Clause 13. The method of any one of Clauses 1 through 12, wherein the surface potential distribution signal width of the treated composite component surface ranges from about 0.01 mV to about 4 V.

Clause 14. The method of any one of Clauses 1 through 13, wherein the surface potential distribution of the treated composite component surface has a maximum value ranging from about 0.01 mV to about 4 V.

Clause 15. A composite component (20) comprising a composite component surface (22) non-destructively inspected according to the method (90) of any one of Clauses 1 through 14, wherein the composite component is made from a material comprising a resin-containing component, said resin-containing component comprising at least one of: a thermoplastic material; a thermoset material, a fluoropolymer material; or a silicone material.

Clause 16. The composite component of Clause 15, wherein the composite component is made from a material comprising a fiber-containing material, said fiber-containing material comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

5 Clause 17. The composite component of any one of Clauses 15 through 16, wherein the composite material comprises a thermoplastic material.

Clause 18. The composite component of any one of Clauses 15 through 17, wherein the composite material comprises PEKK.

10 Clause 19. The composite component of any one of Clauses 15 through 18, wherein the composite material comprises a carbon fiber reinforced polymer.

Clause 20. A composite component assembly (124) comprising the composite component of any one of Clauses 15 through 19.

Clause 21. An aircraft (120) comprising the composite component assembly of Clause 20.

15 Clause 22. A method (100) of non-destructively inspecting a treated composite component surface, said method comprising determining (102) surface potential distribution of the treated composite component surface, wherein the surface potential distribution of the treated composite component surface is indicative of a fracture toughness ranging from about 1 lb./in.² to about 10 lbs./ in.².

20 Clause 23. The method of Clause 22, wherein determining (102) surface potential distribution of the treated composite component surface comprises measuring (104) the treated composite component surface with an atomic force microscope, said atomic force microscope comprising an atomic force microscope probe.

Clause 24. The method of any one of Clauses 22 through 23, wherein
25 determining (102) surface potential distribution of the treated composite component surface comprises measuring the treated composite component surface with a Kelvin force probe.

Clause 25. The method of any one of Clauses 22 through 24, wherein the treated composite component surface comprises at least one of: a physically abraded surface; a chemically abraded surface; a laser treated surface; a chemically etched surface; or a coated
30 surface.

Clause 26. The method of any one of Clauses 22 through 25, wherein the treated composite component surface comprises a plasma treated surface.

Clause 27. The method of any one of Clauses 22 through 26, wherein the treated composite component surface is plasma treated by a plasma treatment, said plasma
35 treatment comprising at least one of: a low intensity plasma treatment; or a medium intensity plasma treatment.

Clause 28. The method of Claims 27, wherein the plasma treatment comprises at least one of a plurality of plasma processing parameters, said plasma processing parameters comprising at least one of: a translation speed ranging from about 5 in./min. to about 300 in./min.; a working height ranging from about 0.1 in. to about 1.0 in.; or an overlap ranging from about 0% to about 50%.

Clause 29. The method of any one of Claims 22 through 28, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of at least one of: a treated thermoplastic composite component; a treated thermoset composite component, a treated fluoropolymer composite component, or a treated silicone composite component.

Clause 30. The method of any one of Claims 22 through 29, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated composite component comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

Clause 31. The method of any one of Claims 22 through 30, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component.

Clause 32. The method of any one of Claims 21 through 31, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising PEKK.

Clause 33. The method of any one of Claims 22 through 32, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising carbon fiber.

Clause 34. The method of any one of Claims 22 through 33, wherein the surface potential distribution signal width of the treated composite component surface ranges from about 0.01 mV to about 4 V.

Clause 35. The method of any one of Claims 22 through 34, wherein the surface potential distribution of the treated composite component surface has a maximum value ranging from about 0.01 mV to about 4 V.

Clause 36. The method of any one of Claims 22 through 35, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated carbon fiber reinforced composite component.

Clause 37. A composite component (20) comprising a composite component surface (22) non-destructively inspected according to the method (100) of any one of Clauses 22 through 36, wherein the composite component is made from a material comprising a resin-containing component, said resin-containing component comprising at least one of: a

5 thermoplastic material; a thermoset material, a fluoropolymer material; or a silicone material.

Clause 38. The composite component of Clause 37, wherein the composite component is made from a material comprising a fiber-containing material, said fiber-containing material comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

10 Clause 39. The composite component of any one of Clauses 37 through 38, wherein the composite material comprises a thermoplastic material.

Clause 40. The composite component of any one of Clauses 37 through 39, wherein the composite material comprises PEKK.

15 Clause 41. The composite component of any one of Clauses 37 through 40, wherein the composite material comprises a carbon fiber reinforced polymer.

Clause 42. A composite component assembly (124) comprising the composite component of any one of Clauses 37 through 41.

Clause 43. An aircraft (120) comprising the composite component assembly of Clause 42.

20 Aspects of the present disclosure can, of course, be carried out in other ways than those specifically set forth herein without departing from essential characteristics of aspects disclosed herein. The presently disclosed aspects are to be considered in all respects as illustrative and not restrictive, and all changes coming within the meaning and equivalency range of the appended claims are intended to be embraced therein.

