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(54) LIGHTNING STRIKE PROTECTION MATERIAL

BLITZSCHUTZMATERIAL

MATERIAU DE PROTECTION CONTRE LA FOUDRE

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention is directed to a lightning strike protection material for composite structures.

Description of the Related Art

[0002] Carbon fibers are light weight materials that can exhibit high strength and high stiffness. Carbon fibers are typically produced by high-temperature pyrolysis of polyacrylonitrile (PAN), pitch, or rayon precursor. High heat treatment (above about 1000°C) of polyacrylonitrile (PAN) based fibers results in essentially 100% carbon as well as a more oriented graphene microstructure and a significantly higher modulus. As the modulus increases, the fibers typically become more difficult to process resulting in increased costs due to heat treatment and subsequent processing (e.g., weaving). For example, at present, intermediate modulus (~270 GPa) fiber in a woven fabric is approximately twice the cost of a standard modulus (~220 GPa) fiber, but only exhibits about a 20% improvement in strength and stiffness.

[0003] In use, the carbon fibers may be processed or woven and then impregnated with resin to form a composite structure. Carbon fiber composites can exhibit a significantly higher strength to weight ratio in comparison to metals, resulting in a potential weight savings of up to about 50%. Carbon fiber composites also can have superior fatigue properties in comparison to metallic structures, and are corrosion resistant. With such advantageous structural properties, carbon fiber composites are suitable for use in various articles including aircraft and aircraft components.

[0004] Attempts have been made to overcome the processing challenges associated with carbon fiber formation while improving the carbon fiber's structural properties for use in various composite structures. These efforts include the use of carbon nanotube reinforcements to improve the strength and stiffness of various types of carbon fibers.

[0005] U.S. Patent No. 7,153,452 references a mesophase pitch-based carbon fiber that includes carbon nanotube reinforcements in an amount ranging from about 0.01 percent to about 1.0 percent by weight. Other efforts have focused on structural improvements utilizing polyacrylonitrile (PAN)-based fibers. Such efforts include the use of an electrospinning process to align and disperse carbon nanotubes before introduction to polyacrylonitrile (PAN) precursors. The dispersion and alignment of the carbon nanotubes is believed by some to directly impact the carbon nanotubes' effectiveness as a reinforcement material. *Titchenal, et al.,* "SWNT and MWNT Reinforced Carbon Nanocomposite Fibrils," Drexel University, Society for the Advancement of Material and Process Engineering. In addition to electrospinning, mechanical and magnetic methods exist to align the carbon nanotubes before addition to the polyacrylonitrile (PAN) precursor.

[0006] There still exists a need for more efficient methods of enhancing or improving the structural properties of carbon and polyacrylonitrile (PAN)-based fibers. There also exists a need for using such fibers in composite structures.

[0007] JP 2003 239171 discloses a carbon fiber reinforced plastic composition. The carbon fiber contains 0.01 to 20 parts by weight of vapour phase epitaxial carbon fiber and/or carbon nanotube adhered with respect to 100 parts by weight of carbon fiber.

[0008] US 4522889 discloses a carbon fibre fabric in a matrix of thermoset plastic that is coated first with a thin layer of nickel, then with a highly conductive second layer, and on the outside once more with nickel. The composite material is suitable for lightning protection.

SUMMARY OF THE INVENTION

[0009] The present invention relates to a lightning strike protection material for composite structures comprising: carbon fibers, wherein the fibers are woven into a fabric for wet lay-up repair of aircraft or aircraft structures, characterised in that each fiber comprises from 5 percent to 20 percent by weight of carbon single wall nanotubes having metallic conductivity, and the nanotubes are in a 10,10 armchair configuration. Herein described are methods of making carbon fibers, including fiber tows and yarns having enhanced strength and stiffness, and composite materials, containing the carbon fibers.

[0010] The fibers include from about 5 to about 20 percent by weight of one or more nanoreinforcement materials.

[0011] In one embodiment of making the fibers, nanoreinforcement materials can be added to a liquid solution containing solvent, adhesive or fiber sizing or a combination thereof, then poured onto one or more fibers. In another embodiment, the nanoreinforcement materials can be powder coated and introduced into one or more fibers. The methods can further include adhering carbon nanotube nanoreinforcement materials in a 10, 10 armchair configuration (Fig 1) into a spread carbon tow or yarn (Fig 3) to form modified fiber tows or yarns. The carbon nanotubes (~1TPa modulus) may be aligned in the direction of micron-sized carbon fibers (i.e. after carbonization of polyacrylonitrile (PAN) precursors). The carbon nanotubes may be coated with metals or functionalized for further modification.

[0012] Carbon fiber tows or yarns including the nanoreinforcement materials may be processed (woven) for impregnation with a thermoset resin or thermoplastic to form various composite structures or materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

Fig.1 illustrates various carbon single wall configurations.

Fig. 2 illustrates a carbon nanofiber as a reference.

Fig. 3 illustrates one embodiment of the method of applying nanoreinforcement materials to the fiber as described herein.

