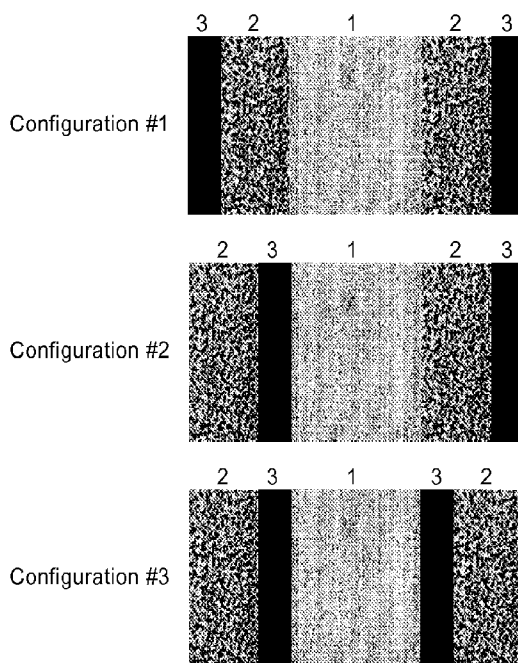




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[Continued on next page]

- (54) **Title:** FIBER REINFORCED POLYMER COMPOSITE COMPOSITION WITH ALIGNED NANOFIBERS



(57) **Abstract:** Embodiments disclosed herein include a fiber reinforced polymer composition comprising a reinforcing fiber, an adhesive composition, and at least a nanofiber sheet. Nanofibers of the nanofiber sheet are spatially located in the fiber reinforced polymer composition, on a plane parallel to the reinforcing fiber, and aligned at an alignment angle with respect to the axis of the reinforcing fiber, such that both mechanical and z-direction electrical conductivity of the composite are substantially improved.



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FIBER REINFORCED POLYMER COMPOSITE COMPOSITION WITH ALIGNED NANOFIBERS

Field of the Invention

[0001] The present application provides an innovative fiber reinforced polymer composition comprising a reinforcing fiber, an adhesive composition, and at least a nanofibers sheet comprising a substantial amount of nanofibers that are in a plane parallel to the reinforcing fiber and aligned at an angle with respect to the reinforcing fiber's axis, such that mechanical and z-direction electrical conductivity of the cured fiber reinforced polymer composition are enhanced simultaneously and substantially.

Background of the Invention

[0002] To increase fracture toughness of a fiber reinforced polymer composite, specifically mode I interlaminar fracture toughness G_{IC} , a conventional approach is to toughen the matrix with a submicrometer-sized or smaller soft polymeric toughening agent. Upon curing of the fiber reinforced polymer composite, the toughening agent is most likely spatially located inside the fiber bed/matrix region, called the *intraply* as opposed to the resin-rich region between two plies, called the *interply*. Uniform distribution of the toughening agent is often expected to maximize G_{IC} . Examples of such resin compositions include, US6063839 (Oosedo et al., Toray Industries, Inc., 2000), EP2256163A1 (Kamae et al., Toray Industries, Inc., 2009) with rubbery soft core/hard shell particles, US6878776B1 (Pascault et al., Cray Valley S.A., 2005) for reactive polymeric particles, US6894113B2 (Court et al., Atofina, 2005) for block copolymers and US20100280151A1 (Nguyen et al., Toray Industries Inc., 2010) for reactive hard core/soft shell particles. For these cases, since a soft material was incorporated in the resin in a large amount either by weight or volume, G_{IC} increased substantially at the expense of resin's modulus and subsequently compressive properties of the composite.

[0003] To increase mode II fracture toughness of the composite, an interlayer toughening technique could be utilized. Typically, a thermoplastic additive (e.g., polyimide, polyamide) having a particle size from 2 μ m-50 μ m could be confined in the *interlayer area* or the resin zone between two bundles of fibers. G_{IIC} is a measure of how well the composite part resists impact loads as opposed to tensile loads in G_{IC} . In this case, cracks generated due to quasi-static bending of the part experience in-plane shear load, which tends to slide one crack face with respect to the other. Examples of such interlayer toughening techniques include US 5,413,847 (Kishi et al., Toray Industries, Inc., Japan) or US 5,605,745 (Recker et al., Cytec Technology Corp., U.S.). Yet, current state-of-the-art materials provide moderate G_{IIC} .

[0004] Recently, some researchers have attempted to use aligned nanofibers to enhance resin's modulus. Cheng et al. (Journal of Material Research 23 (11), 2008) and Ogasawara et al. (Carbon 48, 260, 2010), formed aligned carbon nanotube (CNT) sheets drawn from a 300um tall CNT forest, and 1-2mm tall forest, respectively. An epoxy resin was impregnated into the CNT sheets allowing the resin's modulus to be increased with less than 10wt% CNT. It was found that the taller was the forest, the greater was the improvement in the resin's modulus. Cheng et al. (Advanced Functional Materials 19, 3212, 2009) formed an aligned CNT sheet stretched from a CNT bucky paper, and the aligned CNT sheet showed some promise. Additional studies on aligned CNT sheets and their fabrication techniques include Shanov et al. and Wang et al. (SAMPE Tech, South Carolina, October 22-25, 2012). However, none of these studies including a reinforcing fiber as well as utilizing them as a toughener.

Summary of the Invention

[0005] An embodiment relates to a fiber reinforced polymer composition comprising an adhesive composition, a reinforcing fiber, and at least a nanofiber sheet comprising nanofibers, wherein the nanofiber sheet is in a plane parallel to the reinforcing fiber.

[0006] In one embodiment, the adhesive composition comprises the nanofiber sheet and/or the nanofibers.

[0007] In one embodiment, the nanofibers are carbon nanotubes, carbon nanofibers, carbonaceous nanofibers, organic nanofibers, inorganic nanofibers, metal nanofibers, oxide nanofibers, composite nanofibers of the aforementioned nanofibers and a polymer, or combinations thereof.

[0008] In one embodiment, the nanofibers comprise carbon nanotubes.

[0009] In one embodiment, an alignment angle between the nanofibers and the reinforcing fibers is greater than zero degree and up to 90 degrees.

[0010] In one embodiment, an alignment angle between the nanofibers and the reinforcing fibers is less than about 20 degrees.

[0011] In one embodiment, the adhesive composition comprises at least a thermosetting resin and a curing agent.

[0012] In one embodiment, the adhesive composition comprises further at least one of an accelerator, a thermoplastic resin, a toughener, an interlayer toughener, or a combination thereof.

[0013] In one embodiment, the adhesive composition comprises at least a thermoplastic resin.

[0014] In one embodiment, the nanofiber sheet is located spatially at least one of locations between a layer of the reinforcing fibers and a layer of the adhesive composition, between two

adhesive composition layers of a same or different kinds, between two reinforcing fiber layers of a same or different kinds, or on one or both surfaces of the layer of the reinforcing fibers impregnated by the adhesive composition, wherein at least one of the reinforcing fiber or the nanofiber is dry or partially or fully impregnated by the adhesive composition.

[0015] In one embodiment, the fiber reinforced polymer composition comprises a prepreg.