25

CLAIMS

WHAT IS CLAIMED IS:

1. A method (90) of non-destructively inspecting a treated composite component surface (22), said method comprising:
 - 5 determining (92) surface potential distribution of the treated composite component surface.
2. The method of Claim 1, wherein determining (92) surface potential distribution of the treated composite component surface comprises measuring (94) the treated composite
10 component surface with an atomic force microscope, said atomic force microscope comprising an atomic force microscope probe (12).
3. The method of any one of Claims 1 through 2, wherein determining (92) surface potential distribution of the treated composite component surface comprises measuring the
15 treated composite component surface with a Kelvin force probe.
4. The method of any one of Claims 1 through 3, wherein the treated composite component surface comprises at least one of: a physically abraded surface; a chemically abraded surface; a laser treated surface; a chemically etched surface; or a coated surface.
20
5. The method of any one of Claims 1 through 4, wherein the treated composite component surface comprises a plasma-treated surface.
6. The method of any one of Claims 1 through 5, wherein the treated composite component surface is plasma treated by a plasma treatment, said plasma treatment comprising at least one
25 of: a low intensity plasma treatment; or a medium intensity plasma treatment.
7. The method of Claim 6, wherein the plasma treatment comprises at least one of a plurality of plasma processing parameters, said plasma processing parameters comprising at
30 least one of: a translation speed ranging from about 5 in./min. to about 300 in./min.; a working height ranging from about 0.1 in. to about 1.0 in.; or an overlap ranging from about 0% to about 50%.
8. The method of any one of Claims 1 through 7, wherein determining (92) the surface
35 potential distribution of the treated composite component surface comprises determining the surface potential distribution of at least one of: a treated thermoplastic composite component; a

treated thermoset composite component, a treated fluoropolymer composite component; or a treated silicone composite component.

9. The method of any one of Claims 1 through 8, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated composite component comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

10. The method of any one of Claims 1 through 9, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component.

11. The method of any one of Claims 1 through 10, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising PEKK.

12. The method of any one of Claims 1 through 11, wherein determining (92) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising carbon fiber.

13. The method of any one of Claims 1 through 12, wherein the surface potential distribution signal width of the treated composite component surface ranges from about 0.01 mV to about 4 V.

14. The method of any one of Claims 1 through 13, wherein the surface potential distribution of the treated composite component surface has a maximum value ranging from about 0.01 mV to about 4 V.

15. A composite component (20) (124) comprising a composite component surface (22) non-destructively inspected according to the method (90) of any one of Claims 1 through 14, wherein the composite component is made from a composite material, said composite material comprising a resin-containing component, said resin-containing component comprising at least one of: a thermoplastic material; a thermoset material, a fluoropolymer material; or a silicone material.

16. The composite component of Claim 15, wherein the composite component is made from a material comprising a fiber-containing material, said fiber-containing material comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

5 17. The composite component of any one of Claims 15 through 16, wherein the composite material comprises a thermoplastic material.

18. The composite component of any one of Claims 15 through 17, wherein the composite material comprises PEKK.

10

19. The composite component of any one of Claims 15 through 18, wherein the composite material comprises a carbon fiber reinforced polymer.

15 20. A composite component assembly (122) comprising the composite component of any one of Claims 15 through 19.

21. An aircraft (120) comprising the composite component assembly of Claim 20.

20 22. A method (100) of non-destructively inspecting a treated composite component surface, said method comprising determining (102) surface potential distribution of the treated composite component surface, wherein the surface potential distribution of the treated composite component surface is indicative of a fracture toughness ranging from about 1 lb./in.² to about 10 lbs./ in.².

25 23. The method of Claim 22, wherein determining (102) surface potential distribution of the treated composite component surface comprises measuring (104) the treated composite component surface with an atomic force microscope, said atomic force microscope comprising an atomic force microscope probe.

30 24. The method of any one of Claims 22 through 23, wherein determining (102) surface potential distribution of the treated composite component surface comprises measuring the treated composite component surface with a Kelvin force probe.

35 25. The method of any one of Claims 22 through 24, wherein the treated composite component surface comprises at least one of: a physically abraded surface; a chemically abraded surface; a laser treated surface; a chemically etched surface; or a coated surface.

26. The method of any one of Claims 22 through 25, wherein the treated composite component surface comprises a plasma treated surface.

27. The method of any one of Claims 22 through 26, wherein the treated composite component surface is plasma treated by a plasma treatment, said plasma treatment comprising at least one of: a low intensity plasma treatment; or a medium intensity plasma treatment.

28. The method of Claim 27, wherein the plasma treatment comprises at least one of a plurality of plasma processing parameters, said plasma processing parameters comprising at least one of: a translation speed ranging from about 5 in./min. to about 300 in./min.; a working height ranging from about 0.1 in. to about 1.0 in.; or an overlap ranging from about 0% to about 50%.

29. The method of any one Claims 22 through 28, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of at least one of: a treated thermoplastic composite component; a treated thermoset composite component, a treated fluoropolymer composite component, or a treated silicone composite component.

30. The method of any one of Claims 22 through 29, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated composite component comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

31. The method of any one of Claims 22 through 30, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component.

32. The method of any one of Claims 21 through 31, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising PEKK.

33. The method of any one of Claims 22 through 32, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated thermoplastic composite component comprising carbon fiber.

34. The method of any one of Claims 22 through 33, wherein the surface potential distribution signal width of the treated composite component surface ranges from about 0.01 mV to about 4 V.

5 35. The method of any one of Claims 22 through 34, wherein the surface potential distribution of the treated composite component surface has a maximum value ranging from about 0.01 mV to about 4 V.

10 36. The method of any one of Claims 22 through 35, wherein determining (102) the surface potential distribution of the treated composite component surface comprises determining the surface potential distribution of a treated carbon fiber reinforced composite component.

15 37. A composite component (20) (124) comprising a composite component surface (22) non-destructively inspected according to the method (100) of any one of Claims 22 through 36, wherein the composite component is made from a composite material, said composite material comprising a resin-containing component, said resin-containing component comprising at least one of: a thermoplastic material; a thermoset material, a fluoropolymer material; or a silicone material.

20 38. The composite component of Claim 37, wherein the composite component is made from a material comprising a fiber-containing material, said fiber-containing material comprising at least one of: a carbon fiber; a boron fiber; a glass fiber; or an aramid fiber.

25 39. The composite component of any one of Claims 37 through 38, wherein the composite material comprises a thermoplastic material.

40. The composite component of any one of Claims 37 through 39, wherein the composite material comprises PEKK.

30 41. The composite component of any one of Claims 37 through 40, wherein the composite material comprises a carbon fiber reinforced polymer.