Fig. 4 illustrates a spread tow coated with nanoreinforcement materials and the reconsolidated tow.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Methods of enhancing structural properties and multifunctionality of fibers, including fiber tows or yarns by adhering nanoreinforcements to the individual filaments of the tow or yarn, are disclosed herein. The nanoreinforcements can be added after the tow or yarn has been manufactured (i.e., not during spinning or fabrication of the fibers). The tow or yam can be spread to expose the filaments for subsequent adherence of the nanoreinforcement.

Below is background for several of the terms used herein: Carbon fiber as used herein is defined as fiber produced by pyrolysis of organic precursor fibers, including but not limited to those based on (polyacrylonitrile) PAN, rayon or pitch. Carbon fibers can be used primarily in composites, which are engineered structures or materials containing two or more components having differing chemical or physical properties where the resulting material has structural properties not present in the original materials. Normally, the components can be physically identified and exhibit an interface between one another. In the case of fiber reinforced composites, the components may be a fiber and a resin.

[0015] Honeycomb cores are lightweight, cellular structures typically made from either metallic sheet materials or non-metallic materials (e.g., resin-impregnated paper or woven fabric) and formed into hexagonal nested cells.

[0016] Nanoreinforcements include single wall carbon nanotubes, multi-wall carbon nanotubes, carbon nanofibers, graphite nanoplatelets, fullerenes, nanoparticles of elements, nanoparticles of binary and complex compounds, and the like.

[0017] Polyacrylonitrile (PAN) is a polymer which, when spun into fiber, can be used as a precursor material to make certain carbon fibers.

[0018] Reinforcement materials can be combined with resin matrices to form composite materials. The reinforcements are typically in the form of continuous fibers, which may be woven or non-woven. As used herein, the term "fibers" specifically includes carbon fibers, fiberglass, boron, aramid or other organic fibers. Reinforcement fabrics include woven carbon fiber, fiberglass, boron, aramid or other organic fibers used to prepare prepregs and honeycombs.

[0019] The terms "repair" and "retrofit" refer to the reinforcement or repair of existing structures. When the repair or retrofit is performed with composite materials, the result can be relatively light weight and lower in cost then other alternatives.

[0020] Sizing is a neutral finishing agent (e.g., epoxy) that protects the fibers during further processing (e.g. prepregging) and acts as an interface to the resin system of the composite.

[0021] Structures that can be made from the composite materials described herein include finished components for aircraft and industrial applications. When the structures are present in aeronautical applications, they can be used in primary or secondary external structures. In automotive applications, they can be used in chassis fairings and floors, among other applications.

[0022] A surface treatment operation can form chemical bonds to the carbon surface, and can give better cohesion to the resin system of the composite.

I. Types of Fibers That Can Be Reinforced

[0023] In addition to carbon fibres, various fibers, including tows and yarns may be reinforced with the nanoreinforcements described herein. The types of fiber tows or yarns capable of reinforcement include the following:

Carbon Fibers

[0024] Carbon fiber can be described as a fiber containing at least 90% carbon obtained by the controlled pyrolysis of appropriate fibers. Carbon fibers are used, for example, in commercial and civilian aircraft, recreational, industrial, and transportation markets. Carbon fibers may be present in composites that are typically used in applications requiring strength, stiffness, relatively low weight, fatigue resistance, high temperature resistance, chemical inertness or high damping properties.

[0025] A number of carbon fiber precursors can be pyrolized to produce carbon fibers, and, depending on the precursor used, the resulting carbon fiber will have different morphology and specific characteristics. Typical precursors include polyacrylonitrile (PAN), cellulosic fibers (viscose rayon, cotton), petroleum or coal tar pitch and certain phenolic fibers. Controlled pyrolysis can remove the oxygen, nitrogen and hydrogen from the fibers to form carbon fibers. The mechanical properties can be improved by increasing the crystallinity and orientation, and by reducing defects in the fiber.

[0026] Based on carbon fiber properties, carbon fibers can be grouped into various types, including Ultra-high-modulus (modulus > about 450Gpa), High-modulus (modulus between about 300 and about 450Gpa), Intermediate-modulus (modulus between about 250 and about 300Gpa), and Low-modulus (modulus < about 250GPa). High modulus fiber can be described as a more refined carbon fiber. The term "modulus" refers to "Young's Modulus", a measurement of stiffness, where higher numbers correlate to stiffer fiber. High modulus fibers can be typically produced by stripping off the outer layers of the individual fibers, leaving a stronger core.

[0027] Based on precursor fiber materials, carbon fibers can be classified into a number of groups. There are PAN-based carbon fibers (formed by the pyrolysis of polyacrylonitrile), pitch-based carbon fibers, mesophase pitch-based carbon fibers, isotropic pitch-based carbon fibers, rayon-based carbon fibers, and gas-phase-grown carbon fibers. High strength carbon fiber tows or yarns are usually supplied in 24K, 12K, 6K, 3K and 1K yarn or tow sizes, where K = 1000 filaments (fibers).

Other Fibers

[0028] In addition to the carbon fiber tows, other fiber tows can be reinforced using the nanoreinforcements described herein. Examples include fiberglass such as E glass and S glass, and aramid fibers such as Kevlar. The fibers can be boron fiber, and can be formed of polymers, such as thermoplastic or other organic fibers.

