

# Mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials

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## Abstract

Introducing a uniform distribution of carbon nanotubes into a polymer matrix can yield property enhancements that go beyond that of a simple rule of mixtures. The challenge is to take full advantage of the exceptional properties of carbon nanotubes in the composite material. Carbon nanotubes are ideal reinforcing material for polymer matrices due to their remarkable properties. However, property improvements are not significant due to poor interfacial bonding and severe agglomeration. The present study is focused primarily upon the mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials. The polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites. The effect of hybrid material weight fraction on the modulus of elasticity and hardness is evaluated. Stress-strain responses of the composite tensile deformation are illustrated and the effect of strain on the bond order parameters is investigated. The present study aims to explore how to effectively improve the mechanical properties of polymers by utilizing graphene-carbon nanotube hybrid materials. Particular emphasis is placed upon the effect of weight fraction on the mechanical properties of polymer composites reinforced with graphene and carbon nanotubes. The results indicate that graphene-carbon nanotube multi-stack three-dimensional architectures can overcome the limitations and restricted performance typically encountered with carbon-based materials by using the combined strategies of three-dimensional architecture and low-dimensional nanomaterial characteristics. Poor dispersibility greatly affects the characteristics of the polymer composites. The modulus of elasticity of the polymer composite is enhanced as compared to the neat polymer. The hybrid material exhibits great improvements in hardness and yield strength and major deteriorations in strain at break. The carbon nanotubes exhibit no preferred orientation and are approximately random. The doping permanently increases the charge concentration in semiconducting carbon nanotubes present in the film, thereby decreasing the sheet resistance of the network. The ability to strengthen polymers is limited by the strength of interfacial bonding. The polymer composite differs from a conventional carbon-fiber composite where there is a much higher interface area between reinforcing carbon and polymer matrix phases.

**Keywords:** Graphene; Carbon; Composites; Polymers; Fibers; Hardness

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## 1. Introduction

Carbon nanotubes can be classified by the number of walls in the tube, single-wall, double wall and multi-wall. Each wall of a carbon nanotube can be further classified into chiral or non-chiral forms. Carbon nanotubes are currently manufactured as agglomerated nanotube balls or bundles [1, 2]. Use of carbon nanotubes and graphene as enhanced performance additives in batteries is predicted to have significant utility for electric vehicles, and electrical storage in general. However, utilization of carbon nanotubes in these applications is hampered due to the general inability to reliably produce individualized carbon nanotubes [3, 4]. Single-walled carbon nanotubes are a novel form of carbon. They are closed-caged, cylindrical molecules, approximately 0.5 to 3 nanometers in diameter and a few hundred nanometers long [5, 6]. They are known for their excellent electrical and thermal conductivity and high tensile strength [7, 8]. Since their discovery in 1993, there has been substantial research to describe their properties and develop applications using them [9, 10]. From unique electronic properties and a thermal conductivity higher than diamond to mechanical properties where the stiffness, strength and resilience exceeds any current material, carbon nanotubes offer tremendous opportunities for the development of fundamentally new material systems.

Utilization of carbon nanotubes in conductors has been attempted [11, 12]. However, the incorporation of carbon nanotubes into polymers at high enough concentrations to achieve the desired conductivity typically increases viscosities of the compound containing the carbon nanotubes to very high levels [13]. The result of such a high viscosity is that conductor fabrication is difficult [14]. A typical example of a high concentration is one percent, by weight, of carbon nanotubes mixed with a polymer [15, 16]. Currently, there are no fully developed processes for fabricating wires based on carbon nanotubes [17, 18], but co-extrusion of carbon nanotubes within thermoplastics is being contemplated, either by pre-mixing the carbon nanotubes into the thermoplastic or by coating thermoplastic particles with carbon nanotubes prior to extrusion [19, 20]. Application of carbon nanotubes to films has been used extensively, but not to wires [21, 22]. Utilization of carbon nanotubes with thermosets has also been widely studied in recent years [23, 24]. However, thermosets are crosslinked and cannot be melted at an elevated temperature [25, 26]. Finally, previous methods for dispersion of carbon nanotubes onto films have not focused on metallic carbon nanotubes in order to maximize current-carrying capability or high conductivity [27, 28]. The above-mentioned proposed methods

for fabricating wires that incorporate carbon nanotubes will encounter large viscosities, due to the large volume of carbon nanotubes compared to the overall volume of carbon nanotubes and the polymer into which the carbon nanotubes are dispersed. Another issue with such a method is insufficient alignment of the carbon nanotubes. Finally, the proposed methods will not produce the desired high concentration of carbon nanotubes.

The use of high-performance, fiber-reinforced composites has expanded substantially in recent years [29, 30], as improvements in these composites have allowed them to meet the final performance requirements of advanced material systems [31, 32]. For example, extensive research and development in carbon fiber-reinforced composites has led to significant improvements in the properties of these composites [31, 32], such as in-plane mechanical properties [33, 34]. Furthermore, composites formed using two-dimensional and three-dimensional woven fiber reinforcements can be formed into the final net shapes [35, 36]. However, the out-of-plane properties of fiber-reinforced composites remain problematically low [37, 38]. Out-of-plane properties are dominated by the matrix surrounding the reinforcing fibers, which is relatively weak compared to the fibers [37, 38]. Additionally, fiber-reinforced composites generally possess matrix-rich regions within the interlaminar region between the fibers [39, 40], and these regions have proven difficult to reinforce with fiber reinforcements [41, 42]. As a result, cracks may easily initiate and propagate under load within these regions, leading to composite failure [43, 44]. Therefore, there exists a continued need for improved reinforcements for composite materials so as to form hybrid carbon nanotube fiber reinforcements by depositing of carbon nanotubes on fiber substrates.

Introducing a uniform distribution of carbon nanotubes into a polymer matrix can yield property enhancements that go beyond that of a simple rule of mixtures. The challenge is to take full advantage of the exceptional properties of carbon nanotubes in the composite material. Carbon nanotubes are ideal reinforcing material for polymer matrices because of their high aspect ratio, low density, remarkable mechanical properties, and good electrical and thermal conductivity. However, property improvements are not significant to date, apparently due to poor interfacial carbon nanotube-polymer bonding and severe carbon nanotube agglomeration. The present study is focused primarily upon the mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials. The graphene-carbon nanotube fiber-reinforced polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes. The effect of the hybrid material weight fraction on the modulus of elasticity and hardness is evaluated for the fiber-reinforced polymer composite. Stress-strain responses of the composite tensile deformation are illustrated and the effect of strain on the bond order parameters of the tensile deformation is investigated for the fiber-reinforced polymer composite. The present study aims to explore how to effectively improve the mechanical properties of polymers by utilizing graphene-carbon nanotube hybrid materials. Particular emphasis is placed upon the effect of weight fraction on the mechanical properties of polymer composites reinforced with graphene and carbon nanotubes.

## 2. Experimental methods

A method of fabrication of graphene-carbon nanotube stacks includes the steps of depositing a first graphene layer on a metal foil, transferring the first graphene layer to a current collector, depositing a first layer of a catalytic metal on the first graphene layer, alternately depositing graphene and catalytic metal layers one upon the other so as to form a stack of alternating graphene and catalytic metal layers on the first graphene and catalytic metal layers, transforming the catalytic metal layers into arrays of metal nanoparticles by thermal breakdown of the catalytic metal layers, and precipitating carbon nanotube outward from the metal nanoparticles. The carbon nanotubes are precipitated in a single execution of the precipitating carbon nanotube outward from the metal nanoparticles step, resulting in simultaneous growth of the carbon nanotubes and expansion of the graphene-carbon nanotube stack. The catalytic metal is a transition metal, for example, nickel. The graphene layers are formed by a chemical vapor deposition process. The carbon nanotubes are formed by a chemical vapor deposition process. The catalytic metal layers are formed by a physical vapor deposition process.

The carbon nanotubes may be any length, diameter, or chirality as produced by any of the various production methods [45, 46]. The chirality of the carbon nanotubes is such that the carbon nanotubes are metallic, semi-metallic, semiconducting or combinations thereof [47, 48]. Carbon nanotubes may include, but are not limited to, single-walled carbon nanotubes, double-walled carbon nanotubes, multi-walled carbon nanotubes, shortened carbon nanotubes, oxidized carbon nanotubes, functionalized carbon nanotubes, purified carbon nanotubes, metalized carbon nanotubes and combinations thereof. The carbon nanotubes may be pristine or functionalized. Functionalized carbon nanotubes, as used herein, refer to any of the carbon nanotubes types bearing chemical modification, physical modification or combination thereof. Such modifications can involve the carbon nanotube ends, sidewalls, or both. Illustrative chemical modifications of carbon nanotubes include, for example, covalent bonding and ionic bonding. Illustrative physical modifications include, for example, chemisorption, intercalation, surfactant interactions, polymer wrapping, solvation, and combinations thereof. Unfunctionalized carbon nanotubes are typically isolated as aggregates referred to as ropes or bundles, which are held together through van der Waals forces. The carbon nanotube aggregates are not easily dispersed or solubilized. Chemical modifications, physical modifications, or both can provide individualized carbon nanotubes through disruption of the van der Waals forces between the carbon nanotubes. As a result of disrupting van der Waals forces, individualized carbon nanotubes may be dispersed or solubilized.