42. A composite component assembly (122) comprising the composite component of any one of Claims 37 through 41.

35

43. An aircraft (120) comprising the composite component assembly of Claim 42.

FIG. 1A

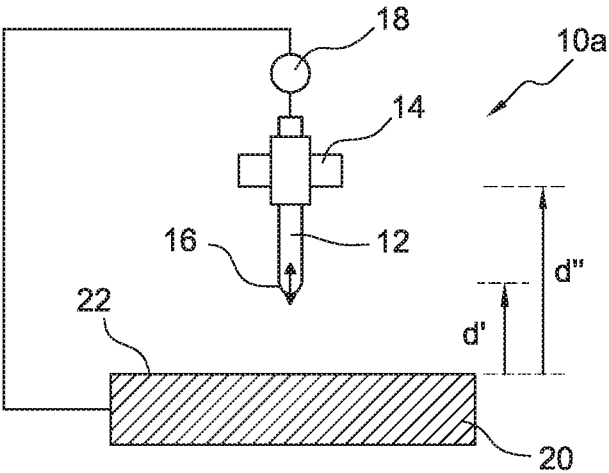


FIG. 1B

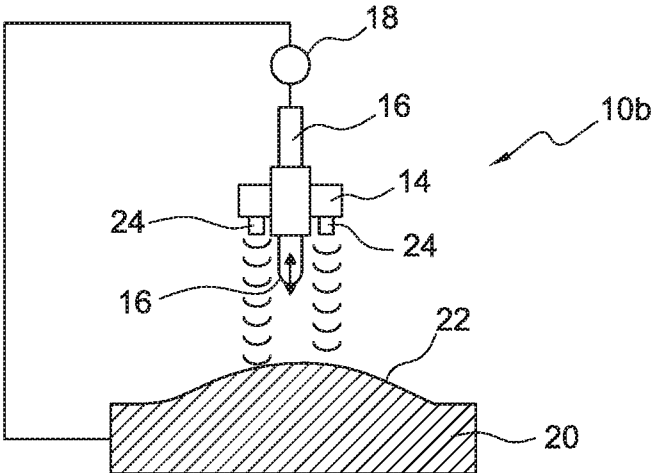
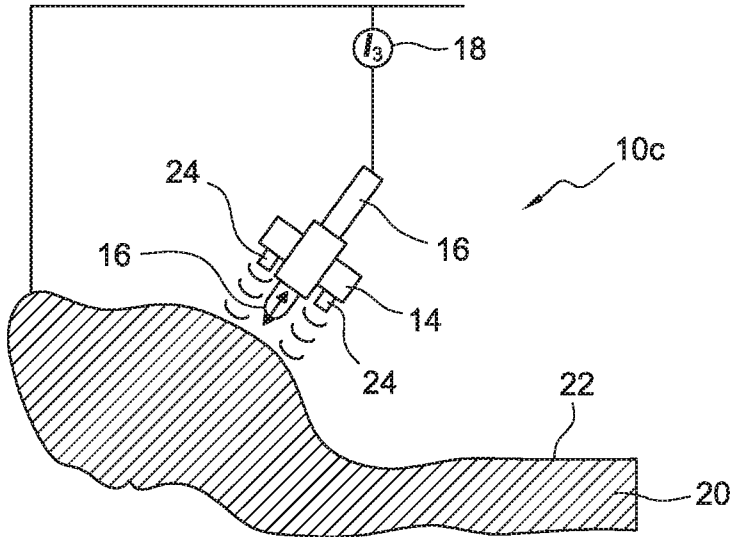