[0029] Boron fiber can be typically produced by chemical vapor deposition. For example, boron can be deposited on a tungsten wire, glass, or graphite filament core. The resulting boron-coated filaments have nominal diameters ranging from about 0.1 to about 0.2 mm. The filaments have low density, high tensile strength as well as a high modulus of elasticity, and stiffness. Their stiffness can make the filaments difficult to weave, braid, or twist, but they can be formed into resin impregnated tapes. Such tapes can be used in hand lay-up and filament winding processes.

[0030] High modulus carbon can be co-mingled with boron fiber, which exhibits high stiffness in compression. When combined with the high tensile stiffness of the carbon, a synergistic result can be achieved where the overall stiffness is greater than that predicted by the properties of the individual fibers. The ultra tough boron fiber also can protect the more brittle high modulus carbon fiber.

Sizing

[0031] Carbon fibers can tend to be brittle, and may need some protection or lubrication as they are handled. The fibers can be "sized" using "size materials" (also known as "sizing" or, simply, "size") selected to protect the carbon fibers. Ideally, the size material is selected to provide consistent handling and to not build up any residue on the processing equipment. Further, the sizing material preferably does not increase friction between the fiber and any point that is touched during handling, and does not impede the penetration of resin into the fiber bundle.

[0032] Size materials should be compatible with the matrix resin. The phrase "compatible with" includes solubility in and reactivity with the formulated resin. The resin should be able to penetrate the fiber bundle and interact with the fiber surface. Typically, sizes that are used with epoxy resins can use an epoxy formulation as the sizing material. The size preferably should not change in chemical or physical characteristics during storage of the sized fiber to allow consistent handling after aging. Some sizes are water-soluble, and can be washed or burned off after weaving or braiding, but before the resin is applied. Others, such as polysiloxane and organosilane finishes, may be less water-soluble.

[0033] Sizes can fall into two categories. The first can be relatively low molecular weight sizes, which allow the tow bundle to be soft and easily spread, and which are typically used for prepregging. The second can be made of film forming materials, which are relatively higher molecular weight polymers that form a tough film after the fiber is dried. The film can offer more protection to the tow bundle and also prevents broken filaments from depositing on process equipment.

[0034] Some size materials, such as epoxy resins, are not water-soluble and must be applied as either an aqueous dispersion or as an emulsion. The size can be uniformly distributed on the surface of the fibers, or can exist as droplets either on the fiber surface or sticking together a number of individual fibers. Accordingly, manufacturers typically strive to control the composition, concentration, and particle size of the emulsion in the sizing bath, as well as the drying conditions, to provide a consistent product.

[0035] Unidirectional prepregs can be prepared using a hot melt process. For this type of process, the fiber preferably needs to spread easily and have consistent incoming width that will eliminate gaps and allow for thin prepregs to be made from less expensive larger tow bundles. For this process, relatively low levels of sizing (< about 1%) can provide adequate protection.

[0036] When carbon fiber is used in operations that subject it to much greater levels of abuse, such as weaving or braiding, a higher level of protection can be required, and so higher levels (> about 1 %) of sizing may be used. Higher size levels may also be used to produce flat tow products, e.g., fiber bundles spread to a highly uniform width on a spool. Carbon fiber that is chopped to be used as a short fiber reinforcement in thermoplastic resins typically has a high (> about 1%) size level.

[0037] Manufacturers can use a solvent to wash or burn off sizing to determine overall size content. Because the sizing is applied at low levels versus the surface area of the fiber bundle, it can be difficult to assess the uniformity of coverage, Secondary characteristics such as friction, fiber damage and spreadability can be correlated to size level and uniformity of coverage.

II. Nanoreinforcements Used to Modify Fiber Tows and Yarns

Carbon Nanotubes

[0038] The carbon nanotubes can be pure or functionalized, and can be metal-coated or polysiloxane-modified. When a polysiloxane coating is applied, there can be ideally at least about 1% polysiloxane per total fiber weight.

[0039] The nanofibers can be aligned along the fiber tows or yarns, to provide the reinforced fiber tows or yarns with advantageous reinforcement properties. The nanotubes can be aligned through various methods, including mechanical, chemical, and magnetic methods. For example, the nanotubes can be mixed with the adhesive and extruded onto the fiber or tow to be coated. The feed screw can be vibrated to improve the alignment of fibers in the flow direction. This operation can be similar to vibration injection molding used with recycled thermoplastics. The nanotubes can be functionalized to react with the tail or head of each nanotube such that it will self-assemble (similar to lipid bi-layer assembly). This can involve optimizing the nanotube loading so that the nanotubes attract each other, while also ensuring that any thermosetting monomers used to adhere the nanotubes to the fibers (i.e., an epoxy resin) do not interfere with the process. Additionally, the nanotubes can be prepared such that a nickel particle is attached to one end. Ferrous alloy nanoparticles and carbon nanotubes (with the nickel particle) can be added to the adhesive, primer, or paint and subjected to a magnetic field to align the nanotubes.