[0016] Another embodiment relates to a method of manufacturing a fiber reinforced polymer composition comprising impregnating one or more adhesive films of the same kind or different kinds onto one side or both sides of a reinforcing fiber layer comprising a plurality of the reinforcing fibers, wherein at least one of the one or more the adhesive films comprises one or more nanofiber sheets comprising a substantial amount the nanofibers that are in a plane parallel to the reinforcing fiber and are aligned at an alignment angle with respect to the reinforcing fiber's axis on one side or both sides of the one or more adhesive films, wherein the nanofibers are sandwiched between two adhesive films, between one side of the reinforcing fiber layer and one adhesive film, on an exposed surface of the impregnated reinforcing fiber by the adhesive composition, or combinations thereof.

[0017] Another embodiment relates to a method of manufacturing a fiber reinforced polymer composition comprising impregnating one or more adhesive films of the same kind or different kinds onto one side or both sides of a reinforcing fiber layer comprising a plurality of the reinforcing fibers, and applying one or more nanofiber sheets on one or more exposed surfaces of the impregnated reinforcing fiber by the adhesive composition such that a substantial amount of the nanofibers are aligned at an alignment angle with respect to the reinforcing fiber's axis.

[0018] In one embodiment of the method of manufacturing the fiber reinforced polymer composition, the nanofibers comprise carbon nanotubes.

[0019] In one embodiment, the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

[0020] In one embodiment, the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

[0020] In one embodiment, the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

[0021] In one embodiment, the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

[0022] In one embodiment, the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

[0023] Another embodiment relates to a method of manufacturing a composite article comprising stacking at least a reinforcing layer, an adhesive composition layer, and a nanofiber sheet comprising a substantial amount of the nanofibers that are in a plane parallel to the reinforcing fiber and are aligned at an alignment angle with respect to the reinforcing fiber's axis in a symmetrical or unsymmetrical sequence with respect to the mid-plane of the stack such that the nanofiber sheet is located at least one of locations between two reinforcing fiber layers of the same kind or different kinds, between one reinforcing layer and one adhesive composition layer or in between two adhesive composition layer of the same kind or different kinds, and curing the stack, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer, or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

Brief Descriptions of the Drawings

[0024] FIG. 1 shows some examples of aligned nanofiber layer configurations in fiber reinforced polymer compositions having at least one adhesive composition (2), reinforcing fibers (1) that are dry or partially or fully impregnated with the at least one adhesive composition, and at least a nanofiber sheet that is dry or partially or fully impregnated with the at least one adhesive composition (3).

[0025] FIG. 2 shows some examples of aligned nanofiber layer configurations in fiber reinforced polymer compositions having at least two different adhesive compositions (2 and 4), reinforcing fibers (1) that are dry or partially or fully impregnated with one of the at least two adhesive compositions, and at least a nanofiber sheet that is dry or partially or fully impregnated with one of the at least two adhesive compositions (3).

Detailed Description of the Invention

[0026] All publications, patents, and patent applications cited in this Specification are hereby incorporated by reference in their entirety.

[0027] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, "a resin" means one resin or more than one resins. Any ranges cited herein are inclusive. The terms "substantially" and "about" used throughout this Specification are used to describe and account for small fluctuations. For example, they can refer to less than or equal to $\pm 5\%$, such as less than or equal to $\pm 2\%$, such as less than or equal to $\pm 1\%$, such as less than or equal to $\pm 0.5\%$, such as less than or equal to $\pm 0.2\%$, such as less than or equal to $\pm 0.1\%$, such as less than or equal to $\pm 0.05\%$.

[0028] A fiber reinforced polymer composition refers to a uncured or cured polymer containing material having reinforcing fibers. Embodiments of a fiber reinforcing polymer composition include a prepreg, an uncured layup for a composite or a composite. A prepreg is a reinforcing or molding material (for example, in the form of a sheet) already impregnated partially or fully with a resin. A composite is a cured material having at least reinforcing fibers and a cured resin.

Nanofibers and aligned nanofiber sheets

[0029] A nanofiber refers to any fibrous material having a diameter of less than 100 nm. The length of the nanofiber could be at least 0.5 micrometers (μm), at least 10 μm , at least 100 μm , or even at least 1 mm. The nanofibers can be carbon nanotubes, carbon nanofibers, carbonaceous nanofibers, organic nanofibers, inorganic nanofibers, metal nanofibers, oxide nanofibers, or combinations thereof.

[0030] The nanofibers could be carbon nanotubes (CNTs), which are produced from a method of a state of the art. Examples of such methods are a chemical vapor deposition (CVD) and its derivatives such as low-pressure CVD, super-growth CVD, plasma activated CVD. Single wall, double wall, more than two wall and multiple wall CNTs could be used.

[0031] An embodiment relates to a method of making aligned nanofiber sheets. The nanofiber sheet could be made from an assembly of CNTs to form a spinnable forest comprising an assembly of vertically aligned CNTs on a substrate, with the height of at least 10 microns, at least 100 microns, or even at least 1 mm. "Spinnable forests" herein and thereafter are referred to substantially vertically aligned nanofiber forests or carpets in that the nanofibers could be drawn into sheets comprising a substantial amount of the nanofibers oriented in the drawing direction. The as-drawn sheets are referred to unidirectional (UD) undensified sheets or simply undensified sheets. These undensified sheets could have a thickness of at least 50 nm, at least 100 nm or even at least 1 μm . Upon contacting a substrate, a solvent, or a polymer solution, the undensified sheets become the densified sheets. These densified sheets could have a thickness of at least 10 nm, at least 20 nm or even at least 50 nm and a density of at least 0.001 g/cm^3 , at least 0.01

g/cm³, or even at least 0.1 g/cm³. Both undensified sheets and densified sheets are referred to nanofiber sheets.

[0032] The term “nanofiber sheet” used in the embodiments herein refers to an assembly of a substantial amount of nanofibers that are aligned in a direction. “Substantial amount” refers to a quantity of at least 20% of the assembly, at least 30% of the assembly, at least 50% of the assembly, or even at least 70% of the assembly by weight.

[0033] When the undensified sheets are densified by a polymer solution, the resulting nanofiber sheet is termed a “nanofiber prepreg”. The nanofiber prepreg could have an amount of the polymer by weight of at least 1%, at least 10%, or even at least 20%. The nanofiber prepreg could have at most 1%, at most 5%, or even at most 10% by weight of the residual amount of the solvent. An embodiment relates to a fiber reinforced polymer composition comprising at least a reinforcing fiber, an adhesive composition and a nanofiber sheet, wherein the nanofiber sheet could be undensified sheets, densified sheets, nanofiber prepreps or combinations thereof. Another embodiment relates to a nanofiber sheet could be made from random CNTs or other nanofiber modified polymer, herein is referred to ‘a mat’, which can be stretched by a mechanical mean to align a substantial amount of these nanofibers in the applied load direction. Yet, another embodiment relates to a nanofiber sheet comprising a mixture of a nanofiber and a polymer such that the mixture can be electrospun to form composite fibers which could be deposited onto a substrate, allowing a substantial amount of the composite fibers to be aligned at an angle.

[0034] Another embodiment relates to functionalization of the aforementioned nanofibers and nanofiber sheets. To make strong bonds between the nanofibers and an adhesive composition, firstly oxygen functional groups are beneficially introduced on the pristine nanofiber’s surface; secondly an adhesion promoter may be selected such that one end of the adhesion promoter is capable of covalently bonding to the oxygen functional groups on the nanofiber’s surface while another end of the adhesion promoter is capable of promoting or participating in chemical interactions with functional groups in the resin. Essentially, the adhesion promoter acts as a bridge connecting the fiber to the bulk resin during curing. A surface treatment such as plasma, UV, corona discharge, vapor of an oxidizing agent, or wet electro-chemical treatment could be used to introduce oxygen functional groups onto the fiber’s surface. Other functional groups such as nitrogen-containing groups (e.g., an amine groups), sulfur-containing functional groups (e.g., a thio groups), amide groups (e.g., organic amides, sulphonamides, or phosphoramides) could be introduced.