FIG. 1C



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FIG. 1D

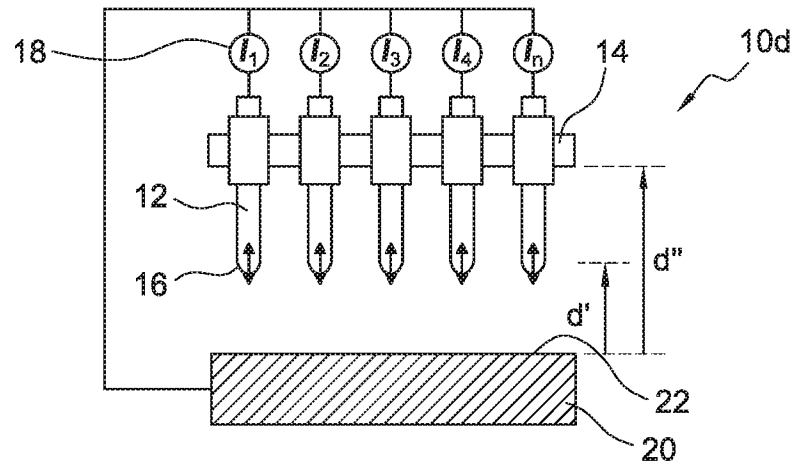


FIG. 1E

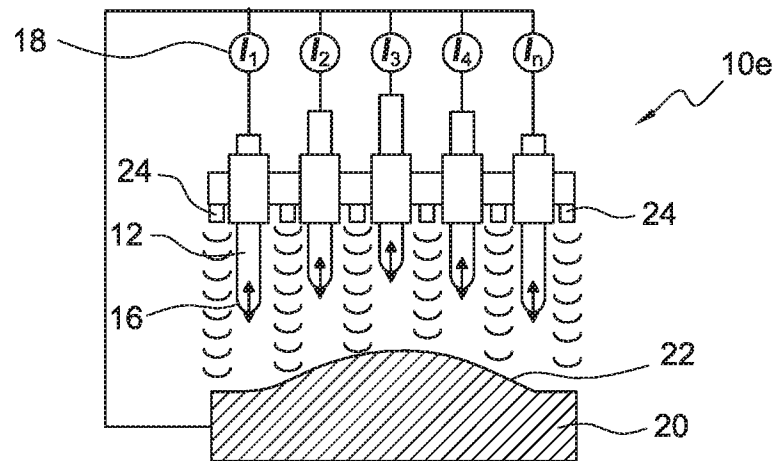
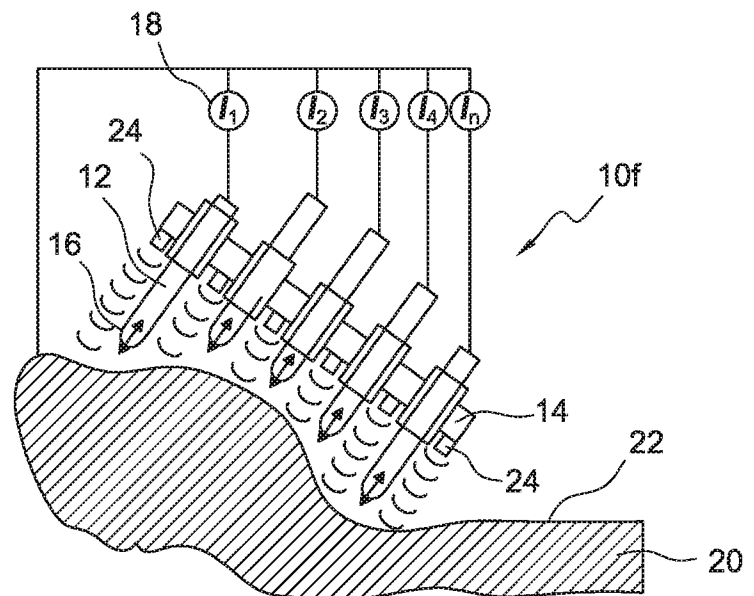


FIG. 1F



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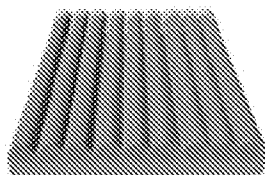


FIG. 2A

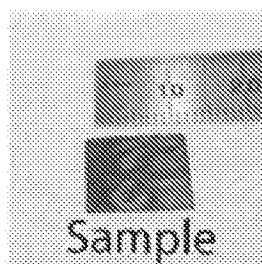


FIG. 2B

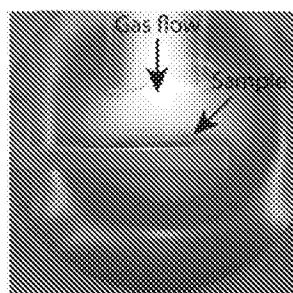


FIG. 2C

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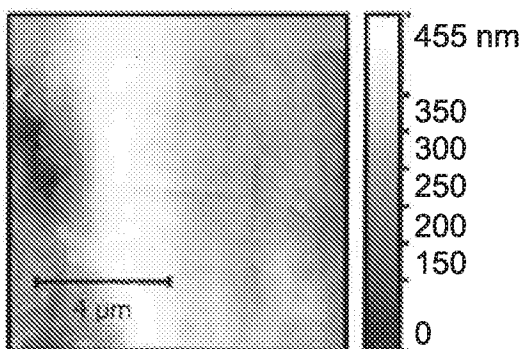