Unfunctionalized carbon nanotubes may be used as-prepared from any of the various production methods, or they may be further purified. Purification of carbon nanotubes typically refers to, for example, removal of metallic impurities, removal of non-nanotube carbonaceous impurities, or both from the carbon nanotubes. Illustrative carbon nanotube purification methods include, for example, oxidation using oxidizing acids, oxidation by heating in air, filtration and chromatographic separation. Oxidative purification methods remove non-nanotube carbonaceous impurities in the form of carbon dioxide. Oxidative purification of carbon nanotubes using oxidizing acids further results in the formation of oxidized, functionalized carbon nanotubes, wherein the closed ends of the carbon nanotube structure are oxidatively opened and terminated with a plurality of carboxylic acid groups. Oxidative purification methods using an oxidizing acid further result in removal of metallic impurities in a solution phase. Depending on the length of time oxidative purification using oxidizing acids is performed, further reaction of the oxidized, functionalized carbon nanotubes results in shortening of the carbon nanotubes, which are again terminated on their open ends by a plurality of carboxylic acid groups. The carboxylic acid groups in both oxidized, functionalized carbon nanotubes and shortened carbon nanotubes may be further reacted to form other types of functionalized carbon nanotubes. For example, the carboxylic acids groups may be reacted to form esters or amides, or they may be reacted in condensation polymerization reactions to form polymers having the carbon nanotubes bound to the polymer chains. Condensation polymers include, for example, polyesters and polyamides.

Functionalized graphene-carbon nanotubes may also be incorporated into polymers using standard polymerization techniques [49, 50]. The functionalized graphene-carbon nanotubes may be dispersed in the polymer and not covalently bound to the polymer chains [51, 52]. Alternately, the functionalized graphene-carbon nanotubes may be dispersed in the polymer and covalently bound to the polymer chains. For example, amino-functionalized graphene-carbon nanotubes may react with epoxy resins through their amino groups. Amino-functionalized graphene-carbon nanotubes are formed by peroxide-mediated introduction of carboxylic acid groups on sidewalls of pristine graphene-carbon nanotubes, followed by amide-functionalization using a diamine. Similarly, fluorinated graphene-carbon nanotubes may react with amino groups of epoxies curing agents to displace fluorine and form a cross-linked epoxy polymer covalently bound to the graphene-carbon nanotubes. Fluorinated graphene-carbon nanotubes are prepared by direct sidewall fluorination of graphene-carbon nanotubes using elemental fluorine. The particular type of functionalized graphene-carbon nanotubes utilized in the various cases herein may be varied across a wide range of functionality. For example, desired solubility or reactivity properties of the functionalized graphene-carbon nanotubes will dictate the choice of functionalized graphene-carbon nanotube type utilized in the various cases herein. The process comprises the steps: providing a porous mat comprising graphene-carbon nanotubes having an average longest dimension in the range of 2 micron to 2000 microns, wherein at least a portion of the graphene-carbon nanotubes are entangled; contacting the mat with one or more condensation polymer precursors, and optionally a catalyst;

polymerizing the one or more polymer precursors in the presence of the mat at a temperature in the range of about 180 °C to about 360 °C to form a nonporous fiber-reinforced polymer composite comprising a mat of graphene-carbon nanotubes embedded in a condensation polymer produced from the polymer precursors, wherein the graphene-carbon nanotubes are present in the composite in an amount ranging from about 0.08 weight percent to about 80 weight percent, based on the weight of the graphene-carbon nanotubes and the condensation polymer; and curing the graphene-carbon nanotube fiber-reinforced polymer composite.

The graphene-carbon nanotube fiber-reinforced polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes. In particular, the graphene-carbon nanotube fiber-reinforced polymer composites provide increased resistance to tension-tension and tension-compression fatigue failure compared to conventional fiber-reinforced polymer composites. Inclusion of graphene-carbon nanotubes at the fiber-matrix interface in graphene-carbon nanotube fiber-reinforced polymer composites provides advantageous resistance to polymer matrix cracking, longitudinal cracking along the fiber-matrix interface, and fiber delamination, all of which are dominant failure mechanisms in conventional fiber-reinforced polymer composites. Thus, the graphene-carbon nanotube fiber-reinforced polymer composites provide a nanotechnology solution to mitigating the evolution of failure mechanisms and extending failure lifetimes under fatigue loading. The graphene-carbon nanotube fiber-reinforced polymer composites include a fiber component, a polymer matrix component, and a quantity of graphene-carbon nanotubes. The polymer matrix component and the fiber component form a fiber-matrix interface. The quantity of graphene-carbon nanotubes coats at least a portion of the fiber component. The fiber-matrix interface further includes the portion of graphene-carbon nanotubes.

Normal fatigue crack progression is suppressed at the fiber-matrix interface where graphene-carbon nanotubes are present. Since fatigue crack progression leads to fiber-matrix longitudinal delamination, the graphene-carbon nanotubes enhance fatigue lifetime under both quasi-static and cyclical fatigue loading conditions. Controlled laboratory testing conditions are used to evaluate the benefits of graphene-carbon nanotube fiber-reinforced polymer composites over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes coating the fiber component. As an initial test of the graphene-carbon nanotube fiber-reinforced polymer composites, the tensile strength and tensile stiffness of graphene-carbon nanotube fiber-reinforced polymer composites and fiber-reinforced polymer composites are evaluated and compared. Testing is conducted by ASTM testing methods ASTM D3039 and ASTM D3039M-17. Graphene-carbon nanotube fiber-reinforced polymer composites utilized in the tensile strength and tensile stiffness studies contain about 0.2 to about 0.8 weight percent graphene-carbon nanotubes coating the carbon fibers. Both tensile stiffness and tensile strength are improved in the graphene-carbon nanotube fiber-reinforced polymer composites, particularly at higher weight percentages of graphene-carbon nanotubes. The improvement for both mechanical properties vary depending on the quantity of graphene-carbon nanotubes used to coat the carbon fibers.

### 3. Results and discussion

The low-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 1 for the production of fiber-reinforced polymer composites. From a mechanical point of view, carbon nanotubes exhibit excellent rigidity, comparable to steel, while being extremely light. In addition, they exhibit excellent electrical and thermal conductivity properties which make it possible to envisage using them as additives to confer these properties on various, particularly macromolecular, materials such as polyamides, polycarbonate, polyesters, polystyrene, and polyethyleneimine, as well as other thermoplastic and thermoset polymers. Carbon-based materials are widely used due to their mechanical and chemical stability, excellent intrinsic electrical conductivity, and large surface area. Graphene-carbon nanotube multi-stack three-dimensional architectures can overcome the limitations and restricted performance typically encountered with carbon-based materials by using the combined strategies of three-dimensional architecture and low-dimensional carbon nanomaterial characteristics. Such graphene-carbon nanotube stacks have one or more of the following characteristics: graphene and carbon nanotubes are active materials that

have unique electrical properties, particularly high surface area and high electrical conductivity, the carbon nanotube array of the graphene- carbon nanotube stack acts as a spacer to prevent graphene self-aggregation, maintaining a large active surface area, and stable electrical and mechanical contact is generated between carbon nanotube and graphene due to the direct growth of carbon nanotube between the graphene layers. A graphene-carbon nanotube stack may be fabricated by sequentially developing a stack of alternating graphene and catalytic metal layers, breaking down the metal layers into catalytic nanoparticles, and causing the simultaneous growth of the carbon nanotube between the graphene layers at the sites of the catalytic nanoparticles and the expansion of the graphene-carbon nanotube stack. The growth tube furnace chemical vapor deposition method is adapted to grow graphene. Graphene synthesis begins when the carbon feedstock is introduced into the furnace tube, where it thermally decomposes into carbon and hydrogen radicals in the presence of the catalyst. In the case of copper, growth is limited to the surface of the metal. The dissociated carbon species diffuse across the surface of the metal, where they nucleate as seeds which grow and coalesce to form a continuous graphene film.