Reinforcing fibers

[0035] A reinforcing fiber is a fiber that provides reinforcement within a composite material. The reinforcing fiber used in the embodiments herein can be, but not limited to, any of the following fibers and their combinations: carbon fibers, organic fibers such as aramide fibers, silicon carbide fibers, metal fibers (e.g., alumina fibers), boron fibers, tungsten carbide fibers, glass fibers, and natural/bio fibers. Among these fibers, carbon fibers, especially graphite fibers, could be used in the embodiments herein. Carbon fibers could have a strength of 2000 MPa or higher, an elongation of 0.5% or higher, and modulus of 200 GPa or higher.

[0036] The morphology and location of the reinforcing fibers used in the embodiments herein are not specifically defined. Any of morphologies and spatial arrangements of fibers such as long fibers in a direction, chopped fibers in random orientation, single tow, narrow tow, woven fabrics, mats, knitted fabrics, and braids can be employed. For applications where especially high specific strength and specific modulus are required, a composite structure where reinforcing fibers could be arranged in a single direction, or cloth (fabric) structures, which are easily handled, could be used in the embodiments herein.

Adhesive composition

[0037] The adhesive composition could be any resin composition and may include different components such as a thermosetting resin and curing agent/optional accelerator, a toughening agent, a thermoplastic resin, and an interlayer toughener. The adhesive composition could also include a nanofiber and/or a nanofiber sheet.

Thermosetting resin and curing agent/optional accelerator

[0038] The thermosetting resin could be any resin which can be cured with a curing agent by means of an external energy such as heat, light, electromagnetic waves such as microwaves, UV, electron beam, or other suitable methods to form a three dimensional crosslink network. A curing agent is defined as any compound having at least an active group which reacts with the thermosetting resin. A curing accelerator can be used to accelerate cross-linking reactions between the thermosetting resin and curing agent.

[0039] The thermosetting resin could be selected from, but not limited, epoxy resin, cyanate ester resin, maleimide resin, bismaleimide-triazine resin, phenolic resin, resorcinolic resin, unsaturated polyester resin, diallylphthalate resin, urea resin, melamine resin, benzoxazine resin (e.g., multi-functional n-phenyl benzoxazine resins such as phenolphthaleine based, thiodiphenyl based, bisphenol A based, bisphenol F based, dicyclopentadiene based benzoxazine resins), polyurethane, and their mixtures thereof. An example of a suitable mixture could be a mixture of an epoxy resin and a benzoxazine resin.

[0040] Of the above thermosetting resins, epoxy resins are suitable for the embodiments herein. The epoxy resins could be di-functional or higher epoxy resins. These epoxies are prepared from precursors such as amines (e.g., tetraglycidyl-diaminodiphenylmethane, triglycidyl-p-aminophenol, triglycidyl-m-aminophenol and triglycidylaminocresol and their isomers), phenols (e.g., bisphenol A epoxy resins, bisphenol F epoxy resins, bisphenol S epoxy resins, phenol-novolac epoxy resins, cresol-novolac epoxy resins and resorcinol epoxy resins), and compounds having a carbon-carbon double bond (e.g., alicyclic epoxy resins). It should be noted that the epoxy resins are not restricted to the examples above. Halogenated epoxy resins prepared by halogenating these epoxy resins can also be used. Furthermore, mixtures of two or more of these epoxy resins, and monoepoxy compounds can be employed in the formulation of the thermosetting resin.

[0041] In certain embodiments of the invention, selected epoxy resins are combined to make 100 parts by weight of an epoxy resin mixture comprising at least a difunctional epoxy resin and a higher than two functional epoxy resin. The combined epoxy equivalent weight of the epoxy resin mixture could be at least 50, at least 80, at least 100, or even at least 120. In other embodiments, an epoxy resin or a mixture of epoxy resins with different functionalities could be mixed with a benzoxazine resin or a mixture of benzoxazines of different kinds. The weight ratio of the epoxy resin to the benzoxazine resin could be between 0.01 to 100.

[0042] Examples of suitable curing agents for epoxy resins include, but not limited to, benzoxazines, polyamides, dicyandiamide, amidoamines (in particular, aromatic amidoamines, e.g., aminobenzamides, aminobenzanilides, aminobenzenesulfonamides), aromatic diamines (e.g., diaminodiphenylmethane, diaminodiphenylsulfone), aminobenzoates (e.g., trimethylene glycol di-p-aminobenzoate and neopentyl glycol di-p-amino-benzoate), aliphatic amines (e.g., triethylenetetramine, isophoronediamine), cycloaliphatic amines (e.g., isophoron diamine), imidazole derivatives, tetramethylguanidine, carboxylic acid anhydrides (e.g., methylhexahydrophthalic anhydride, carboxylic acid hydrazides (e.g., adipic acid hydrazide), phenol-novolac resins and cresol-novolac resins, carboxylic acid amides, polyphenol compounds, polysulfide and mercaptans, and Lewis acid and base (e.g., boron trifluoride ethylamine, tris-(diethylaminomethyl) phenol). Note that a mixture of two or more of the above mentioned curing agents such as DICY and DDS could be utilized. Typically, the curing agent(s) could be employed in an amount ranging from about 15 to about 50 parts by weight per 100 parts by weight of total thermosetting resin.

[0043] Depending on the desired properties of a fiber reinforced epoxy composite, a suitable curing agent is selected from the above list. For examples, if dicyandiamide is used, it will

provide the product good elevated-temperature properties, good chemical resistance, and good combination of tensile and peel strength. Aromatic diamines, on the other hand, will give moderate heat and chemical resistance and high modulus. Aminobenzoates will provide excellent tensile elongation though they have inferior heat resistance compared to aromatic diamines. Acid anhydrides will provide the resin matrix low viscosity and excellent workability, and subsequently, high heat resistance after cured. Phenol-novolac resins or cresol-novolac resins provide moisture resistance due to the formation of ether bonds, which have excellent resistance to hydrolysis. Above all, a curing agent having two or more aromatic rings such as 4,4'-diaminodiphenyl sulfone (DDS) could provide high heat resistance, chemical resistance and high modulus.

[0044] Examples of suitable accelerator/curing agent pairs for epoxy resins are borontrifluoride piperidine, p-t-butylcatechol, or a sulfonate compound for aromatic amine such as DDS, urea or imidazole derivatives for dicyandiamide, and tertiary amines or imidazole derivatives for carboxylic anhydride or polyphenol compound. If an urea derivative is preferably used, urea derivatives may be compounds obtained by reacting with secondary amines with isocyanates. Such accelerators are selected from the group of 3-phenyl-1,1-dimethylurea, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU) and 2,4-toluene bis-dimethyl urea. High heat resistance and water resistance of the cured material are achieved, though it is cured at a relatively low temperature.