FIG. 3A

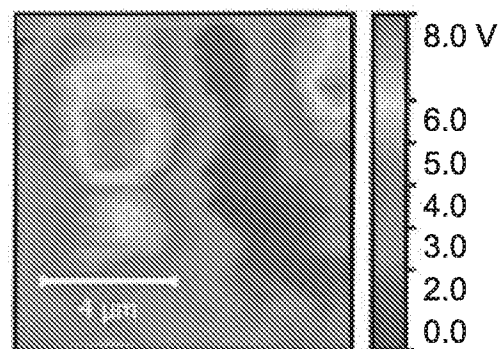


FIG. 3B

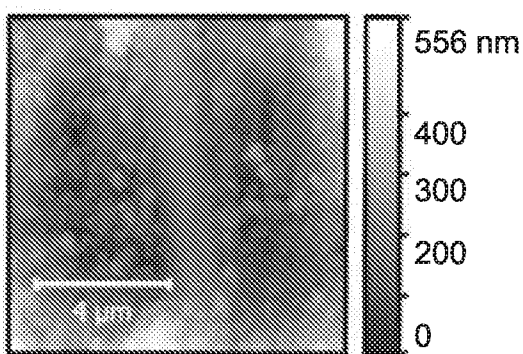


FIG. 3C

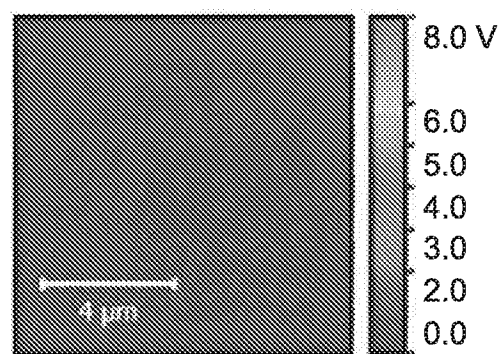


FIG. 3D

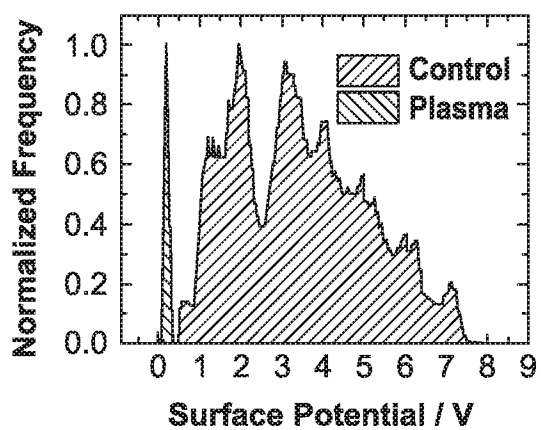


FIG. 3E

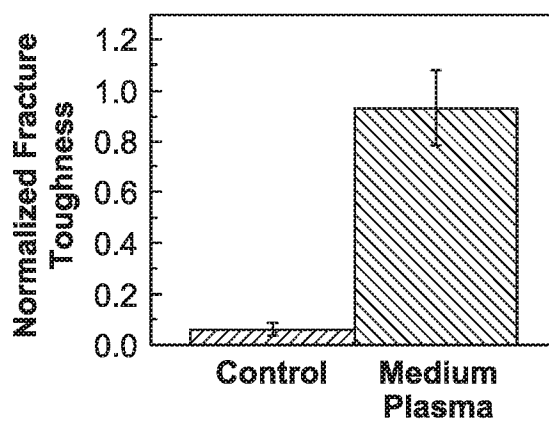


FIG. 3F

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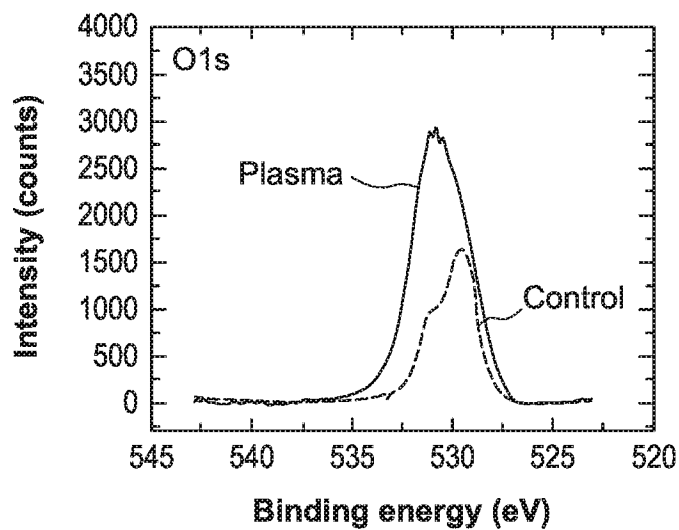


FIG. 4A

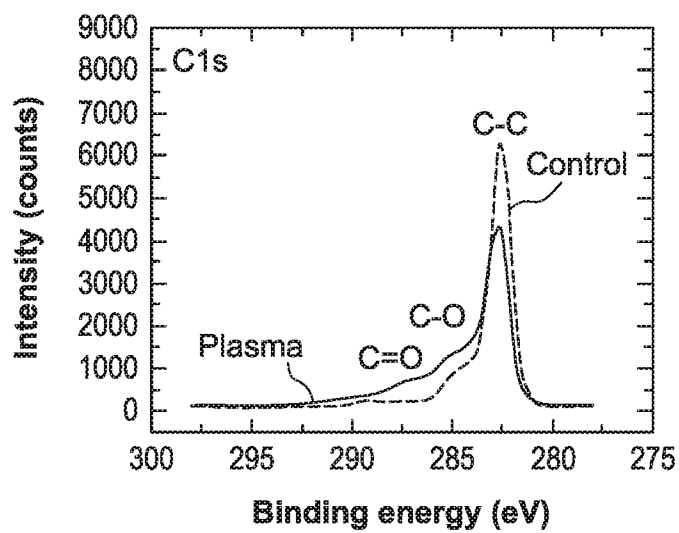


FIG. 4B

Sample	Water	DIM	EG
Control	64.8±2.2°	55.2±0.56°	50.4±1.6°
Plasma	25.±2.5°	201.±0.42°	8.0±1.0°