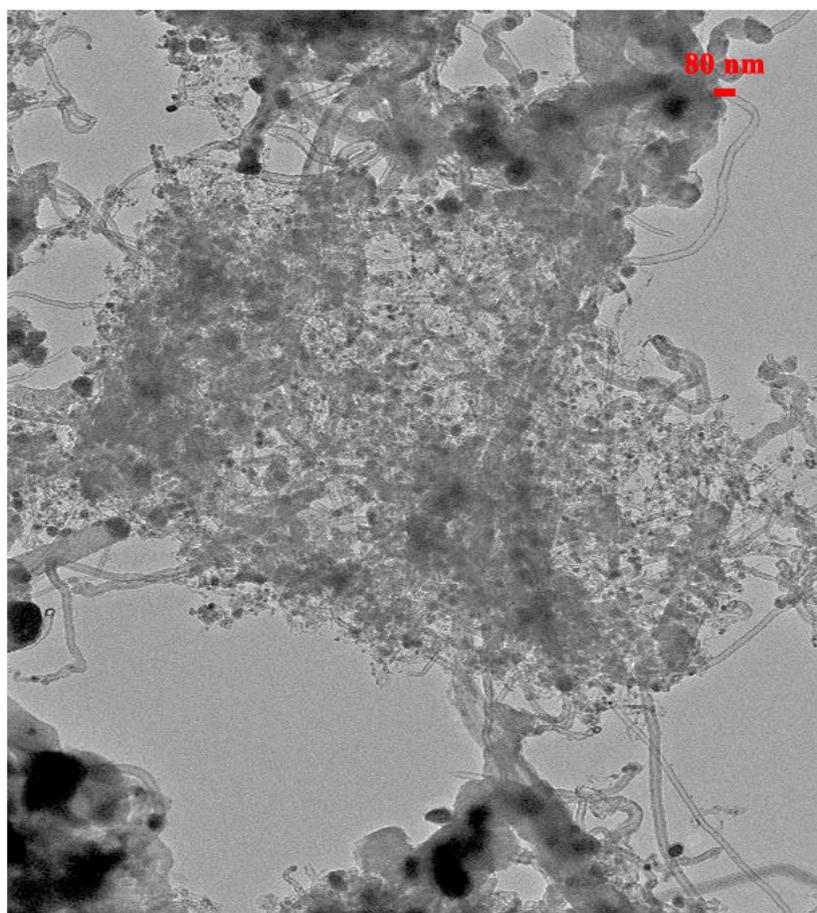


Figure 1. Low-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The high-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 2 for the production of fiber-reinforced polymer composites. The porous mat comprising graphene-carbon nanotubes is contacted with one or more condensation polymer precursors, and optionally

a catalyst. Under polymerization conditions, the condensation polymer precursors undergo in situ polymerization to produce a condensation polymer which forms the polymer component of the graphene-carbon nanotube fiber-reinforced polymer composite. As the polymerization step is performed in the presence of the mat, the mat of entangled graphene-carbon nanotubes maintains its nanostructured sheet form and becomes embedded in the condensation polymer, and a nonporous graphene-carbon nanotube fiber-reinforced polymer composite is formed. The composite is nonporous as a result of the condensation polymer occupying the openings previously present between adjacent graphene-carbon nanotubes, or between adjacent ropelike structures of graphene-carbon nanotubes, within the mat. The condensation polymer precursors are polymerized in the presence of the mat under suitable polymerization conditions to form a nonporous fiber-reinforced polymer composite comprising a mat of graphene-carbon nanotubes embedded in the condensation polymer produced from the polymer precursors. Suitable polymerization conditions include sufficient pressure, temperature, time, and other process conditions for polymerization of the polymer precursors to occur. Suitable polymerization conditions can include addition of a catalyst. The poor dispersibility of graphene-carbon nanotubes greatly affects the characteristics of the composites which they form with the polymer matrices into which they are introduced. There is observed in particular the appearance of nano-cracks, formed in aggregates of graphene-carbon nanotubes, which lead to the composite becoming fragile. Moreover, since graphene-carbon nanotubes are poorly dispersed, it is necessary to increase their amount in order to reach a given electrical and thermal conductivity, which has the effect of increasing the viscosity of the mixture for manufacturing the composite, leading to self-heating of this mixture which may result in degradation of the polymer and a reduction in productivity. Thermal properties refer to a material's response to applied heat. Non-limiting examples include thermal conductivity, thermal diffusivity, coefficient of thermal expansion, emissivity, specific heat, melting point, glass transition temperature, boiling point, flash point, triple point, heat of vaporization, heat of fusion, pyrophoricity, autoignition temperature, and vapor pressure.

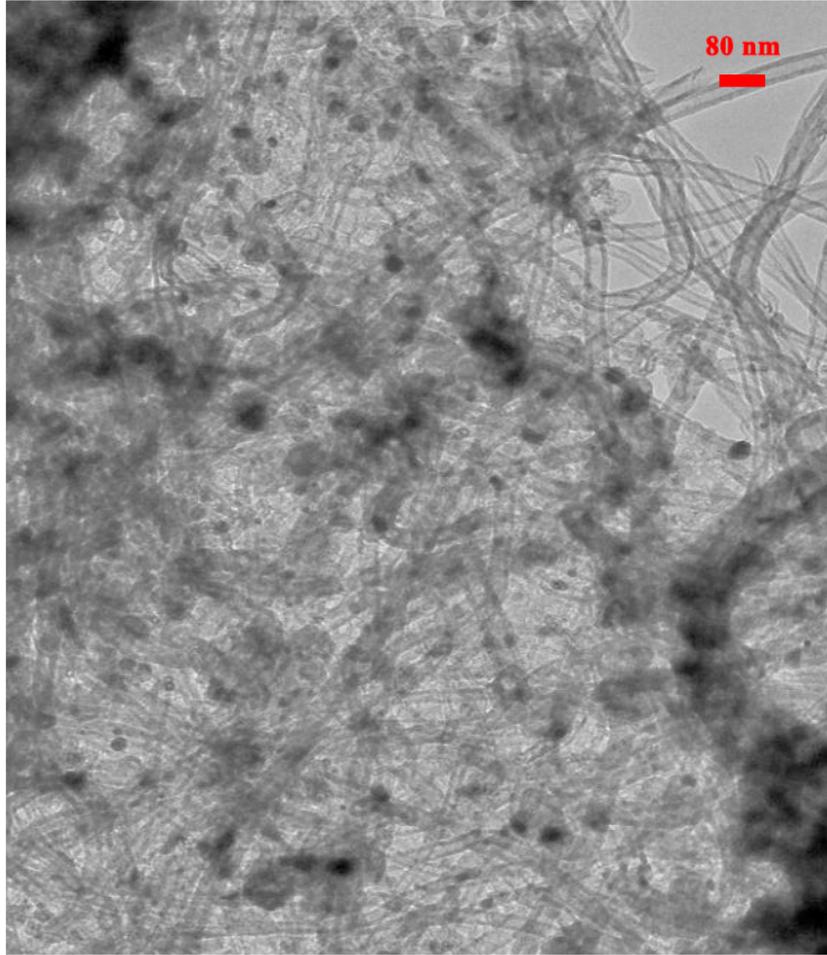


Figure 2. High-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The effect of the weight fraction of the graphene-carbon nanotube hybrid material on the modulus of elasticity is illustrated in Figure 3 for the fiber-reinforced polymer composite. Intense research has been focused on polymer nanocomposites because of their potential to dramatically enhance properties relative to neat polymer and to yield multifunctional materials [53, 54]. Carbon nanotubes have been extensively studied as nanofillers because of their low density, high aspect ratio, and excellent mechanical, electrical, and thermal properties [55, 56]. However, major challenges remain in the development of polymer-carbon nanotube nanocomposites, especially as related to carbon nanotube dispersion via industrially scalable, environmentally friendly methods and understanding the relationship between dispersion and optimum properties [57, 58]. Several strategies have been studied to achieve well-dispersed polymer-carbon nanotube nanocomposites, including melt mixing, polymer-carbon nanotube blending in solvent, and in situ polymerization [59, 60]. Use of melt mixing alone often leads to limited carbon nanotube dispersion in polymer. Blending polymer and in situ polymerization methods can lead to better dispersion, but the former is not environmentally friendly and both methods have limited applicability and scalability. One or more mechanical or physical properties of the graphene-carbon nanotube fiber-reinforced polymer composite are enhanced, including but not limited to increased Young's modulus and increased yield strength, electrical conductivity, thermal stability and crystallization rate, as compared to the corresponding neat polymer. For example, the modulus

of elasticity of the composite is enhanced as compared to the corresponding neat polymer. The method of preparing the composite comprises providing a polymer component and a graphene-carbon nanotube mixture; applying a mechanical energy thereto through solid-state shear pulverization in the presence of cooling at least partially sufficient to maintain such a polymer component in a solid state, such pulverization at least sufficient to provide a pulverization product comprising a graphene-carbon nanotube component at least partially homogeneously dispersed therein; and melt-mixing such a pulverization product, to provide a graphene-carbon nanotube fiber-reinforced polymer composite. Crystallization kinetic effect can be selected from increased rate of isothermal crystallization and decreased distribution of crystallization time. Solid-state shear pulverization and melt-mixing can be at least partially sufficiently to affect a mechanical and physical property of such a mixture, such a property as can be selected from Young's modulus, yield strength, electrical conductivity, and thermal stability. Dispersion can be characterized by field-emission scanning electron microscopy and the absence of agglomeration at micron-length scales under microscopy conditions.