Toughening agent

[0045] A toughening agent is any material that could be added to the thermosetting resin to enhance the fracture toughness of the thermosetting resin. Polymeric and/or inorganic toughening agent can be used to enhance fracture toughness of the thermosetting resin. The toughening agent could be uniformly distributed in the cured thermosetting resin or a cured bonded structure comprising the cured thermosetting resin. Particles could be less than 5micron in diameter, less than 1 micron, or even less than 300nm for the shortest dimension. Such toughening agents include, but not limited to, branched polymer, hyperbranched polymer, dendrimer, block copolymer, core-shell rubber particles, core-shell (dendrimer) particles, hard core-soft shell particles, soft core-hard shell particles, oxides or inorganic materials with or without surface modification such as clay, polyhedral oligomeric silsesquioxane (POSS), carbonaceous materials (e.g., carbon black, carbon nanotube, carbon nanofiber, fullerene), ceramic and silicon carbide.

[0046] Examples of block copolymers whose composition as described in US 6894113 (Court et al., Atofina, 2005) and include "Nanostrength®" SBM (polystyrene-polybutadiene-

polymethacrylate), and AMA (polymethacrylate-polybutylacrylate-polymethacrylate), both produced by Arkema. Other block copolymers include Fortegra® and amphiphilic block copolymer described in US 7820760B2 by Dow Chemical. Examples of known core-shell particles include core-shell (dendrimer) particles whose compositions as described in US20100280151A1 (Nguyen et al., Toray Industries, Inc., 2010) for an amine branched polymer as shell grafted a core polymer polymerized from a polymerizable monomers containing unsaturated carbon-carbon bonds, core-shell rubber particles whose compositions described in EP 1632533A1 and EP 2123711A1 by Kaneka Corporation, and “KaneAce MX” product line of such particle/epoxy blends whose particles have a polymeric core polymerized from polymerizable monomers such as butadiene, styrene, other unsaturated carbon-carbon bond monomer, or their combinations, and a polymeric shell compatible with the epoxy, typically polymethylmethacrylate, polyglycidylmethacrylate, polyacrylonitrile or the alike and similar. “JSR SX” series of carboxylated polystyrene/polydivinylbenzene produced by JSR Corporation. “Kureha Paraloid” EXL-2655 (produced by Kureha Chemical Industry Co., Ltd.), which is a butadiene alkyl methacrylate styrene copolymer; “Stafileid” AC-3355 and TR-2122 (both produced by Takeda Chemical Industries, Ltd.), each of which are acrylate methacrylate copolymers; “PARALOID” EXL-2611 and EXL-3387 (both produced by Rohm & Haas), each of which are butyl acrylate methyl methacrylate copolymers. Examples of known oxide particles include Nanopox® produced by nanoresins AG. This is a master blend of functionalized nanosilica particles and an epoxy.

Thermoplastic resin

[0047] A thermoplastic resin is a non-metallic material that does not undergo a substantial chemical change in its composition when heated and can be repeatedly softened by heating and hardened by cooling. A thermoplastic resin could be a synthetic or natural material generally derived from petrochemicals or natural products. A thermoplastic resin could be, but is not limited to, the following thermoplastic materials such as polyethylene, polypropylene, polyethylene terephthalate, polyvinyl formal, polyamide, polycarbonate, polyacetal, polyphenyleneoxide, poly phenylene sulfide, polyarylate, polyester, polyamideimide, polyimide, polyetherimide, polyimide having phenyltrimethylindane structure, polysulfone, polyethersulfone, polyetherketone, polyetheretherketone, polyaramid, polyethernitrile, polybenzimidazole, their derivatives and their mixtures thereof.

[0048] One could use one or more thermoplastic additives which do not impair the high thermal resistance and high elastic modulus of the resin. The selected thermoplastic additive could be soluble in the resin to a large extent to form a homogeneous mixture. The thermoplastic

additives could be compounds having an aromatic skeleton or a ring structure selected from the group consisting of polysulfones, polyethersulfones, polyamides, polyamideimides, polyimides, polyetherimides, polyetherketones, polyetheretherketones, and polyvinyl formals, their derivatives, similar polymers, and mixtures thereof.

[0049] In another embodiment, the migrating agent is selected from the group consisting of polyethersulfones, polyetherimides and mixtures thereof. Suitable polyethersulfones, for example, may have a number average molecular weight of from about 10,000 to about 75,000.

Interlayer tougheners

[0050] An interlayer toughener is a material located primarily between interlayers of a composite material to maximize damage tolerance and resistance of the composite material. In the embodiments herein, the materials could be thermoplastics, elastomers, or combinations of an elastomer and a thermoplastic, or combinations of an elastomer and an inorganic such as glass. The size of interlayer tougheners is preferably no more than 100 μm , more preferably 10-50 μm to keep them in the interlayer after curing. Such particles are generally employed in amounts of up to about 30%, preferably up to about 15% by weight (based upon the weight of total resin content in the composite composition).

[0051] An example of the thermoplastic materials includes polyamides. Known polyamide particles include SP-500, produced by Toray Industries, Inc., "Orgasole" produced by Atochem, and Grilamid TR-55 produced by EMS-Grivory, nylon-6, nylon-12, nylon 6/12, nylon 6/6, and Trogamid CX by Evonik.

[0052] Another embodiment relates to an interlayer toughener which is a conductive material having an electrical conductivity of at least 10^{-13} S/m, at least 10^{-10} S/m, or even 10^{-5} S/m, a mixture of a conductive material and a non-conductive material having an electrical conductivity of less than 10^{-13} S/m, or a combination thereof. Examples of conductive materials include, but are not limited to, carbonaceous materials (e.g., carbon particles such as Bellpearl by Airwater Inc., carbon back, carbon nanofibers, carbon nanotubes, graphite, graphene, graphene oxide, graphite nanoplatelets), metal particles, metal oxide particles, indium titanium oxides and conductive material coated organic or inorganic particles such as Micropearl® by Sekisui Chemical Co., Ltd. Both the conductive and the non-conductive materials could have a shortest dimension of up to 100 μm , up to 50 μm , or even up to 20 μm .

Fiber reinforced polymer compositions

[0053] A fiber reinforced polymer composition comprising a reinforcing fiber, one or more adhesive compositions of same or different kinds and at least one aforementioned nanofiber sheet, wherein the nanofiber sheets could be located somewhere spatially in the fiber reinforced

polymer composition after cured. The nanofiber sheets can be located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two adhesive composition layers of the same kind or different kinds.

[0054] FIG. 1 shows some examples of spatial location of a nanofiber sheet (3) with respect to a reinforcing fiber layer (1) and an adhesive composition layer (2). The reinforcing fiber layer and/or the nanofiber sheet in configurations 1-3 can be partially or fully impregnated by the adhesive composition. Configuration 1 can be made by impregnating two resin films on a release backing paper of the adhesive composition onto both sides of the dry reinforcing fiber bed by heat and pressure followed by attaching the nanofiber sheet on both sides of the impregnated reinforcing fiber bed. Configuration 3 can be made by attaching the nanofiber sheet onto a film on a release backing paper of the adhesive composition and impregnating the resulting film onto each side of the dry fiber bed by heat and pressure. Configuration 2 can be made by impregnating one film with the nanofiber sheet onto one side of the dry reinforcing fiber bed and another film without the nanofiber sheet onto the other side of the reinforcing fiber bed by heat and pressure. The nanofiber sheet can be attached on the exposed side of the impregnated fiber bed.