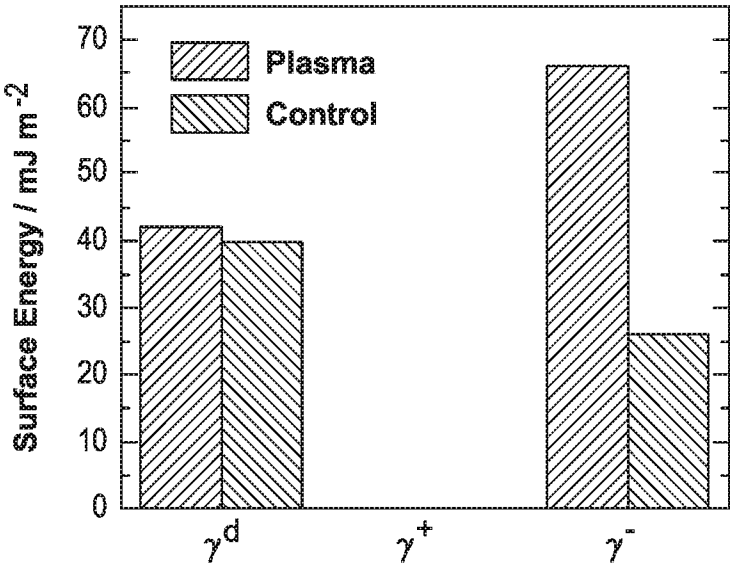


FIG. 5

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FIG. 6A

FIG. 6B

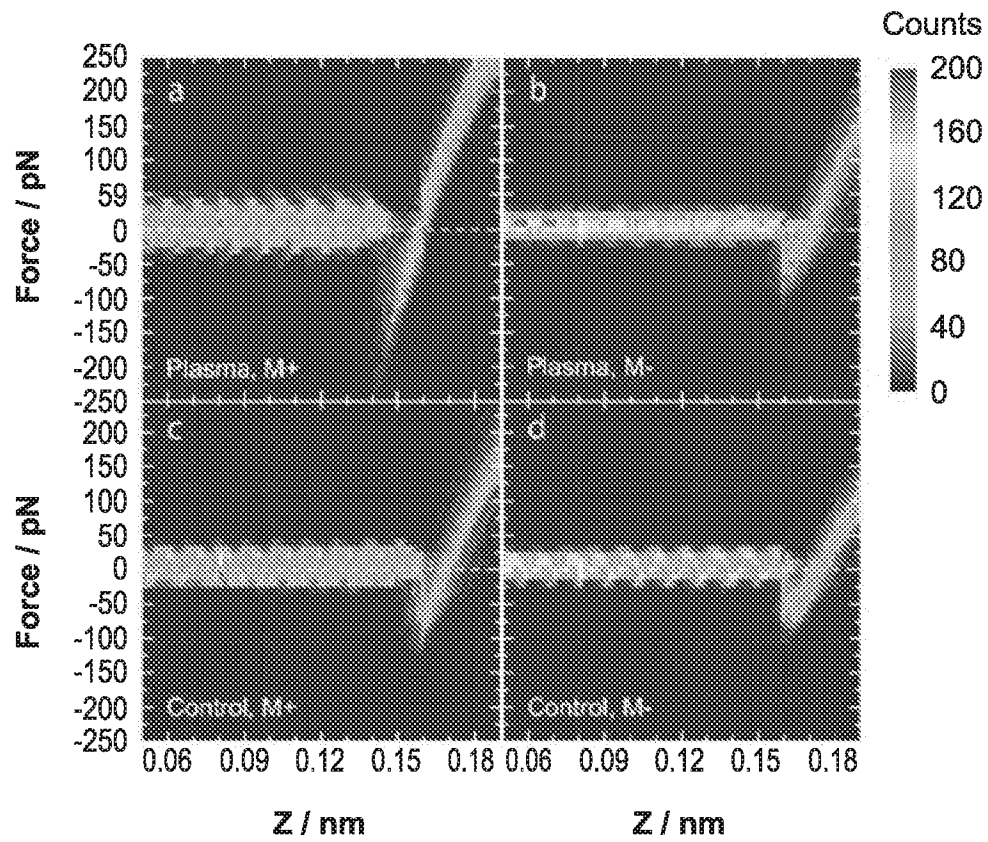


FIG. 6C

FIG. 6D

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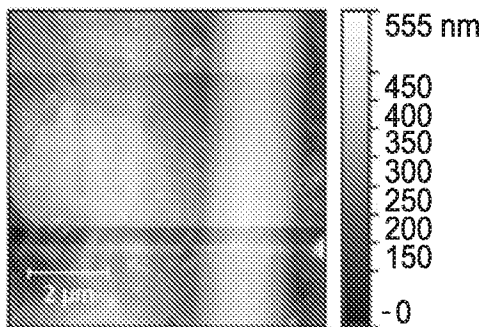