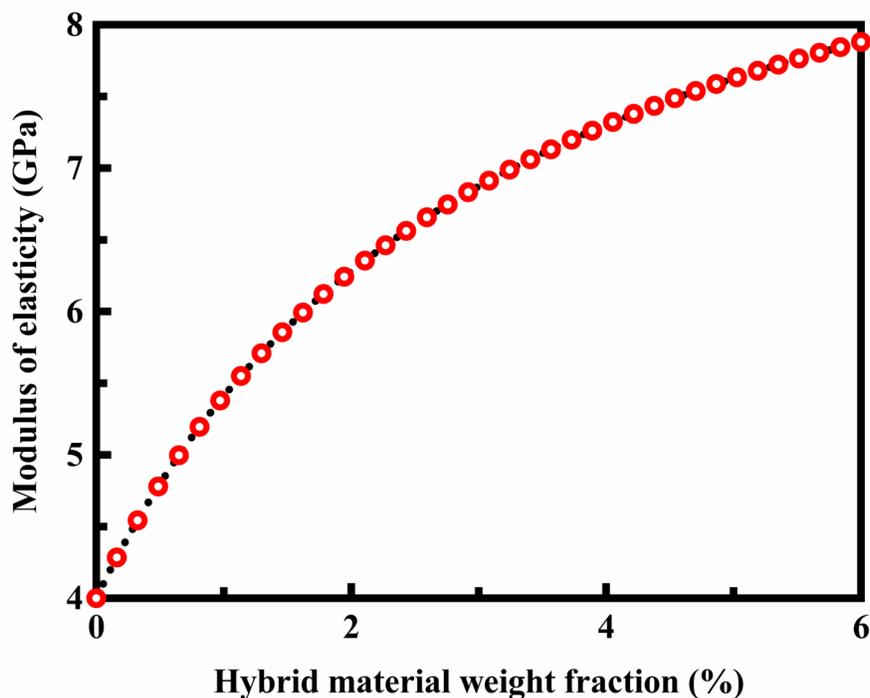


Figure 3. Effect of the weight fraction of the graphene-carbon nanotube hybrid material on the modulus of elasticity for the fiber-reinforced polymer composite.

The effect of the weight fraction of the graphene-carbon nanotube hybrid material on the hardness is illustrated in Figure 4 for the fiber-reinforced polymer composite. Regarding the enhancement of mechanical properties, superior dispersion relates to the maximization of Young's modulus, which may be expected if the graphene-carbon nanotubes are dispersed homogeneously at the level of individual graphene and carbon nanotubes. However, as can relate to other considerations, when enhanced electrical conductivity is the goal, the development of a contiguous, cellular graphene-carbon nanotube structure yielding electrical percolation can result in greater property enhancement than a relatively homogeneous graphene-carbon nanotube dispersion. The hybrid material exhibits great improvements in hardness and yield strength and major deteriorations in strain at break. A modest degree of chemical attachment between the derivatized graphene-carbon nanotubes and the polymer matrix could be tolerated, while retaining the thermoplastic properties. Physical blending of the graphene-carbon nanotubes with the polymer can be enhanced by the derivatization process. For instance, a polymer composite material containing pure graphene-carbon

nanotubes may be desired so that the polymer would have certain enhanced conductive properties; however, the pure and underivatized graphene-carbon nanotubes may not sufficiently disperse in the polymer. By derivatizing the graphene-carbon nanotubes with a particular moiety, the derivatized graphene-carbon nanotubes could then be dispersed adequately. In this manner, the conductivity of the material can be recovered. Polymer properties are enhanced by incorporating therein a combination of graphene or carbon nanotubes. Additionally, graphene-carbon nanotubes prevent delamination and provide structural stability in polymer composites. Because graphene-carbon nanotubes have uniquely high strength to mass ratio, intrinsic light weight, thermal conductivity, electrical conductivity, and chemical functionality, and prevent delamination and provide structural stability in polymer composites, they can impart these properties to polymers when effectively combined therewith. Incremental additions of graphene-carbon nanotubes to the polymer matrix are necessary to produce a composite that contains a high fraction of graphene-carbon nanotubes. It is important to ensure that mixing parameters remain as stable as possible. The rapid increase in melt viscosity during mixing is attributed to chemical bonding between dispersed graphene-carbon nanotubes and the polymer matrix. After completion of the mixing process, the composite material, now having a rubber-like consistency, is extracted from the barrel at the mixing temperature. Larger samples of the fiber-reinforced polymer composite can be prepared using an integrated high shear mixing and injection molding apparatus. ASTM standard test bars can be fabricated and evaluated for mechanical properties. Preliminary tests performed on small samples indicate significant improvements in stiffness and strength. Typically, fiber-reinforced thermoplastic composites suffer from lower impact resistance than the polymer alone. Additionally, the high-shear mixing process can efficiently disperse the graphene-carbon nanotube agglomerates, forming a uniform distribution of graphene-carbon nanotubes in the polymer matrix.

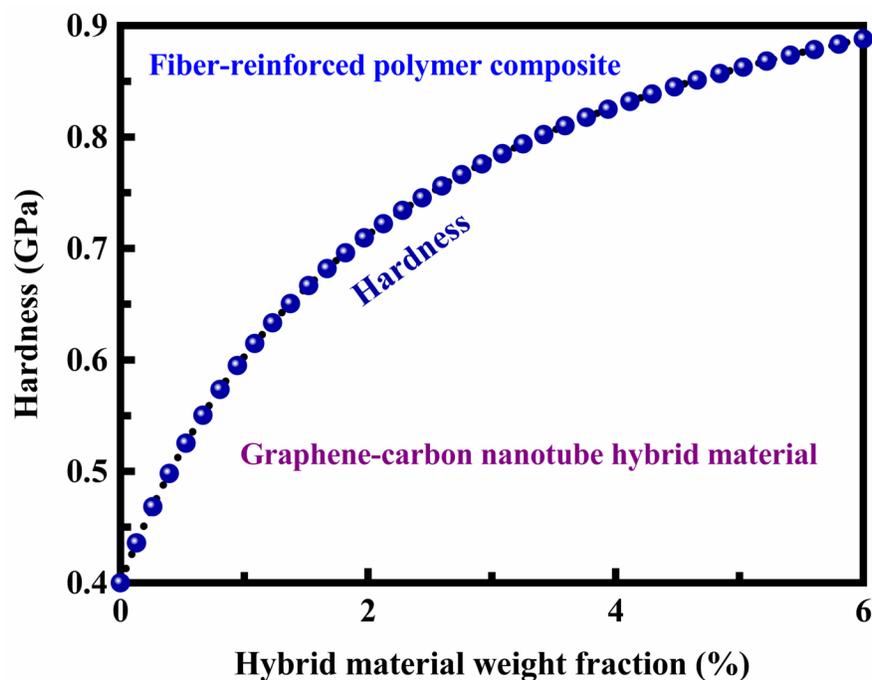


Figure 4. Effect of the weight fraction of the graphene-carbon nanotube hybrid material on the hardness for the fiber-reinforced polymer composite.

The low-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 5 for the production of fiber-reinforced polymer composites. Graphene is the term for a modification of carbon having a two-dimensional structure in which each carbon atom is surrounded by three further carbon atoms so as to form a honeycomb-like pattern. In this respect, graphene may be regarded as

a single graphite layer. However, the term graphene also includes thin stacks of single graphite layers which owing to their small thickness have physical properties which differ substantially from those of graphite bulk material. Each graphene platelet has a length and a width parallel to the graphite plane and a thickness perpendicular to the graphite plane. The largest dimension is here referred to as the length, the smallest dimension as the thickness and the last dimension as the width. The carbon nanotubes and the graphene platelets are advantageously dispersed separately or together in an aqueous medium and the dispersions obtained are subsequently combined. The dispersing step can be carried out with the aid of ultrasound and jet dispersers. Material property refers to the response of a material to an external stimulus [61, 62]. Non-limiting examples of material properties include mechanical properties, electrical properties, magnetic properties, thermal properties, chemical properties, and acoustical properties. Mechanical properties refer to the response of a material to an applied load or force [63, 64]. Non-limiting examples of mechanical properties include Young's modulus, specific modulus, strength, for example, tensile, compressive, shear, yield, bearing, and creep, ductility, Poisson's ratio, hardness, impact toughness, resilience, fatigue limit, and fracture toughness. Thermal properties refer to a material's response to applied heat. Non-limiting examples include thermal conductivity, thermal diffusivity, coefficient of thermal expansion, emissivity, specific heat, melting point, glass transition temperature, boiling point, flash point, triple point, heat of vaporization, heat of fusion, pyrophoricity, autoignition temperature, and vapor pressure. Electrical properties refer to the response of a material to an applied electric or electromagnetic field. Non-limiting examples include electrical conductivity, electrical resistivity, permittivity, dielectric constant, dielectric strength, and piezoelectric constant. Composite or composite material refer to a material composed of two or more materials, where each material possesses a distinct phase at a length scale of interest and a distinct interface is present between each of the two or more materials [65, 66]. Reinforced composite refers to a composite including at least two phases, a matrix phase that is continuous and that surrounds at least a portion of a dispersed phase [67, 68]. The composite is formed from a free mixture of graphene, carbon nanotube, and porous carbon. The graphene self-aligns in a plurality of sheets approximately parallel to a substrate upon which the mixture is deposited, while at least a portion of the carbon nanotubes are aligned at a defined angle to the graphene sheets. The carbon nanotubes exhibit no preferred orientation and are approximately random. Concurrently, the plurality of graphene sheets is oriented approximately horizontally, that is approximately parallel to the substrate surface. Depositing a layer of graphene over the cleaned layer of carbon nanotube film to form a carbon nanotube-graphene hybrid film includes transferring chemical vapor deposition grown graphene using several known transfer processes, such as polymer assisted transfer. The graphene films can also be directly obtained from bulk graphite through a scotch tape transfer process. Graphene can also be deposited through solution in the form of dissolved graphene oxide. This can be accomplished through spraying the solution or spinning graphene oxide flakes suspending in a solvent over the substrate containing carbon nanotubes, and graphene oxide flakes can later be reduced to graphene through gas or solution phase reducing treatments. The polymer interacts with solvents. The combination of the Van der Waals inhibition and polymer-solvent interaction causes the wrapped carbon nanotubes to be much more readily suspended at high concentrations in solvents. This enables creation of high-concentration carbon nanotube solutions and suspensions, which in turn substantially enables manipulation of carbon nanotubes into the bulk material. The novel electrical properties are isotropic in compositions where the carbon nanotubes are essentially randomly oriented with one another, such as in an electrically-insulating matrix.