Preparation of Carbon Nanotube and Metal Powder Blends

[0040] A carbon nanotube-copper composite powder can be prepared by an electrodeposition process using a copper plating bath. The bath contains homogenously dispersed carbon nanotubes. Particles of the composite with a "spiky" ball structure are accumulated on the plating electrode during the initial stage of electroplating, and can be separated to produce a carbon nanotube-copper powder. In the present invention, the nanotubes may be embedded into the copper particles.

Metal-coated Microspheres and Carbon Nanotubes

[0041] Carbon nanotubes can be coated with metals, such as silver, using techniques known in the art. Metallic conducting 10,10 armchair configuration single wall nanotubes are used in the micron size fiber tows or yarns, for example, to improve the conductivity for EMI shielding or lightning strike protection. These modified fiber tows or yarns can also improve the thermal conductivity of the resulting composite prepared from the tows or yarns.

[0042] Typically, carbon nanotubes are pre-treated, for example, by oxidation, hydrophilic treatment, sensitizing treatment, activating treatment or a combination thereof. Such treatment may be required because carbon nanotubes typically have low chemical reactivity, and do not act as a catalyst for the deposition of metal coatings. The pre-treatment provides activated sites that permit plating of metals such as silver. Other pre-treatment steps that provide such activated sites can also be used.

[0043] Oxidation can be performed, for example, using nitric acid. Sensitization and activation can be carried out, for example, by immersing the tubes in an acidic tin chloride solution, rinsing, and then immersing the tubes in an acidic palladium chloride solution. During sensitization, activation, and electroless plating, the reaction mixtures can be agitated using ultrasound. These steps provide the surface of the nanotubes with various functional groups, such as carboxylic acid, ketone and hydroxyl groups.

[0044] Electroless plating can provide a metal coating layer roughly about 10 to about 20 nm in thickness. The metal atoms aggregate laterally and vertically to form a continuous layer. In one embodiment, silver-coated carbon nanotubes can be used to provide an electrically conductive layer.

[0045] The density of the microspheres, nanotubes or combination thereof, preferably is close to the density of the fibers that are being reinforced. For example, the density of silver-coated microspheres is about 0.13 lb/in^3 (3.5 g/cm^3) for about 70 micron average diameter with a about 5 micron silver coating. An ultrasonic horn or roller may be used to help mix and disperse the particles.

Single-Wall Carbon Nanotubes

[0046] Carbon nanotubes in a 10,10 configuration can have a resistivity close to copper and can be six times lighter than copper. These carbon nanotubes can preferably be aligned in-plane to conduct electricity. The nanotubes may be aligned through various methods. Mechanical, chemical, and magnetic methods can be used to align the nanotubes. For example, the nanotubes can be mixed with the adhesive and extruded onto the fiber tows or yarns to be coated. The feed screw can be vibrated to improve the alignment of fiber tows or yarns in the flow direction. The nanotubes can be functionalized to react with the tail or head of each nanofiber such that it will self-assemble (similar to lipid bi-layer assembly). This typically requires optimizing the nanotube loading so that the nanotubes attract each other, while also ensuring that the epoxy does not substantially interfere with the process. Finally, the nanotubes can be made such that a nickel particle is attached to one end. Ferrous alloy nanoparticles and carbon nanotubes (with the nickel particle) can be added to the adhesive, primer, or paint and subjected to a magnetic field to align the nanotubes.

Modified Carbon Nanotubes

[0047] Carbon nanotubes may be modified to decrease their resistivity. By bonding metal atoms to the end or sides of carbon nanotubes the electron pathways are increased or made more efficient, hence lowering their resistivity. These modified nanotubes can be oriented in-plane or used within a two-phase polymer.

III. Methods for Applying the Nanoreinforcements to Fiber Tows or Yarns

[0048] The nanoreinforcement materials recited herein may be applied to carbon fiber tows or yarns. In one embodiment, the nanoreinforcement materials are coated with a thermoplastic powder, and then are electrostatically sprayed onto the fiber tows or yarns. In another embodiment, the nanoreinforcement materials are mixed into a liquid, for example, a solution that includes a solvent including adhesive, sizing, or a combination thereof, which is then sprayed onto the fiber tows or yarns. In either embodiment, the nanoreinforcement materials may be introduced to micron size carbon fibers derived from (polyacrylonitrile) PAN precursors (i.e. after carbonization of (polyacrylonitrile) PAN).

[0049] The nanoreinforcement materials can be applied in a random orientation, or an ordered orientation. When they are to be applied in an ordered manner, this can be accomplished using a variety of means, including electric field orientation, a moving tow, a special (i.e., spinning, vibration, etc.) nozzle or combing with grooved feeder or platen. Such application techniques are either as described herein or as known in the art, and can be applied singularly or in combination with other techniques.

[0050] The application of nanoreinforcement materials onto spread fiber tows or yarns can form modified fibers, tows or yarns, where the nanoreinforcement is adhered to or trapped within the tow yarn. Figure 4 illustrates a nanoreinforced tow wherein the nanoreinforcement material is adhered or trapped within the carbon tow. In one embodiment, aligning the nanoreinforcement materials in the direction of micron-sized carbon fibers in the tows or yarns improves the carbon fiber tows or yarns strength or stiffness or a combination thereof. The carbon nanotubes can optionally be coated with metals, or functionalized for further modification. While not wishing to be bound to a particular theory, it is believed that the improvement in structural properties such as tensile strength through the use of nanoreinforcement materials such as nanotubes and nanofibers is dependent, at least in part, on the gaps and overlaps between the ends of the nanofibers or nanotubes.