FIG. 7A

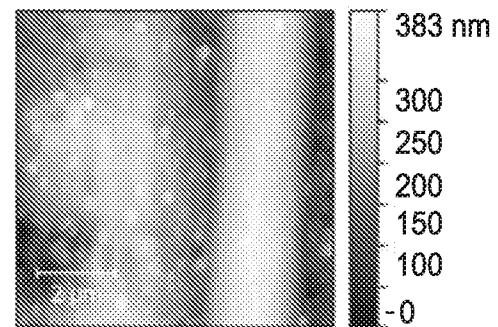


FIG. 7B

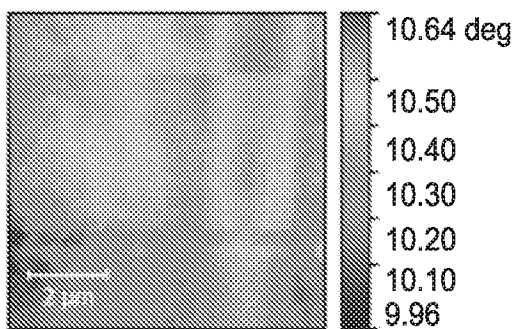


FIG. 7C

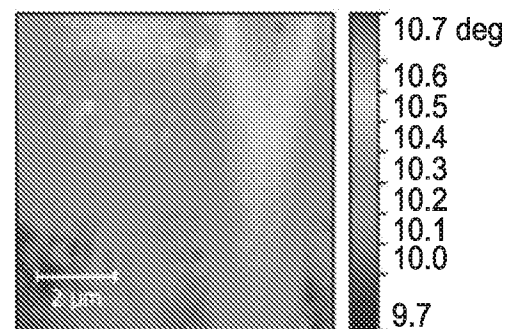


FIG. 7D

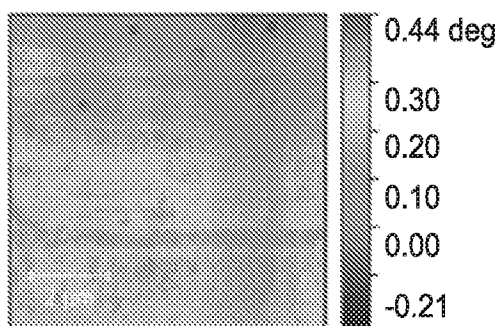


FIG. 7E

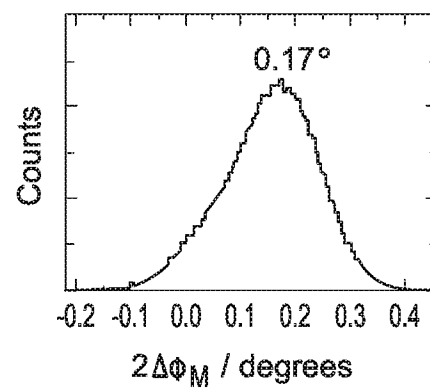


FIG. 7F

FIG. 8A

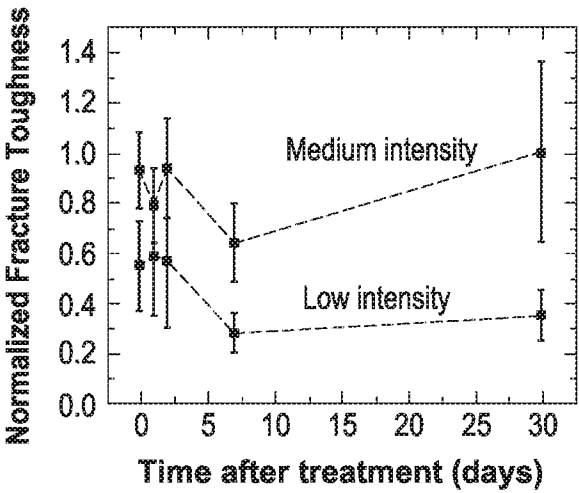


FIG. 8B

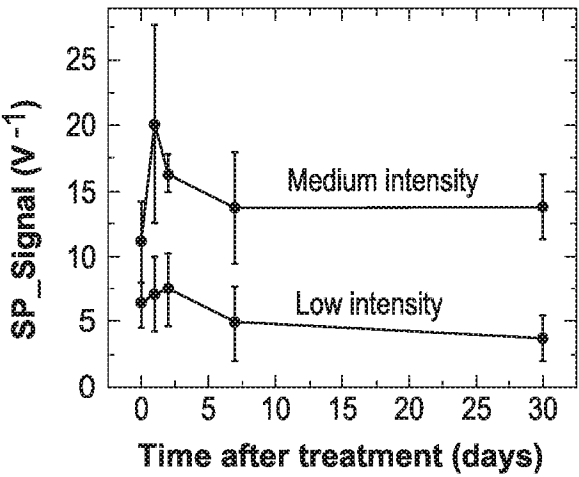
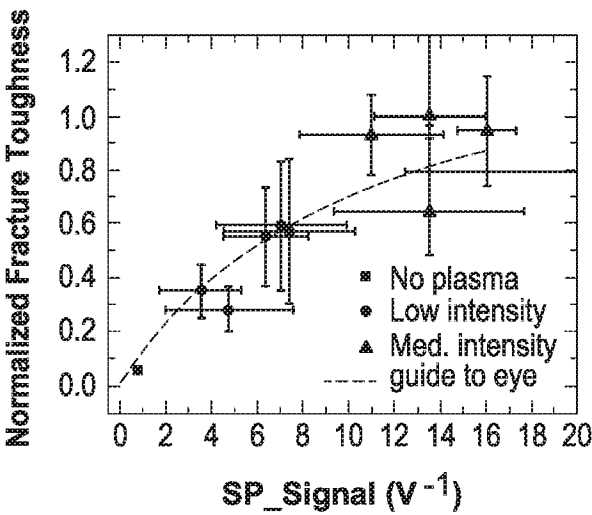


FIG. 8C



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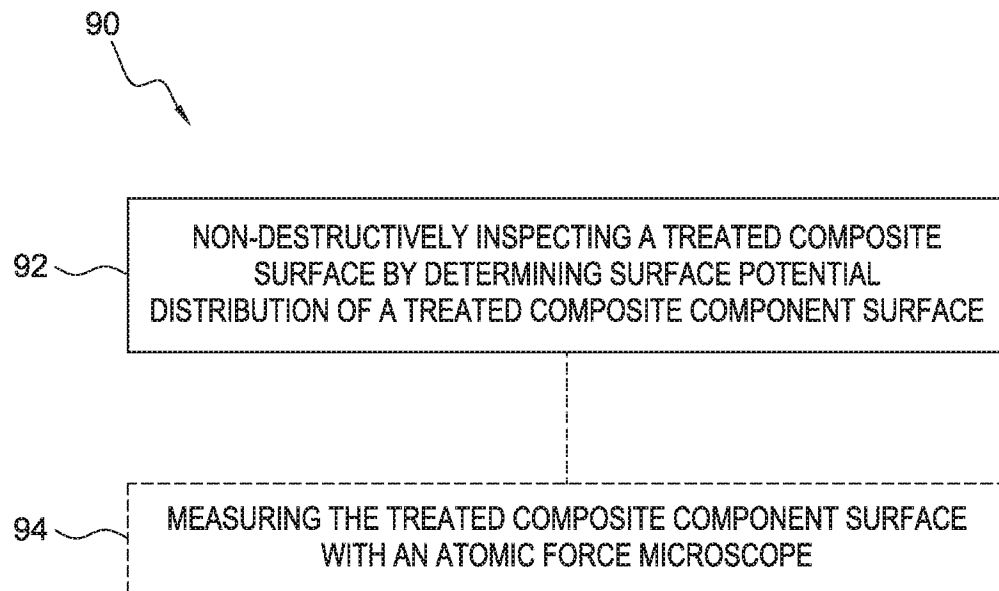


FIG. 9

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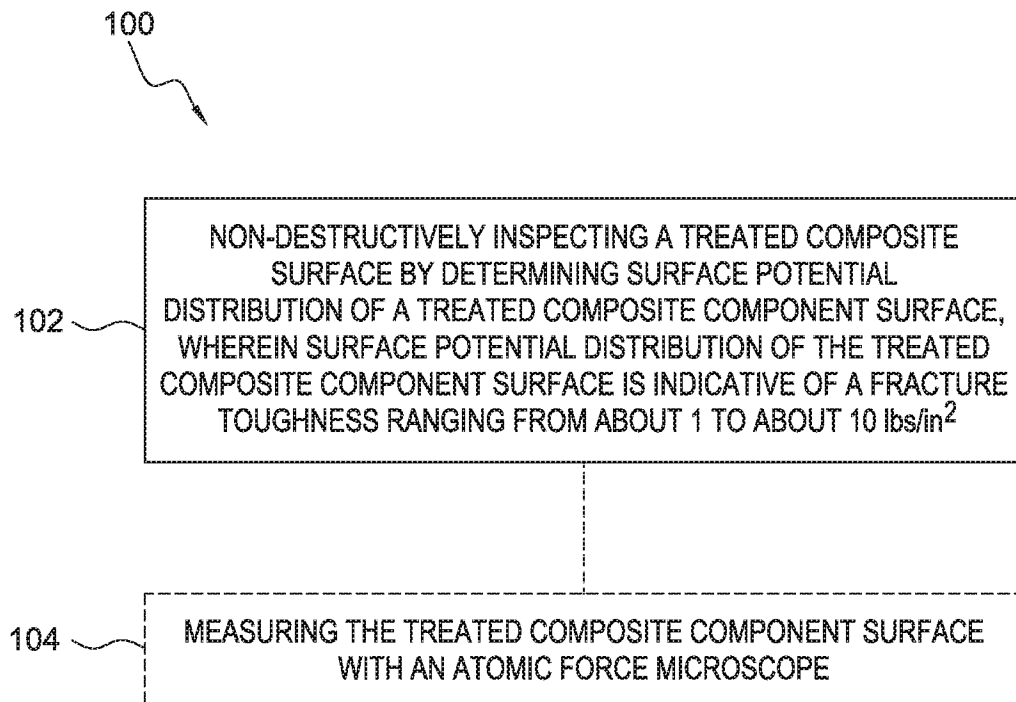