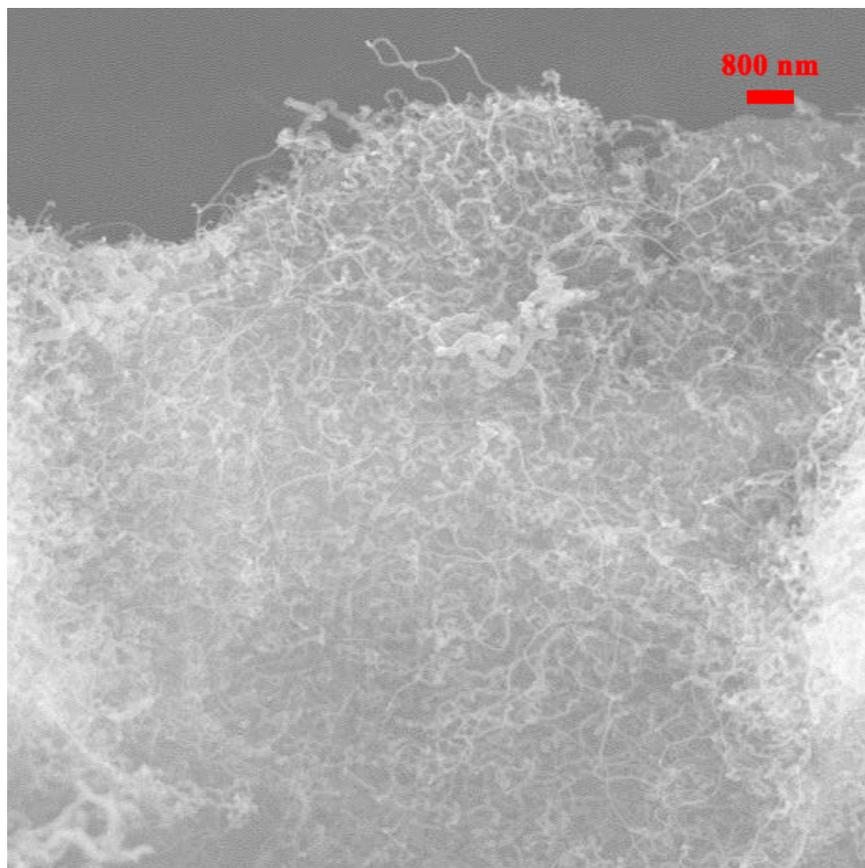


Figure 5. Low-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The high-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 6 for the production of fiber-reinforced polymer composites. A key difficulty of using graphene-carbon nanotubes in many applications is their poor adhesion to the substrate which can give rise to reliability issues and also compromise good electrical contacts. In chemical vapor deposition of both graphene and carbon nanotube, a metal catalyst is used which is susceptible to environmental poisoning, such as oxidation, prior to the growth process and hence degrades the material properties. The poisoned catalyst may further poison underneath materials. Furthermore, many in-situ graphene and carbon nanotubes-based device fabrication processes involve patterning where etching is performed. In a buried catalyst arrangement, the catalyst is also attacked by etchants during the etching process. Protection of the catalyst film from etchants attack, process poisoning, and growth of reliably attached material with the substrate is highly favorable for the applications of graphene-carbon nanotubes in various areas. The techniques may include chemically doping the cleaned carbon nanotube-graphene hybrid film to increase conductivity. A carbon nanotube film can be a mixture of semiconducting and metallic carbon nanotubes. The doping permanently increases the charge concentration in semiconducting carbon nanotubes present in the film, thereby decreasing the sheet resistance of the network. The doping step also increases the electrical performance of the film. Doping the nanotube-graphene hybrid film can include using a solution doping technique. Carbon nanotubes can be doped in solution before getting deposited over the substrate. Similarly, solution suspended graphene oxide flakes can be doped before getting deposited over carbon nanotubes. The dopants can be acid solutions such as nitric acid and sulfuric acid, or the dopants can be metal-organic compounds which can form charge-transfer complexes with the bonded carbon atoms in carbon nanotube and graphene. The resultant structure

can appear as nanotubes scattered over or under a single or multiple large area graphene sheet reducing the sheet resistance of graphene. Doping is preferably conducted in solution phase, although gas phase doping is also feasible. For solution processes, organic solvents such as dichlorobenzene, dichloromethane, ethanol, acetonitrile, chloroform, methanol, butanol, among others, are suitable. Doping can be accomplished via charge transfer from the dopants to the nano-components, for example, interaction of the lone electron pairs of doping molecules with the quantum confined orbitals of semiconductor nanowires and nanocrystals which affects the concentration of carriers involved in charge transport.

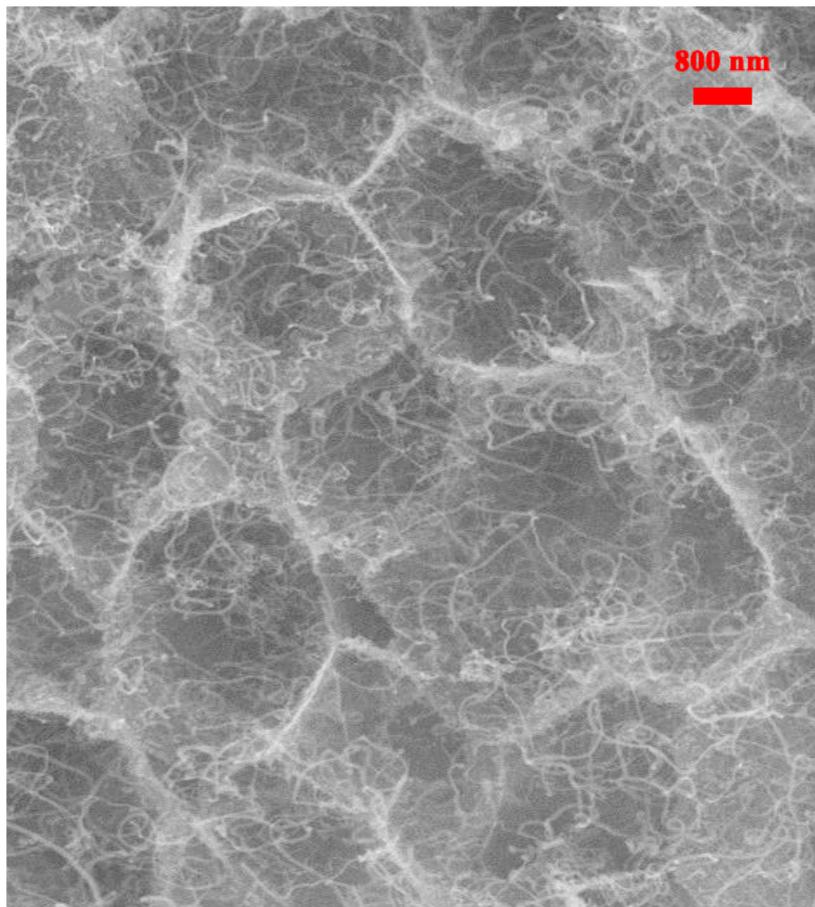


Figure 6. High-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The stress-strain responses of tensile deformation are illustrated in Figure 7 for the graphene-carbon nanotube fiber-reinforced polymer composite system. Carbon nanotubes can be functionalized via covalent or non-covalent bonding, to either the ends of the carbon nanotubes or to the sidewalls [69, 70]. Covalent functionalization often requires beginning with modified carbon nanotubes, such as fluorinated carbon nanotubes [71, 72], or with purified carbon nanotubes where defect sites in the carbon nanotubes are produced by oxidation [73, 74]. Because these modifications often result in the disruption of the bonds along the carbon nanotubes themselves [75, 76], covalent functionalization can degrade the mechanical and electrical properties of the carbon nanotubes [77, 78] and, thus, is not ideal for all applications. Though graphene and carbon nanotubes have extraordinary mechanical properties, their ability to strengthen polymers and epoxies