Powder Coating

[0051] In one embodiment of the methods described herein, nanoreinforcement materials may be applied to carbon nanotubes. The carbon nanotubes can be aligned for deposition into the tows or yarns using mechanical (e.g., vibration plated) or electrical means before powder coating. Alternatively, one can powder coat the nanotube with thermoplastic, then align the nanotubes or nanofibers.

[0052] The powder coated nanotubes can then be spread onto micron size carbon fiber tows or yarns. The tows or yarns can then be heated, pressed, or a combination thereof to ensure the carbon nanotubes or nanofibers adhere to the tow or yarn for subsequent processing. In an alternative embodiment, the powder coated carbon nanotubes or nanofibers may be electrostaticly sprayed into a spread tow or yarn. A moving tow or yarn may be used with a special (e.g., spinning, vibration, etc.) nozzle that may be used to help control orientation during spraying.

Liquid Application

[0053] The nanoreinforcement can also be applied using a liquid media. In one embodiment, the materials are added to a liquid solution and sprayed or poured onto the fiber tows or yarns. The solution includes solvent and can optionally also include sizing and adhesive. The liquids may be applied to a moving tow or yarn. Optionally, the nanoreinforcement liquid may be applied using a special (e.g., spinning or vibrating) nozzle, a grooved feeder, a platen or a combination thereof.

[0054] When a liquid solution containing the nanoreinforcement materials, solvent, adhesive, and fiber sizing is poured onto the spread tow or yarn, the dispensing head or the tow or yarn can be vibrated or moved to help orient the nanotubes or nanofibers. The feeder may can contain grooves that simulate a comb. After the spread tow or yarn is coated, the feeder can be pulled through platens with the grooves placed on the platens. Combing orients the nanotubes. In one embodiment, the nanotube sizing is the same epoxy-compatible sizing used on the micron sized carbon fibers. This embodiment permits the nanoreinforcement materials to adhere to the micron sized carbon fiber in the tows or yarns with the application of heat, pressure or a combination thereof. The nanoreinforcement materials may be coated with or contain ferromagnetic metals, which can enable the materials to be aligned in a subsequent magnetic field.

[0055] In another embodiment, the carbon nanotubes can be coated with ferromagnetic metals such as nickel or cobalt, or the nickel catalyst can be left in the grown nanotube and aligned in a subsequent magnetic field in a polystyrene solution. Magnetic alignment methods typically require very strong magnets. Accordingly, this approach may be less desirable than mechanical or electric field alignment.

[0056] One example of the nanoreinforcement process is shown in Fig. 3. In this process, a tow or yarn spool is unrolled into a tow or yarn spread, which can include an air comb, a vacuum comb, tensioning rollers, or an ultrasonic roller. A nanoreinforcement feeder is placed above the tow spreader to feed the nanoreinforcement materials onto the spread tow. The feeder can be or include, for example, a vibratory feeder, an electrostatic sprayer, a grooved comb, or an electric field column. Following application of the nanoreinforcement materials to the spread tow, the coated fiber tows or yarns pass through a heater, which can be an infrared heater, an oven, or heated rollers. The coated, heated fibers then can pass through a set of compaction rollers, and are reconsolidated into a tow using a collimator or an orifice. The reconsolidated tow can then be respooled.

IV. Preparation of Composite Materials

[0057] The resulting nanoreinforced fiber tows or yarns can be molded into high strength composite materials for structural applications. For example, the nanoreinforced fiber tows or yarns can be processed into composite materials using either thermoset or thermoplastic polymers, via conventional methods (e.g., prepreg lay-up, towpreg, filament winding, resin transfer molding, fiber placement, and the like).

[0058] In one embodiment, fiber tows or yarns including the reinforced fibers described herein can be processed for impregnation with a thermoset resin or thermoplastic to form a composite structure. The resin- applied modified fiber tows or yarns (prepreg or towpreg) can then be shaped into a composite structure before curing. The woven fiber tows or yarns can also be used in a dry form for resin transfer molding or resin film infusion of the composite structure. In another aspect, the thermoplastic-impregnated fibers are shaped and the thermoplastic is consolidated.

[0059] The performance increase of the modified fiber tows or yarns relative to the unmodified fiber tows or yarns can be greater than the weight increase caused by the modification. Increased fiber stiffness and strength can result in a significant weight saving, which can be particularly important in applications, e.g., airborne structures, where low weight and high strength are desired. The cost savings of adding a low percentage of carbon nanotubes to the tow bundle may be lower than switching to a higher performance micron size carbon fiber tow or yarn.

V. Articles of Manufacture Including the Composite Materials

[0060] The nanoreinforced fiber tows or yarns can be used to prepare virtually any composite materials commonly made using the fiber tows or yarns themselves. Examples include products in the aerospace field.