[0055] FIG. 2 shows some examples of spatial location of a nanofiber sheet (3) with respect to a reinforcing fiber layer (1) and two layers of two different kinds of adhesive compositions (2, 4). The reinforcing fiber layer and/or the nanofiber sheet in configurations 4-6 can be partially or fully impregnated by the adhesive composition (s). Configuration 4 can be made by impregnating two resin films on a release backing paper of the adhesive composition 2 followed by impregnating two resin films on a release backing paper of the adhesive composition 4 onto both sides of the dry reinforcing fiber bed by heat and pressure. The nanofiber sheet is attached on both sides of the impregnated reinforcing fiber bed. Configuration 5 can be made by impregnating two resin films on a release backing paper of the adhesive composition 2 onto both sides of the dry reinforcing fiber bed by heat and pressure, followed by impregnating two resin films of the adhesive composition 4 containing the nanofiber sheet on both sides of the impregnated reinforcing fiber bed. Configuration 6 can be made by impregnating two resin films on a release backing paper of the adhesive composition 2 containing the nanofiber sheet onto both sides of the dry reinforcing fiber bed by heat and pressure, followed by impregnating two resin films of the adhesive composition 4 on both sides of the impregnated reinforcing fiber bed.

[0056] To make a composite article one of more units of configurations 1-6 or their combinations are stacked in a desired sequence and cured by an external energy source such as heat. Alternatively, dry reinforcing fiber layers, adhesive composition layers and the nanofiber

sheets can be stacked in a sequence with as-shown configurations 1-6, similar configurations, or their combinations and are cured under heat and pressure to make a composite article. In any case, the nanofiber sheet (s) in the cured article can be located between a reinforcing fiber layer and a cured adhesive composition layer or sandwiched between two adhesive composition layers of the same kind or different kinds.

Fabrication techniques for fiber reinforced polymer composition

[0057] For manufacturing a fiber reinforced polymer composition, one embodiment relates to combining an adhesive composition with a reinforcing fiber to produce a curable fiber reinforced polymer composition such as a prepreg that could be subsequently cured to produce a composite. Employable is a wet method in which reinforcing fibers are soaked in a bath of the resin matrix dissolved in a solvent such as methyl ethyl ketone or methanol, and withdrawn from the bath to remove solvent. Nanofibers, nanofiber sheets, or nanofiber prepregs can be applied to the exposed surface of the prepreg such that the nanofibers are aligned at an angle with respect to the reinforcing fiber's axis.

[0058] Another method is hot melt method, wherein an adhesive composition is heated to lower its viscosity, directly applied to a layer of a reinforcing fiber to obtain a resin-impregnated prepreg; or alternatively as another method, the adhesive composition is coated on a release paper to obtain a thin film. One or more adhesive compositions of same or different kinds could be used. Nanofibers, nanofiber sheets, or nanofiber prepregs can be applied to the exposed surface of the adhesive films such that the nanofibers are aligned at an angle with respect to the reinforcing fiber's axis. The nanofiber modified films of one or more different kinds could be consolidated onto both surfaces of the layer of the reinforcing fiber by heat and pressure such that the nanofibers are aligned at an angle with respect to the reinforcing fiber's axis.

Alternatively, films of the adhesive composition could be impregnated onto the dry reinforcing fiber bed, and nanofibers, nanofiber sheets or nanofiber prepregs can be applied to the exposed surface of the impregnated fiber bed such that the nanofibers are aligned at an angle with respect to the reinforcing fiber's axis. The nanofibers could be located in between two films of the same kind or of different kinds, in between the layer of the reinforcing fiber and a film, or on top of the layer of the reinforcing fiber covered by one of the resin compositions. Examples of such prepregs are illustrated in Figures 1-2. Note that other configurations than configurations 1-6 having a symmetrical or unsymmetrical arrangement of adhesive composition layers and nanofiber sheets with respect to the mid-plane of the reinforcing fiber bed could be suitable in the present invention. The reinforcing fiber layer and/or the nanofiber sheet can be partially or fully impregnated by the adhesive composition (s).

[0059] To produce a composite article from the aforementioned prepregs, for example, one or more plies are applied onto to a tool surface or mandrel with a desired stacking sequence. This process is often referred to as tape-wrapping. Heat and pressure are needed to laminate the plies. The tool is collapsible or removed after cured. Curing methods such as autoclave and vacuum bag could be used. However, other suitable methods such as conductive heating, microwave heating, electron beam heating and similar or the alike, can also be employed. In autoclave method pressure is provided to compact the plies, while vacuum-bag method relies on the vacuum pressure introduced to the bag when the part is cured in an oven. Autoclave method could be used for manufacturing high quality composite parts. The nanofiber sheet could be located somewhere spatially in the cured composite part, in between the reinforcing fiber layer and the cured adhesive composition or in between two cured layers of one or more adhesive compositions of the same kind or different kinds.

[0060] Without forming prepregs, an adhesive composition may be directly applied to reinforcing fibers which were conformed onto a tool or mandrel for a desired part's shape, and cured under heat. The methods include, but not limited to, filament-winding, pultrusion molding, resin injection molding and resin transfer molding/resin infusion. One could use resin transfer molding, resin infusion, resin injection molding, vacuum assisted resin transfer molding or the alike or similar. Nanofiber sheets can be applied to the exposed surface of the impregnated reinforcing fibers such that they aligned at an angle with respect to a reinforcing fiber's axis.

[0061] An embodiment relates to resin film infusion to make a composite article in which dry reinforcing fiber layers, adhesive composition layers and the nanofiber sheets can be stacked in a sequence with as-shown configurations 1-6, similar configurations, or their combinations and are cured under heat and pressure to make a composite article. The nanofiber sheet (s) in the cured article can be located between a reinforcing fiber layer and a cured adhesive composition layer or sandwiched between two adhesive composition layers of same or different kinds.

Examination of nanofibers in a cured composite article

[0062] Several methods are known to one skilled in the art to examine and locate the presence of the nanofibers, their distribution, and alignment in a cured composite article. An example is to cut the composite at 90° , 45° or other angles of interest with respected to a fiber's axis to obtain a cross section. The cut cross-section is polished mechanically or by an ion beam such as argon, and examined under any high magnification electron microscopes such as SEM or TEM.

[0063] The sample can also be fractured to expose the fiber's surface and SEM or TEM can be used to document the alignment of these nanofibers with respect to the fiber's axis.

Examples

[0064] The embodiments herein are described in detail by means of the following examples with the following components:

Component	Product name	Manufacturer	Description
Epoxy	ELM434	Sumitomo Chemical Co., Ltd.	Tetra glycidyl diamino diphenyl methane with a functionality of 4, having an average EEW of 120 (ELM434)
	Epon™ 825	Hexion Specialty Chemicals, Inc.	Diglycidyl ether of bisphenol A with a functionality of 2, having an average EEW of 177 (EPON825)
	Epicon 830	Dainippon Ink and Chemicals, Inc.	Diglycidyl ether of bisphenol F with a functionality of 2, having an average EEW of 177 (EPc830)
Thermoplastic resin	Sumika Excel PES5003P	Sumitomo Chemical Co., Ltd.	Polyethersulfone, MW 38,200 (PES1)
	VW-10700RP	Solvay	Polyethersulfone, MW 21,000 (PES2)
Thermoplastic particle	Gilamid TR55	Emzaberk Co.	Polyamide (PA)
Curing agent	ARADUR 9664-1	Huntsman Advanced Materials	4,4'-diaminodiphenyl sulfone (4,4-DDS)
Toughener material	Kane Ace MX416	Kaneka Texas Corporation	25wt% core-shell rubber (CSR) particles having core composition of polybutadiene (CSR) in epoxy
	C S1-25	Arkema	25wt% unfunctionalized multi-wall carbon nanotubes (1-10 um long) in bisphenol A epoxy, solid (rCNT2)
	CNT-X	Toray Industries, Inc.	3wt% MWCNT (1-5 um long) functionalized with epoxy functional group in an epoxy mixture (rCNT1)
	CNT-S1		Nonfunctionalized aligned CNT sheet (aCNT1)

	CNT-S2		Functionalized aligned CNT sheet (aCNT2)
Carbon fiber	T800SC-24K-10E	Toray Industries, Inc.	24,000 fibers, tensile strength 5.9 GPa, tensile modulus 290 GPa, tensile strain 2.0% (T800S-10)
	T800GC-24K-31E	Toray Industries, Inc.	24,000 fibers, tensile strength 5.9 GPa, tensile modulus 290 GPa, tensile strain 2.0%, type-3 sizing for epoxy resin systems (T800G-31).