is limited by the strength of interfacial bonding. As a result, when incorporated into polymeric resin without cross-linking or functionalization, they lack the ability to transfer loads across the structure. Generally, single-walled carbon nanotubes are preferred over multi-walled carbon nanotubes for use in these applications because they have fewer defects and are therefore stronger and more conductive than multi-walled carbon nanotubes of similar diameter. Defects are less likely to occur in single-walled carbon nanotubes than in multi-walled carbon nanotubes because multi-walled carbon nanotubes can survive occasional defects by forming bridges between unsaturated carbon valences, while single-walled carbon nanotubes have no neighboring walls to compensate for defects. Single-walled carbon nanotubes exhibit exceptional chemical and physical properties that have opened a vast number of potential applications. However, the availability of these new single-walled carbon nanotubes in quantities and forms necessary for practical technology is still problematic. Large scale processes for the production of high-quality single-walled carbon nanotubes are still needed, and suitable forms of the single-walled carbon nanotubes for application to various technologies are still needed. The fibers are broken in the presence of molten polymers during melt processing. Fiber breakage can be accomplished either by having a specially designed cutting tool in the melt processing equipment, or through high shear during melt processing, or by a combination of the two. The opening up of new fiber ends by breaking the fibers while surrounded by liquid polymers introduces dangling bonds, or reactive free radicals, on the fiber ends that represent sites for strong bonding by the polymers with the graphene-carbon nanotube hybrid material. The resulting solid composites have improved mechanical properties.

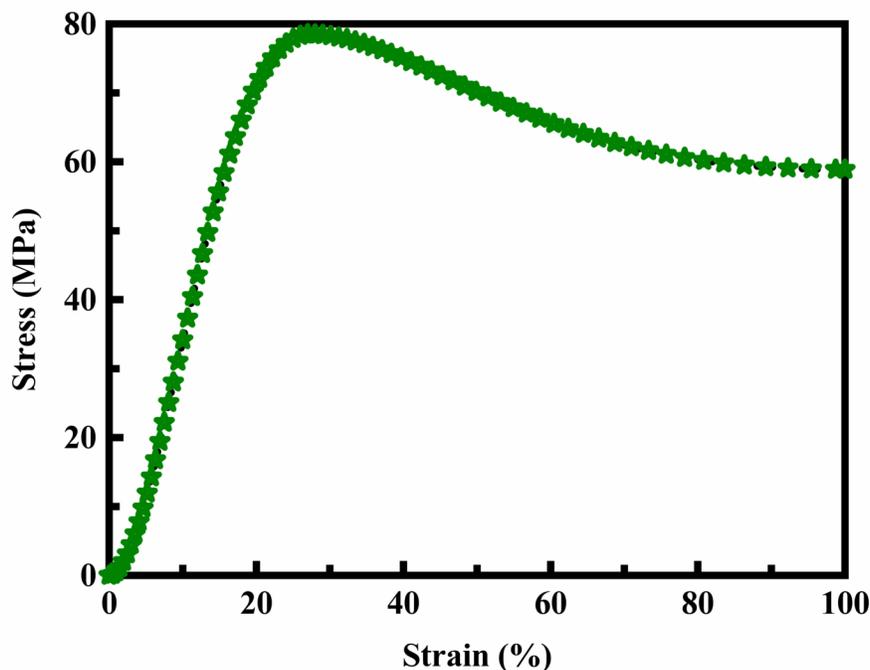


Figure 7. Stress-strain responses of the tensile deformation of the graphene-carbon nanotube fiber-reinforced polymer composite system.

The effect of strain on the bond order parameters of the tensile deformation is illustrated in Figure 8 for the graphene-carbon nanotube fiber-reinforced polymer composite system. Non-covalent functionalization to the sidewalls of carbon nanotubes can be attained by exploiting the van der Waals and pi-pi bonding between the pi electrons of the carbon nanotubes and that of a polyaromatic molecule, for example, a polyaromatic hydrocarbon [79, 80]. This type of functionalization results in higher degrees of functionalization as the entire length of the carbon nanotubes can be functionalized rather than just the ends and specific active sites [81, 82]. Like end-functionalization, non-covalent functionalization also opens up the possibility for

tailoring the functionalization via the choice of molecule [83, 84]. The methods may be used to create light weight, high strength structures [85, 86]. This results in improving the mechanical properties of the interface between the carbon nanotubes and the polymer thereby imparting many of the valuable properties of carbon nanotubes into the polymer matrix resulting in a significantly improved polymer-carbon nanotube composite [87, 88]. Carbon nanotubes are ideal reinforcing material for polymer matrices because of their high aspect ratio, low density, remarkable mechanical properties, and good electrical and thermal conductivity. The graphene-carbon nanotube fiber-reinforced polymer composite differs from a conventional carbon-fiber composite in that there is a much higher interface area between reinforcing carbon and polymer matrix phases. Introducing a uniform distribution of graphene-carbon nanotubes into a polymer matrix should yield property enhancements that go beyond that of a simple rule of mixtures. The challenge is to take full advantage of the exceptional properties of graphene-carbon nanotubes in the composite material. However, property improvements are not significant to date, apparently due to poor interfacial graphene-carbon nanotube-polymer bonding and severe graphene-carbon nanotube agglomeration. These obstacles can be overcome by utilizing a new processing route that involves high-shear mixing in a molten polymer to induce deagglomeration and dispersal of graphene-carbon nanotubes, while enhancing adhesive bonding and covalent bonding by creating new sites on the graphene-carbon nanotubes to which the polymer chains can bond. The polymer matrix in the near vicinity to the interface behaves differently than the polymer in the bulk, which is attributed to the outer diameter of a graphene-carbon nanotube having the same magnitude as the radius of gyration of the polymer chain.

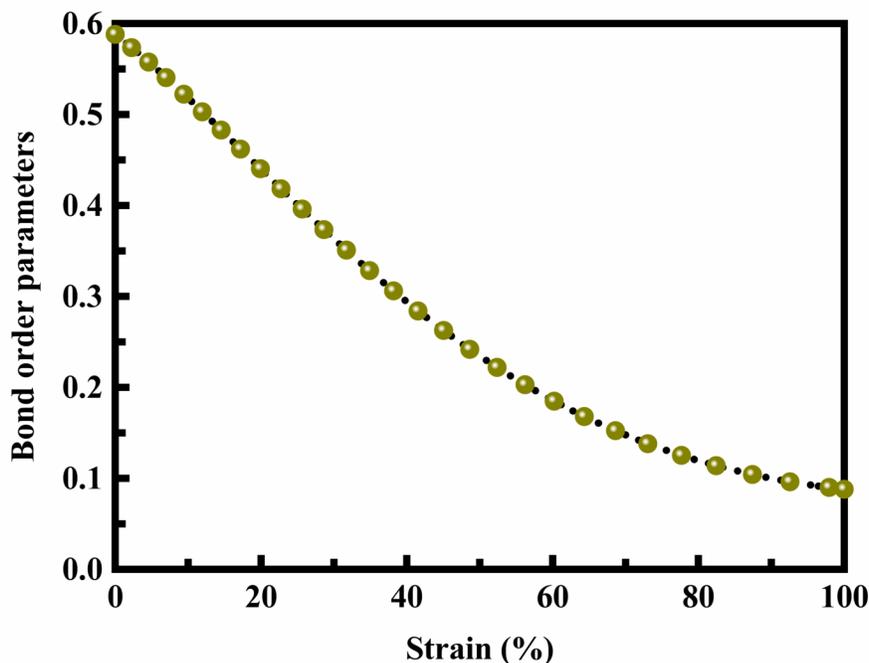


Figure 8. Effect of strain on the bond order parameters of the tensile deformation of the graphene-carbon nanotube fiber-reinforced polymer composite system.

#### 4. Conclusions

The present study is focused primarily upon the mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials. The graphene-carbon nanotube fiber-reinforced polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes. The effect of the hybrid material weight fraction on the modulus of elasticity and

hardness is evaluated, stress-strain responses of the composite tensile deformation are illustrated, and the effect of strain on the bond order parameters is investigated for the fiber-reinforced polymer composite. The major conclusions are summarized as follows:

- Graphene-carbon nanotube multi-stack three-dimensional architectures can overcome the limitations and restricted performance typically encountered with carbon-based materials by using the combined strategies of three-dimensional architecture and low-dimensional carbon nanomaterial characteristics.
- The poor dispersibility of graphene-carbon nanotubes greatly affects the characteristics of the composites which they form with the polymer matrices into which they are introduced.
- The modulus of elasticity of the composite is enhanced as compared to the neat polymer.
- The hybrid material exhibits great improvements in hardness and yield strength and major deteriorations in strain at break.
- The carbon nanotubes exhibit no preferred orientation and are approximately random.
- The doping permanently increases the charge concentration in semiconducting carbon nanotubes present in the film, thereby decreasing the sheet resistance of the network.
- Though graphene and carbon nanotubes have extraordinary mechanical properties, their ability to strengthen polymers and epoxies is limited by the strength of interfacial bonding.
- The graphene-carbon nanotube fiber-reinforced polymer composite differs from a conventional carbon-fiber composite in that there is a much higher interface area between reinforcing carbon and polymer matrix phases.