FIG. 10

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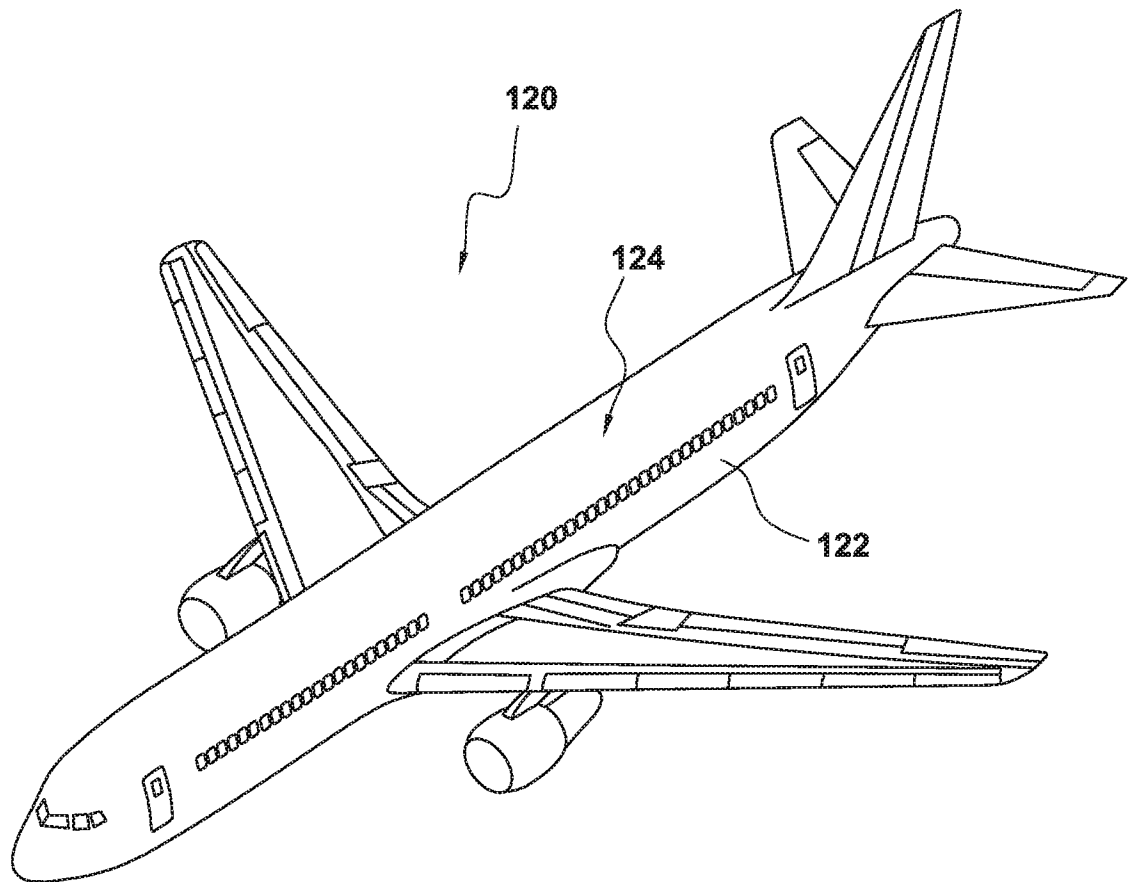


FIG. 11

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/012125

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	G01Q60/30 B64F5/60	B29C70/06 G01N27/20 G01Q70/06 G01N27/61
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) G01Q B29C G01N B64F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KEISUKE FUNATSU ET AL: "Quantitative evaluation of initial galvanic corrosion behavior of CNTs reinforced Mg-Al alloy", ADVANCED POWDER TECHNOLOGY, vol. 24, no. 5, 28 February 2013 (2013-02-28), pages 833-837, XP055568861, NL ISSN: 0921-8831, DOI: 10.1016/j.appt.2013.02.002	1-7,9, 13,14, 22-28, 30,34-36
Y	figures 2, 5-7	10-12, 31-33
A	paragraph [0002] - paragraph [0003]	8,15-21, 29,37-43
	----- -/--	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 14 March 2019		Date of mailing of the international search report 26/03/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Polesello, Paolo

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2019/012125

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 3 002 106 A1 (BOEING CO [US]) 6 April 2016 (2016-04-06)	15-21, 37-43
Y	figures 1-5 paragraph [0009] - paragraph [0026] -----	10-12, 31,33
X	FR 2 872 779 A1 (AIRBUS FRANCE SAS [FR]) 13 January 2006 (2006-01-13)	15-21, 37-43
Y	figure 2 page 11, line 11 - line 15 page 11, line 25 - line 30 -----	11,32
X	SEILER JOHANNES ET AL: "Insight into the interphase in polymer nanocomposites", IEEE TRANSACTIONS ON DIELECTRICS AND ELECTRICAL INSULATION, IEEE SERVICE CENTER, PISCATAWAY, NJ, US, vol. 21, no. 2, 1 April 2014 (2014-04-01), pages 537-547, XP011545061, ISSN: 1070-9878, DOI: 10.1109/TDEI.2013.004388 [retrieved on 2014-04-03]	1,2,8, 13-15, 22,23, 29,34, 35,37
A	figures 18,19,21 paragraph [0003] - paragraph [0006] paragraph [07.2] -----	3-7, 9-12, 16-21, 24-28, 30-33, 36,38-43

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2019/012125

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 3002106	A1	06-04-2016	BR 102015024024 A2	04-10-2016
			CN 105482723 A	13-04-2016
			EP 3002106 A1	06-04-2016
			SG 10201507971V A	30-05-2016
			US 2016098826 A1	07-04-2016

FR 2872779	A1	13-01-2006	NONE	