[0065] CNT-S1 was made as follows. MWCNT forests were synthesized according to a CVD method as follows. A smooth quartz substrate was placed in a horizontal quartz tube furnace. Iron chloride and acetylene gas were used as catalyst and carbon source, respectively. CVD growth was carried out at the furnace temperature of 820C at 10 Torr. Maximum forest height was about 2mm. However, for the following examples a forest height of about 500um was used to draw aligned CNT sheets, which are densified upon contacting a resin film's surface or a prepreg' surface. Multiple CNT sheets can be placed on the resin film to achieve a desired weight fraction.

[0066] Alternatively, an aligned CNT sheet was made by a method such that a CNT sheet drawn from the CNT forest was attached to a release paper on a roller and rotated to form a desired stack of multiple aligned CNT sheets or a web. A solvent such as ethanol or a solvent containing a binder polymer (e.g., 5wt% epoxy in ethanol) was applied to the web to densify CNTs to form an aligned CNT paper. Alternatively, the web can be infused with a polymer or a mixture of polymers by an available method in the art such as resin infusion, vacuum assisted resin infusion, hot-melt, resin transfer molding, vacuum assisted resin transfer molding, pultrusion molding, resin injection molding, the similar and the alike. The CNT paper is ready to be applied on the surface of a resin film or a prepreg.

[0067] CNT-S2 was made in a similar fashion as CNT-S1. Yet, the functionalized CNTs were obtained by either a corona discharge or a plasma method after they were drawn from a CNT forest to make a CNT sheet.

[0068] CNT-X material was made from short length epoxy functionalized MWCNT (Multi-wall carbon nanotubes) of 1-5µm and a mixture of epoxies according to the below recipes in Table 1. Oxidized MWCNT and glycidoxypopyltrimethoxy silane (GPS) were purchased from U.S. Research Nanomaterials and Gelest, respectively. The CNTs were placed in a solution of 3wt%

GPS in methanol/DI water (95/5wt%) and stirred for 90 min. The solids were removed by a centrifuge and redispersed into fresh methanol. The procedure was repeated two times to obtain a final dispersion of epoxy-functionalized CNT in methanol. The dispersion was mixed with the epoxy mixture and methanol was removed under heat and vacuum.

Examples 1-3 and Comparative Examples 1-3

[0069] Examples 1-3 and Comparative Examples 1-3 demonstrate the effects of the CNTs on mechanical and electrical properties of composites without other types of tougheners.

[0070] To make a resin in Comparative Examples 1-3, appropriate amounts of epoxies, CNT and thermoplastic resin as shown in Table 1 were charged into a mixer preheated at 100°C. After charging, the temperature was increased to 160 °C while the mixture was agitated, and held for 1hr. After that, the mixture was cooled to 70 °C and 4,4-DDS was charged. The final resin mixture was agitated for 1 hr, then discharged and some were stored in a freezer.

[0071] To make a prepreg, the hot resin was first casted into a thin film using a knife coater onto a release paper. The film was consolidated onto a bed of fibers on both sides by heat and compaction pressure. A UD prepreg having carbon fiber area weight of about 190g/m² and resin content of about 35% was obtained. The prepregs were cut and hand laid up with the sequence listed in Table 2 for each type of mechanical test, followed an ASTM procedure. Panels were cured in an autoclave at 180°C for 2 hr with a ramp rate of 1.7 °C/min and a pressure of 0.59 MPa.

[0072] The exposed surface of the resin film in Comparative Example 1 was deposited with multiple aligned CNT sheets to obtain the desired weight fraction in Examples 1-2. The CNT modified films were then impregnated onto a fiber bed on both sides such that a substantial amount of CNTs aligned in the fiber's axis to make each corresponding prepreg.

[0073] To make the prepreg of Example 3 CNT sheets were deposited on the prepreg of Comparative Example 1 at the desired weight fraction.

[0074] As shown in Table 1, when aligned CNTs were presented in the composite of Examples 1-3, tensile strength and z-direction conductivity were increased compared to Comparative Example 1 such that the higher the amount of CNT was in the prepreg, the higher the increase in these properties could be observed. Tensile strength improvement could possibly be explained by the alignment of CNTs parallel to the fiber's axis and perhaps shear strength improvement as CNTs reinforced the interphase between the resin and fiber. The effect of CNT alignment could be seen when compared tensile strength with Comparative Examples 2-3 that utilize random CNTs.

[0075] Yet, while G_{IIC} increase was not observed for these cases, G_{IC} seemed to be decreased with non-functionalized CNTs but increased when functionalized CNT were used. Good adhesion between CNTs and the resin in the latter could explain the observation.

Examples 4-7 and Comparative Example 4

[0076] These examples document the synergistic effect of aligned CNTs on fracture toughness when used with other tougheners. Comparative Example 4 is the control.

[0077] Resin mixing procedure was similar to previous examples. However, two pots of resin with and without PA particles were made. PA particles were charged to the resin before adding DDS. Two types of resins films with and without PA particles, designated film #2 and film #1, respectively, were made with the desired area weight to achieve target resin content in the prepreg. To make the prepreg of Comparative Example 4, two films #1 were first impregnated onto both sides of the fiber bed followed by two films #2.

[0078] To make the prepreg of Example 4, multiple aligned CNT sheets were deposited onto the surface of the prepreg of Comparative Example 4 to achieve the desired weight fraction. To make the prepreg of Example 5 or Example 7, multiple aligned CNT sheets were first deposited onto the film #2 to achieve the desired weight fraction and the resulting film was impregnated onto the fiber bed that was already impregnated with the film #1. To make the prepreg of Example 6, multiple aligned CNT sheets were deposited onto the film #1 to achieve the desired weight fraction. It was then impregnated onto a fiber bed followed by impregnation of the film #2.

[0079] Synergistic effects were found on G_{IIC} of the composites when aligned CNTs were present with PA particles in the interlayer. A substantial improvement was observed with higher amount of CNTs. This could be explained that the presence of CNT sheets helped confine crack growth in the interlayer. There was not a significant effect of location of CNT sheets with respect to the fiber bed on G_{IIC} .

[0080] It was anticipated that with the presence of CNTs in the interlayer, this layer became conductive and therefore promoted z-direction electrical conductivity substantially, compared to the control.