[0061] There are many applications that can take advantage of carbon fiber's physical strength, specific toughness, and light weight. Specific examples include nacelles (and components thereof) for use to house and operate with aircraft engines.

[0062] Examples of nacelle components include monolithic carbon fiber thrust reverser cascades, nacelle cowling (such as inlet, fan, side, upper, lower, core, or nose cowls), acoustic panels, nacelle duct systems including engine build up (EBU) components, starter, cowl anti-ice, oil cooler and vent ducts, nacelle mounting and attach rings, thrust reversing systems such as fan reversers, flight control panels, airframe structures, fans, actuation accessories (pneumatic, electric, and hydraulic), exhaust nozzles, centerbodies, nose lipskins, nozzles surround the engine, fuel systems, lubrication systems, air-conditioning systems and fire warning systems.

[0063] There are applications which can take advantage of carbon fiber's high dimensional stability, low coefficient of thermal expansion, and low abrasion.

[0064] There are applications which can take advantage of carbon fiber's electrical conductivity.

[0065] There are applications which can take advantage of carbon fiber's biological inertness and x-ray permeability.

[0066] There are applications which can take advantage of carbon fiber's fatigue resistance, self-lubrication, and high damping.

[0067] Additional applications can take advantage of carbon fiber's chemical inertness and high corrosion resistance.

[0068] Other applications can take advantage of carbon fiber's electromagnetic properties.

[0069] Non-polymer materials can also be used as the matrix for carbon fibres.

[0070] The composites can be used in a variety of repair and retrofit applications in the aerospace industry.

Lightning Strike Protection

[0071] The nanoreinforced fibers, including tows and yarns described herein, are used to form lightning strike protection composite materials. As used herein, a lightning strike protection material provides lightning strike protection to various structures, including those employed in the aircraft and aerospace industry. Various airworthiness certification authorities set forth or practice standards to which aircraft manufactures must comply. Based on the probability of a lightning strike and the probable intensity of the lightning current generated in the strike, various authorities designate different potential strike zones for each aircraft and the probable current waveforms to which structures and systems in these zones must be resistant. These are generally identified as Zones 1A and 1B, Zones 2A and 2B and Zone 3, as is known in the aircraft industry.

[0072] The location of strike zones on any aircraft is dependent on the geometry of the aircraft and operational factors, and often varies from one aircraft to another. Airworthiness authorities designate standards with which the aircraft manufacturers must comply. Different potential strike zones are assigned for each aircraft component and the current wave component is designated. The structure must be resistant to this strike without penetration through the thickness of the component.

[0073] Aircraft components are subjected to thermal cycling during ground to air to ground service. This thermal cycling may cause microcracking within the surface film. This microcracking may extend into the composite structure causing premature failure from exposure to moisture and/or other chemicals. Hence it is desirable to formulate the surface film such that it does not microcrack for at least 2000 cycles when exposed to thermal cycling from about -65°F (-55°C) to about 160°F (70°C).

[0074] According to one aspect of the invention, composite materials include an outer layer of a lightning strike protection layer prepared using the nanoreinforced carbon fibers of this invention. Such reinforced composite materials can form a part of an exterior portion of an aircraft or aircraft components. In one aspect of the invention, the composite materials are prepared from carbon fiber tows or yarns which are reinforced using metal nanoparticles, nanowires, and the like, or metal-coated carbon nanotubes or nanofibers, and a carrier.

[0075] According to one embodiment of the invention, the carrier may include a thermoset or thermoplastic polymer. In another aspect, the carrier can be a monomer that forms a thermoset polymer. One example of a suitable polymer is an epoxy resin that, when cured, can form a thermoset polymer on the surface of the composite material, aircraft or aircraft part to which it is applied. In use, the material can be applied as the top layer of a composite material used to form structural elements of an airplane, which may optionally include an overcoat of primer or paint or a combination thereof. In this aspect, the nanoreinforcements can be ideally sized to provide adequate electrical properties (i.e., resistance) for use as a lightning strike protection material.

[0076] The concentration of nanoreinforcements may be sufficient such that the surface resistivity of the airplane to which the material is applied may be low enough to dissipate the energy from a strike without damage to the underlying plies (i.e., the plies in the composite material underlying the lightning strike protection layer). The composite material can optionally include an isolation ply, particularly where the resistivity of the material is not sufficiently low to provide adequate protection Without the use of such an isolation ply. For most aspects, multiple layers can be used to achieve a desired lightning protection effect. For example, the composite material can include one or more layers of the nanoreinforced fiber tows or yarns, optionally with one or more fiberglass isolation plies.

[0077] In one aspect, carbon nanotubes in the 10, 10 armchair configuration can be used as all or part of the nanoreinforcement in the reinforced tows or yarns, these carbon nanotubes can have a resistivity close to copper and can be six times lighter than copper. The nanotubes may be aligned on the yarn or fiber through various methods including mechanical, chemical, and magnetic methods, as discussed above.

[0078] In another aspect, graphene platelets or metal nanorods, nanowires, or nanostrands (collectively called nanowires) can be used as part of the nanoreinforcement of the fiber tows or yarns. In a further aspect, carbon nanotubes that have been modified to decrease their resistivity can be used as nanoreinforcement materials for the fiber tows or yarns.