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# Mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials

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## Abstract

Introducing a uniform distribution of carbon nanotubes into a polymer matrix can yield property enhancements that go beyond that of a simple rule of mixtures. The challenge is to take full advantage of the exceptional properties of carbon nanotubes in the composite material. Carbon nanotubes are ideal reinforcing material for polymer matrices due to their remarkable properties. However, property improvements are not significant due to poor interfacial bonding and severe agglomeration. The present study is focused primarily upon the mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials. The polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites. The effect of hybrid material weight fraction on the modulus of elasticity and hardness is evaluated. Stress-strain responses of the composite tensile deformation are illustrated and the effect of strain on the bond order parameters is investigated. The present study aims to explore how to effectively improve the mechanical properties of polymers by utilizing graphene-carbon nanotube hybrid materials. Particular emphasis is placed upon the effect of weight fraction on the mechanical properties of polymer composites reinforced with graphene and carbon nanotubes. The results indicate that graphene-carbon nanotube multi-stack three-dimensional architectures can overcome the limitations and restricted performance typically encountered with carbon-based materials by using the combined strategies of three-dimensional architecture and low-dimensional nanomaterial characteristics. Poor dispersibility greatly affects the characteristics of the polymer composites. The modulus of elasticity of the polymer composite is enhanced as compared to the neat polymer. The hybrid material exhibits great improvements in hardness and yield strength and major deteriorations in strain at break. The carbon nanotubes exhibit no preferred orientation and are approximately random. The doping permanently increases the charge concentration in semiconducting carbon nanotubes present in the film, thereby decreasing the sheet resistance of the network. The ability to strengthen polymers is limited by the strength of interfacial bonding. The polymer composite differs from a conventional carbon-fiber composite where there is a much higher interface area between reinforcing carbon and polymer matrix phases.

**Keywords:** Graphene; Carbon; Composites; Polymers; Fibers; Hardness

## 1. Introduction

Carbon nanotubes can be classified by the number of walls in the tube, single-wall, double wall and multiwall. Each wall of a carbon nanotube can be further classified into chiral or non-chiral forms. Carbon nanotubes are currently manufactured as agglomerated nanotube balls or bundles [1, 2]. Use of carbon nanotubes and graphene as enhanced performance additives in batteries is predicted to have significant utility for electric vehicles, and electrical storage in general. However, utilization of carbon nanotubes in these applications is hampered due to the general inability to reliably produce

individualized carbon nanotubes [3, 4]. Single-walled carbon nanotubes are a novel form of carbon. They are closed-caged, cylindrical molecules, approximately 0.5 to 3 nanometers in diameter and a few hundred nanometers long [5, 6]. They are known for their excellent electrical and thermal conductivity and high tensile strength [7, 8]. Since their discovery in 1993, there has been substantial research to describe their properties and develop applications using them [9, 10]. From unique electronic properties and a thermal conductivity higher than diamond to mechanical properties where the stiffness, strength and resilience exceeds any current material, carbon nanotubes offer tremendous opportunities for the development of fundamentally new material systems.

Utilization of carbon nanotubes in conductors has been attempted [11, 12]. However, the incorporation of carbon nanotubes into polymers at high enough concentrations to achieve the desired conductivity typically increases viscosities of the compound containing the carbon nanotubes to very high levels [13]. The result of such a high viscosity is that conductor fabrication is difficult [14]. A typical example of a high concentration is one percent, by weight, of carbon nanotubes mixed with a polymer [15, 16]. Currently, there are no fully developed processes for fabricating wires based on carbon nanotubes [17, 18], but co-extrusion of carbon nanotubes within thermoplastics is being contemplated, either by pre-mixing the carbon nanotubes into the thermoplastic or by coating thermoplastic particles with carbon nanotubes prior to extrusion [19, 20]. Application of carbon nanotubes to films has been used extensively, but not to wires [21, 22]. Utilization of carbon nanotubes with thermosets has also been widely studied in recent years [23, 24]. However, thermosets are crosslinked and cannot be melted at an elevated temperature [25, 26]. Finally, previous methods for dispersion of carbon nanotubes onto films have not focused on metallic carbon nanotubes in order to maximize current-carrying capability or high conductivity [27, 28]. The above-mentioned proposed methods for fabricating wires that incorporate carbon nanotubes will encounter large viscosities, due to the large volume of carbon nanotubes compared to the overall volume of carbon nanotubes and the polymer into which the carbon nanotubes are dispersed. Another issue with such a method is insufficient alignment of the carbon nanotubes. Finally, the proposed methods will not produce the desired high concentration of carbon nanotubes.

The use of high-performance, fiber-reinforced composites has expanded substantially in recent years [29, 30], as improvements in these composites have allowed them to meet the final performance requirements of advanced material systems [31, 32]. For example, extensive research and development in carbon fiber-reinforced composites has led to significant improvements in the properties of these composites [31, 32], such as in-plane mechanical properties [33, 34]. Furthermore, composites formed using two-dimensional and three-dimensional woven fiber reinforcements can be formed into the final net shapes [35, 36]. However, the out-of-plane properties of fiber-reinforced composites remain problematically low [37, 38]. Out-of-plane properties are dominated by the matrix surrounding the reinforcing fibers, which is relatively weak compared to the fibers [37, 38]. Additionally, fiber-reinforced composites generally possess matrix-rich regions within the interlaminar region between the fibers [39, 40], and these regions have proven difficult to reinforce with fiber reinforcements [41, 42]. As a result, cracks may easily initiate and propagate under load within these regions, leading to composite failure [43, 44]. Therefore, there exists a continued need for improved reinforcements for composite materials so as to form hybrid carbon nanotube fiber reinforcements by depositing of carbon nanotubes on fiber substrates.

Introducing a uniform distribution of carbon nanotubes into a polymer matrix can yield property enhancements that go beyond that of a simple rule of mixtures. The challenge is to take full advantage of the exceptional properties of carbon nanotubes in the composite material. Carbon nanotubes are ideal reinforcing material for polymer matrices because of their high aspect ratio, low density, remarkable mechanical properties, and good electrical and thermal conductivity. However, property improvements

are not significant to date, apparently due to poor interfacial carbon nanotube-polymer bonding and severe carbon nanotube agglomeration. The present study is focused primarily upon the mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials. The graphene-carbon nanotube fiber-reinforced polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes. The effect of the hybrid material weight fraction on the modulus of elasticity and hardness is evaluated for the fiber-reinforced polymer composite. Stress-strain responses of the composite tensile deformation are illustrated and the effect of strain on the bond order parameters of the tensile deformation is investigated for the fiber-reinforced polymer composite. The present study aims to explore how to effectively improve the mechanical properties of polymers by utilizing graphene-carbon nanotube hybrid materials. Particular emphasis is placed upon the effect of weight fraction on the mechanical properties of polymer composites reinforced with graphene and carbon nanotubes.

## 2. Experimental methods

A method of fabrication of graphene-carbon nanotube stacks includes the steps of depositing a first graphene layer on a metal foil, transferring the first graphene layer to a current collector, depositing a first layer of a catalytic metal on the first graphene layer, alternately depositing graphene and catalytic metal layers one upon the other so as to form a stack of alternating graphene and catalytic metal layers on the first graphene and catalytic metal layers, transforming the catalytic metal layers into arrays of metal nanoparticles by thermal breakdown of the catalytic metal layers, and precipitating carbon nanotube outward from the metal nanoparticles. The carbon nanotubes are precipitated in a single execution of the precipitating carbon nanotube outward from the metal nanoparticles step, resulting in simultaneous growth of the carbon nanotubes and expansion of the graphene-carbon nanotube stack. The catalytic metal is a transition metal, for example, nickel. The graphene layers are formed by a chemical vapor deposition process. The carbon nanotubes are formed by a chemical vapor deposition process. The catalytic metal layers are formed by a physical vapor deposition process.