Examples 8-10 and Comparative Example 5

[0081] These examples document the synergistic effect of aligned CNTs on fracture toughness when used with both intralayer and interlayer tougheners. Comparative Example 5 is the control. Resins and prepregs were made in a similar fashion as previous examples.

[0082] With the presence of CNT sheets significant synergistic effects were observed on many observed properties of the corresponding composites.

[0083] The above description is presented to enable a person skilled in the art to make and use the invention, and is provided in the context of a particular application and its requirements.

Various modifications to the embodiments will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the invention. Thus, this invention is not intended to be limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein.

[0084] This application discloses several numerical range limitations. The numerical ranges disclosed inherently support any range within the disclosed numerical ranges though a precise range limitation is not stated verbatim in the specification because this invention can be practiced throughout the disclosed numerical ranges. Finally, the entire disclosure of the patents and publications referred in this application are hereby incorporated herein by reference.

Table 1

		Example										Comparative Example				
		1	2	3	4	5	6	7	8	9	10	1	2	3	4	5
Resin formulation	Epoxy (phr)	ELM434	60	60	60	60	60	60	60	60	60	60	60	60	60	60
		EPON825	20	20	20	20	20	20	20	20	20	20	20	20	20	20
		EPe830	20	20	20	20	20	20	20	20	20	20	20	20	20	20
	Nanofiber (wt%) in resin	rCNT1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9	0.0	0.0
		rCNT2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9	0.0	0.0	0.0
		aCNT1	1.0	3.9	0.0	1.0	3.9	3.9	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		aCNT2	0.0	0.0	5.0	0.0	0.0	0.0	0.0	5.0	10.0	0.0	0.0	0.0	0.0	0.0
	Curing agent (phr)	4,4-DDS	45	45	45	45	45	45	45	45	45	45	45	45	45	45
	Toughener (phr)	CSR	0	0	0	0	0	0	5	5	5	0	0	0	0	5
	Thermoplastic resin (phr)	PES1 (5003P)	0	0	6	0	0	0	6	6	6	0	0	0	0	6
Fiber (wt%)		PES2 (10700)	12	12	0	12	12	12	0	0	0	12	12	12	12	0
	Optional (phr)	PA	0	0	0	30	30	30	30	30	30	0	0	0	30	30
	Type-1 sizing	T800S-10	100	100	100	100	100	100	0	0	0	100	100	100	100	0
	Type-3 sizing	T800G-31	0	0	0	0	0	0	100	100	100	0	0	0	0	100
Prepreg	CNT Location **	S1	S1	S3	S3	S2	S1	S2	S2	S3	S3	-	-	-	-	-
Composite properties	Tensile	Strength* (ksi)	415	440	460	425	444	450	400	417	415	400	412	392	405	380
	Fracture toughness	G _{IC} (lb.in/in ²)	1.4	0.8	3.3	1.1	1.3	0.5	3.5	4.0	4.5	2.6	1.1	2.3	2.6	3.0
		G _{IIIC} (lb.in/in ²)	4.5	4.3	4.8	11.0	15.6	17.7	20.0	19.5	19.5	4.4	3.5	4.6	11.1	11.1
	z-direct conductivity (S/m)		2.3	3.0	3.5	0.8	1.1	1.0	1.2	1.3	1.3	2.0	4.4	5.0	0.5	0.5

* Normalized to V_f = 60%

** S1=between fiber layer and resin layer (e.g., configuration #3 or #6); S2=between two resin layers (e.g., configuration #5); S3= on prepreg surface (e.g., configuration #1 or #4)

Table 2

Test Panel	Test method	Panel Size (mm x mm)	Ply Lay-up Configuration	Test Condition
0deg-Tensile	ASTM D 3039	300 x 300	(0) ₆	RTD
DCB (for G _{IC})	ASTM D 5528	350 x 300	(0) ₂₀	RTD
ENF (for G _{IIc})	JIS K 7086*	350 x 300	(0) ₂₀	RTD
z-conductivity	(4-point probe)**	300x300	(0) ₁₆	RTD

* Japanese Industrial Standard Test Procedure

**Z-direction conductivity measurement. 25 mm x 25 mm coupons ($W_1 \times W_2$) are prepared from the panel. Both top and bottom surfaces of a coupon are polished mechanically to remove the top layers up to 50 μ m and the coupon's thickness (t) is determined. A silver paint (Dotite D-550) is painted on polished surfaces, followed by applying a 25-mm wide copper tape (3M 1181). The volumetric resistivity (RV) is determined from the below. Electrical conductivity is $1/RV$ where R is the resistance measured by a digital multimeter with four probe method between the top and bottom surfaces of the coupon (Advantest R6581)

$$RV = \frac{W_1 \times W_2}{t} \times R$$

What is claimed is:

1. A fiber reinforced polymer composition comprising an adhesive composition, a reinforcing fiber, and at least a nanofiber sheet comprising nanofibers, wherein the nanofiber sheet is in a plane parallel to the reinforcing fiber.
2. The fiber reinforced polymer composition of claim 1, wherein the adhesive composition comprises the nanofiber sheet and/or the nanofibers.
3. The fiber reinforced polymer composition of claim 2, wherein the nanofibers are carbon nanotubes, carbon nanofibers, carbonaceous nanofibers, organic nanofibers, inorganic nanofibers, metal nanofibers, oxide nanofibers, composite nanofibers of the aforementioned nanofibers and a polymer, or combinations thereof.
4. The fiber reinforced polymer composition of claim 3, wherein the nanofibers comprise carbon nanotubes.
5. The fiber reinforced polymer composition of claim 1, wherein an alignment angle between the nanofibers and the reinforcing fibers is greater than zero degree and up to 90 degrees.
6. The fiber reinforced polymer composition of claim 5, wherein an alignment angle between the nanofibers and the reinforcing fibers is less than about 20 degrees.
7. The fiber reinforced polymer composition of claim 1, wherein the adhesive composition comprises at least a thermosetting resin and a curing agent.
8. The fiber reinforced polymer composition of claim 7, wherein the adhesive composition comprises further at least one of an accelerator, a thermoplastic resin, a toughener, an interlayer toughener, or a combination thereof.

9. The fiber reinforced polymer composition of claim 1, wherein the adhesive composition comprises at least a thermoplastic resin.
10. The fiber reinforced polymer composition of claim 1, wherein the nanofiber sheet is located spatially at least one of locations between a layer of the reinforcing fibers and a layer of the adhesive composition, between two adhesive composition layers of a same or different kinds, between two reinforcing fiber layers of a same or different kinds, or on one or both surfaces of the layer of the reinforcing fibers impregnated by the adhesive composition, wherein at least one of the reinforcing fiber or the nanofiber is dry or partially or fully impregnated by the adhesive composition.
11. The fiber reinforced polymer composition of claim 10, wherein the fiber reinforced polymer composition comprises a prepreg.
12. A method of manufacturing a fiber reinforced polymer composition comprising impregnating one or more adhesive films of the same kind or different kinds onto one side or both sides of a reinforcing fiber layer comprising a plurality of the reinforcing fibers, wherein at least one of the one or more the adhesive films comprises one or more nanofiber sheets comprising a substantial amount the nanofibers that are in a plane parallel to the reinforcing fiber and are aligned at an alignment angle with respect to the reinforcing fiber's axis on one side or both sides of the one or more adhesive films, wherein the nanofibers are sandwiched between two adhesive films, between one side of the reinforcing fiber layer and one adhesive film, on an exposed surface of the impregnated reinforcing fiber by the adhesive composition, or combinations thereof.
13. A method of manufacturing the fiber reinforced polymer composition of claim 12, wherein the nanofibers comprise carbon nanotubes.
14. A method of manufacturing a fiber reinforced polymer composition comprising impregnating one or more adhesive films of the same kind or different kinds onto one

side or both sides of a reinforcing fiber layer comprising a plurality of the reinforcing fibers, and applying one or more nanofiber sheets on one or more exposed surfaces of the impregnated reinforcing fiber by the adhesive composition such that a substantial amount of the nanofibers are aligned at an alignment angle with respect to the reinforcing fiber's axis.