[0079] In a preferred embodiment, the composite materials prepared using the nanoreinforced tows or yarns can provide sufficient lightning strike protection to pass at least a Zone 2A lightning strike test, and, more preferably, can pass a Zone 1A lightning strike test. Also, the materials ideally will have desirable thermal cycling properties for use in aircraft manufacture and use. For example, it is preferred that the composite material does not microcrack for at least 2,000 cycles when exposed to thermal cycling from about -65°F (-55°C) to about 160°F (70°C).

[0080] The present invention can be better understood with reference to the following non-limiting examples.

Example 1

[0081] Carbon fiber is reinforced with about 5 to about 20% by weight carbon single wall nanotube with metallic conductivity (10, 10 armchair configuration). This fiber is then woven into a fabric for use as the top layer of a composite structure for lightning strike protection for aircraft structures. This layer also provides increased strength, stiffness, and thermal conductivity in the composite structure.

Example 2

[0082] Carbon fiber can be reinforced with about 5 to about 20% by weight carbon single wall nanotubes with metallic conductivity. These fibers are woven into a fabric to use for wet lay-up repair of aircraft structures. This layer can be used on the top surface to provide repair of the lightning strike material without using an additional layer of wire screen for aircraft structures.

[0083] Whereas particular embodiments of this invention have been described above for purposes of illustration, it will be evident to those skilled in the art that numerous variations of the details of the present invention may be made without departing from the scope of the invention as defined in the appended claims.

Claims

1. A lightning strike protection material for composite structures comprising: carbon fibers, wherein the fibers are woven into a fabric for wet lay-up repair of aircraft or aircraft structures,
characterised in that
each fiber comprises from 5 percent to 20 percent by weight of carbon single wall nanotubes having metallic conductivity, and
the nanotubes are in a 10,10 armchair configuration.

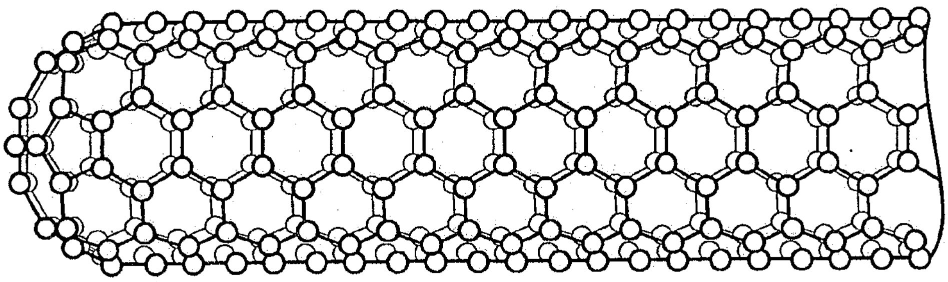
Patentansprüche

1. Blitzschutzmaterial für Verbundstrukturen, umfassend:

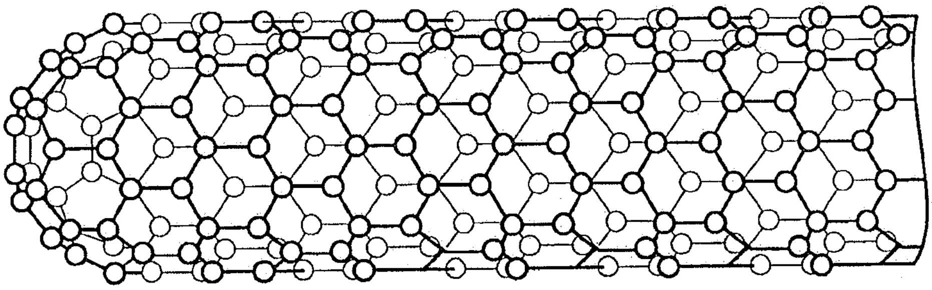
   Kohlenstofffasern, wobei die Fasern zu einem Stoff für die Nasslaminierungsreparatur von Luftfahrzeugen oder Luftfahrzeugstrukturen verwebt sind,
   dadurch gekennzeichnet, dass
   jede Faser 5 Gewichtsprozent bis 20 Gewichtsprozent einwandige Kohlenstoffnanoröhrchen umfasst, die eine metallische Leitfähigkeit aufweisen; und
   die Nanoröhrchen in einer 10,10-Lehnstuhlkonfiguration sind.

Revendications

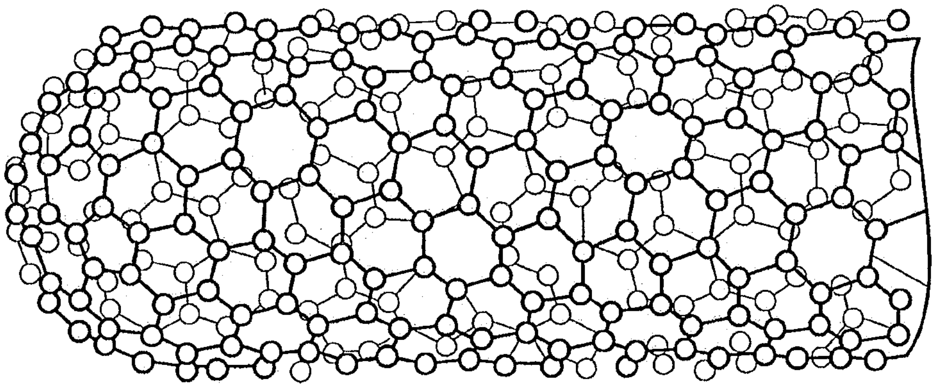
1. Matériau de protection contre la foudre pour des structures composites comprenant : des fibres de carbone, dans lequel les fibres sont tissées pour former un tissu pour la réparation en couches humides des aéronefs ou des structures des aéronefs,
   caractérisé en ce que
   chaque fibre est comprise entre 5 pourcent et 20 pourcent en poids des nanotubes à paroi simple de carbone ayant une conductivité métallique, et les nanotubes sont dans une configuration 10,10 de type « armchair ».



ARMCHAIR ($\alpha = 30^\circ$)



ZIGZAG ($\alpha = 0^\circ$)



INTERMEDIATE ($0< \alpha = 30^\circ$)

FIG. 1

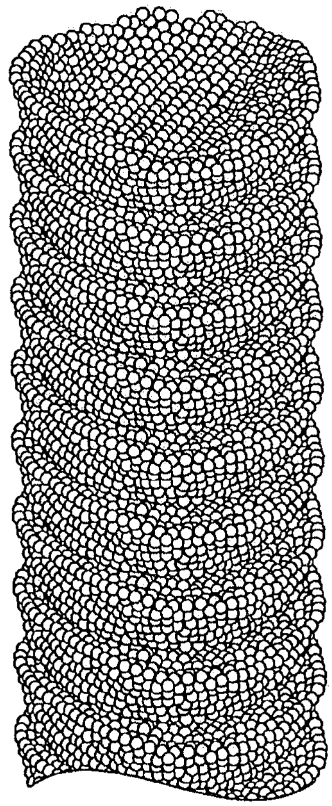


FIG. 2

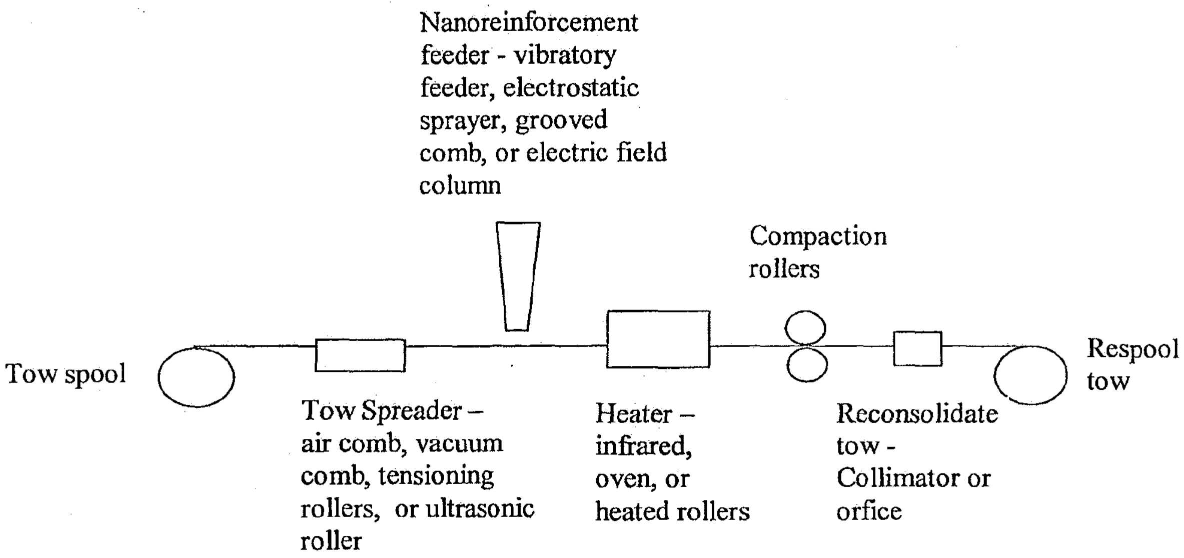
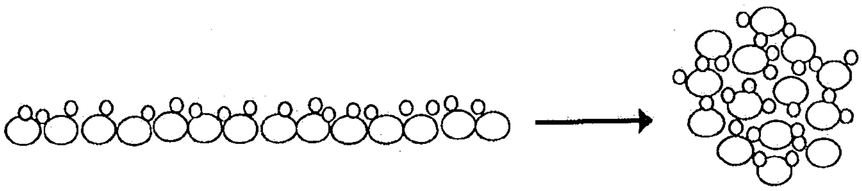


Figure 3. Nanoreinforcement coating process



Spread tow coated with nanoreinforcement

Reconsolidated tow with bulk of nanoreinforcement trapped inside

Figure 4. Nanoreinforced tow bundle (~usually 3K, 6K, or 12K filaments)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 7153452 B **[0005]**
- JP 2003239171 A **[0007]**
- US 4522889 A **[0008]**