15. A method of manufacturing the fiber reinforced polymer composition of claim 14, wherein the nanofibers comprise carbon nanotubes.
16. A method of manufacturing a composite article comprising curing the fiber reinforced polymer composition of claim 1, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.
17. A method of manufacturing a composite article comprising curing the fiber reinforced polymer composition of claim 8, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.
18. A method of manufacturing a composite article comprising curing the fiber reinforced polymer composition of claim 11, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.
19. A method of manufacturing a composite article comprising curing the prepreg of claim 13, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.

20. A method of manufacturing a composite article comprising curing the prepreg of claim 15, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer or sandwiched between two cured adhesive composition layers of the same kind or different kinds.
21. A method of manufacturing a composite article comprising stacking at least a reinforcing layer, an adhesive composition layer, and a nanofiber sheet comprising a substantial amount of the nanofibers that are in a plane parallel to the reinforcing fiber and are aligned at an alignment angle with respect to the reinforcing fiber's axis in a symmetrical or unsymmetrical sequence with respect to the mid-plane of the stack such that the nanofiber sheet is located at least one of locations between two reinforcing fiber layers of the same kind or different kinds, between one reinforcing layer and one adhesive composition layer or in between two adhesive composition layer of the same kind or different kinds, and curing the stack, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured adhesive composition layer, or sandwiched between two cured adhesive composition layers of the same kind or different kinds.
22. A method of manufacturing a composite article comprising stacking a reinforcing layer impregnated with at least one adhesive composition and a nanofiber sheet comprising a substantial amount of the nanofibers that are in a plane parallel to the reinforcing fiber and are aligned at an alignment angle with respect to the reinforcing fiber's axis in a symmetrical or unsymmetrical sequence with respect to the mid-plane of the stack, and curing the stack, wherein the nanofiber sheet in the cured article is located between the reinforcing fiber layer and the cured at least one adhesive composition layer, or sandwiched between two cured adhesive composition layers of the same kind or different kinds.
23. The fiber reinforced polymer composition of claim 1, wherein a substantial amount of nanofibers that are aligned in a direction.

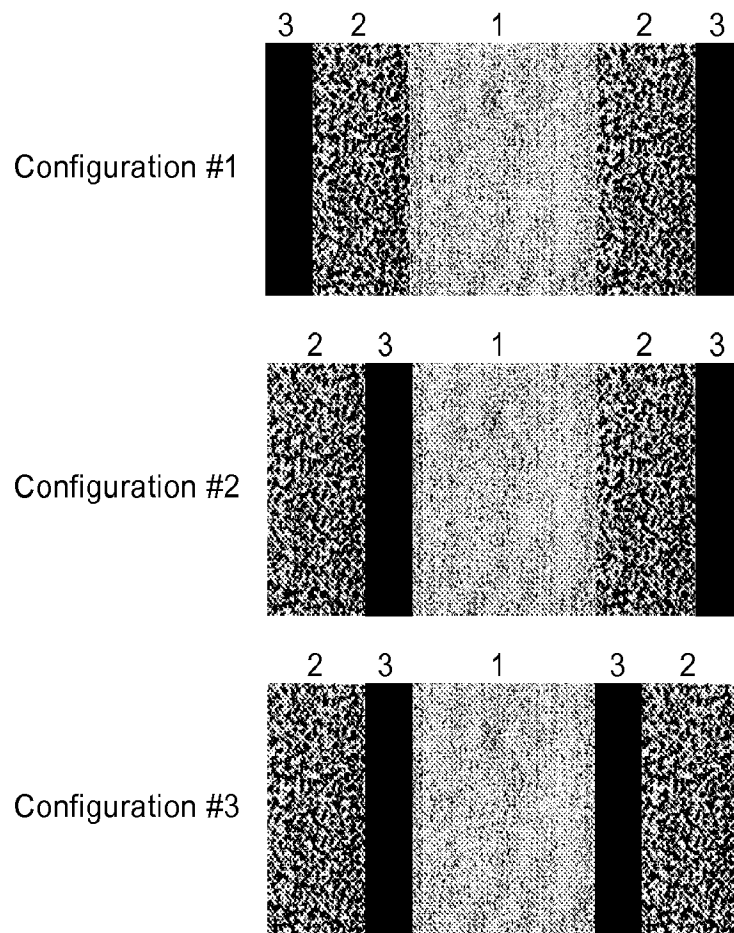


FIG. 1

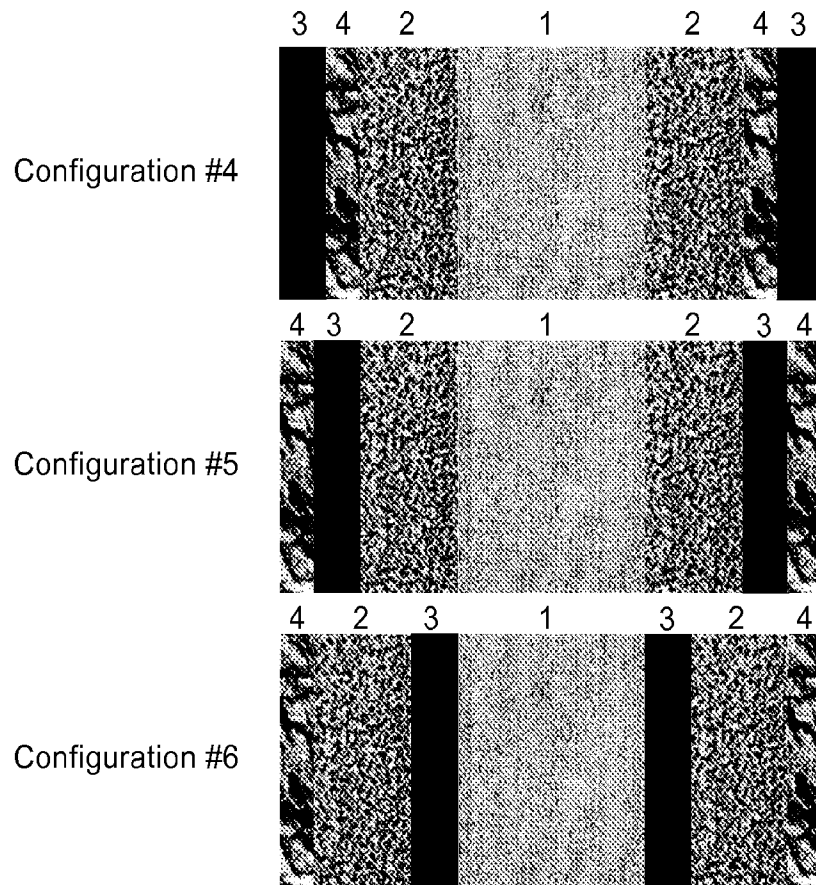


FIG. 2