The carbon nanotubes may be any length, diameter, or chirality as produced by any of the various production methods [45, 46]. The chirality of the carbon nanotubes is such that the carbon nanotubes are metallic, semi-metallic, semiconducting or combinations thereof [47, 48]. Carbon nanotubes may include, but are not limited to, single-walled carbon nanotubes, double-walled carbon nanotubes, multi-walled carbon nanotubes, shortened carbon nanotubes, oxidized carbon nanotubes, functionalized carbon nanotubes, purified carbon nanotubes, metalized carbon nanotubes and combinations thereof. The carbon nanotubes may be pristine or functionalized. Functionalized carbon nanotubes, as used herein, refer to any of the carbon nanotubes types bearing chemical modification, physical modification or combination thereof. Such modifications can involve the carbon nanotube ends, sidewalls, or both. Illustrative chemical modifications of carbon nanotubes include, for example, covalent bonding and ionic bonding. Illustrative physical modifications include, for example, chemisorption, intercalation, surfactant interactions, polymer wrapping, solvation, and combinations thereof. Unfunctionalized carbon nanotubes are typically isolated as aggregates referred to as ropes or bundles, which are held together through van der Waals forces. The carbon nanotube aggregates are not easily dispersed or solubilized. Chemical modifications, physical modifications, or both can provide individualized carbon nanotubes through disruption of the van der Waals forces between the carbon nanotubes. As a result of disrupting van der Waals forces, individualized carbon nanotubes may be dispersed or solubilized.

Unfunctionalized carbon nanotubes may be used as-prepared from any of the various production methods, or they may be further purified. Purification of carbon nanotubes typically refers to, for example, removal of metallic impurities, removal of non-nanotube carbonaceous impurities, or both

from the carbon nanotubes. Illustrative carbon nanotube purification methods include, for example, oxidation using oxidizing acids, oxidation by heating in air, filtration and chromatographic separation. Oxidative purification methods remove non-nanotube carbonaceous impurities in the form of carbon dioxide. Oxidative purification of carbon nanotubes using oxidizing acids further results in the formation of oxidized, functionalized carbon nanotubes, wherein the closed ends of the carbon nanotube structure are oxidatively opened and terminated with a plurality of carboxylic acid groups. Oxidative purification methods using an oxidizing acid further result in removal of metallic impurities in a solution phase. Depending on the length of time oxidative purification using oxidizing acids is performed, further reaction of the oxidized, functionalized carbon nanotubes results in shortening of the carbon nanotubes, which are again terminated on their open ends by a plurality of carboxylic acid groups. The carboxylic acid groups in both oxidized, functionalized carbon nanotubes and shortened carbon nanotubes may be further reacted to form other types of functionalized carbon nanotubes. For example, the carboxylic acids groups may be reacted to form esters or amides, or they may be reacted in condensation polymerization reactions to form polymers having the carbon nanotubes bound to the polymer chains. Condensation polymers include, for example, polyesters and polyamides.

Functionalized graphene-carbon nanotubes may also be incorporated into polymers using standard polymerization techniques [49, 50]. The functionalized graphene-carbon nanotubes may be dispersed in the polymer and not covalently bound to the polymer chains [51, 52]. Alternately, the functionalized graphene-carbon nanotubes may be dispersed in the polymer and covalently bound to the polymer chains. For example, amino-functionalized graphene-carbon nanotubes may react with epoxy resins through their amino groups. Amino-functionalized graphene-carbon nanotubes are formed by peroxide-mediated introduction of carboxylic acid groups on sidewalls of pristine graphene-carbon nanotubes, followed by amide-functionalization using a diamine. Similarly, fluorinated graphene-carbon nanotubes may react with amino groups of epoxies curing agents to displace fluorine and form a cross-linked epoxy polymer covalently bound to the graphene-carbon nanotubes. Fluorinated graphene-carbon nanotubes are prepared by direct sidewall fluorination of graphene-carbon nanotubes using elemental fluorine. The particular type of functionalized graphene-carbon nanotubes utilized in the various cases herein may be varied across a wide range of functionality. For example, desired solubility or reactivity properties of the functionalized graphene-carbon nanotubes will dictate the choice of functionalized graphene-carbon nanotube type utilized in the various cases herein. The process comprises the steps: providing a porous mat comprising graphene-carbon nanotubes having an average longest dimension in the range of 2 micron to 2000 microns, wherein at least a portion of the graphene-carbon nanotubes are entangled; contacting the mat with one or more condensation polymer precursors, and optionally a catalyst; polymerizing the one or more polymer precursors in the presence of the mat at a temperature in the range of about 180 °C to about 360 °C to form a nonporous fiber-reinforced polymer composite comprising a mat of graphene-carbon nanotubes embedded in a condensation polymer produced from the polymer precursors, wherein the graphene-carbon nanotubes are present in the composite in an amount ranging from about 0.08 weight percent to about 80 weight percent, based on the weight of the graphene-carbon nanotubes and the condensation polymer; and curing the graphene-carbon nanotube fiber-reinforced polymer composite.

The graphene-carbon nanotube fiber-reinforced polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes. In particular, the graphene-carbon nanotube fiber-reinforced polymer composites provide increased resistance to tension-tension and tension-compression fatigue failure compared to conventional fiber-reinforced polymer composites. Inclusion of graphene-carbon nanotubes at the fiber-matrix interface in graphene-carbon nanotube fiber-reinforced polymer composites provides advantageous

resistance to polymer matrix cracking, longitudinal cracking along the fiber-matrix interface, and fiber delamination, all of which are dominant failure mechanisms in conventional fiber-reinforced polymer composites. Thus, the graphene-carbon nanotube fiber-reinforced polymer composites provide a nanotechnology solution to mitigating the evolution of failure mechanisms and extending failure lifetimes under fatigue loading. The graphene-carbon nanotube fiber-reinforced polymer composites include a fiber component, a polymer matrix component, and a quantity of graphene-carbon nanotubes. The polymer matrix component and the fiber component form a fiber-matrix interface. The quantity of graphene-carbon nanotubes coats at least a portion of the fiber component. The fiber-matrix interface further includes the portion of graphene-carbon nanotubes.

Normal fatigue crack progression is suppressed at the fiber-matrix interface where graphene-carbon nanotubes are present. Since fatigue crack progression leads to fiber-matrix longitudinal delamination, the graphene-carbon nanotubes enhance fatigue lifetime under both quasi-static and cyclical fatigue loading conditions. Controlled laboratory testing conditions are used to evaluate the benefits of graphene-carbon nanotube fiber-reinforced polymer composites over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes coating the fiber component. As an initial test of the graphene-carbon nanotube fiber-reinforced polymer composites, the tensile strength and tensile stiffness of graphene-carbon nanotube fiber-reinforced polymer composites and fiber-reinforced polymer composites are evaluated and compared. Testing is conducted by ASTM testing methods ASTM D3039 and ASTM D3039M-17. Graphene-carbon nanotube fiber-reinforced polymer composites utilized in the tensile strength and tensile stiffness studies contain about 0.2 to about 0.8 weight percent graphene-carbon nanotubes coating the carbon fibers. Both tensile stiffness and tensile strength are improved in the graphene-carbon nanotube fiber-reinforced polymer composites, particularly at higher weight percentages of graphene-carbon nanotubes. The improvement for both mechanical properties vary depending on the quantity of graphene-carbon nanotubes used to coat the carbon fibers.

### **3. Results and discussion**

The low-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 1 for the production of fiber-reinforced polymer composites. From a mechanical point of view, carbon nanotubes exhibit excellent rigidity, comparable to steel, while being extremely light. In addition, they exhibit excellent electrical and thermal conductivity properties which make it possible to envisage using them as additives to confer these properties on various, particularly macromolecular, materials such as polyamides, polycarbonate, polyesters, polystyrene, and polyethyleneimine, as well as other thermoplastic and thermoset polymers. Carbon-based materials are widely used due to their mechanical and chemical stability, excellent intrinsic electrical conductivity, and large surface area. Graphene-carbon nanotube multi-stack three-dimensional architectures can overcome the limitations and restricted performance typically encountered with carbon-based materials by using the combined strategies of three-dimensional architecture and low-dimensional carbon nanomaterial characteristics. Such graphene-carbon nanotube stacks have one or more of the following characteristics: graphene and carbon nanotubes are active materials that have unique electrical properties, particularly high surface area and high electrical conductivity, the carbon nanotube array of the graphene- carbon nanotube stack acts as a spacer to prevent graphene self-aggregation, maintaining a large active surface area, and stable electrical and mechanical contact is generated between carbon nanotube and graphene due to the direct growth of carbon nanotube between the graphene layers. A graphene-carbon nanotube stack may be fabricated by sequentially developing a stack of alternating graphene and catalytic metal layers, breaking down the metal layers into catalytic nanoparticles, and causing the simultaneous growth of the carbon nanotube between the graphene layers at the sites of the

catalytic nanoparticles and the expansion of the graphene-carbon nanotube stack. The growth tube furnace chemical vapor deposition method is adapted to grow graphene. Graphene synthesis begins when the carbon feedstock is introduced into the furnace tube, where it thermally decomposes into carbon and hydrogen radicals in the presence of the catalyst. In the case of copper, growth is limited to the surface of the metal. The dissociated carbon species diffuse across the surface of the metal, where they nucleate as seeds which grow and coalesce to form a continuous graphene film.

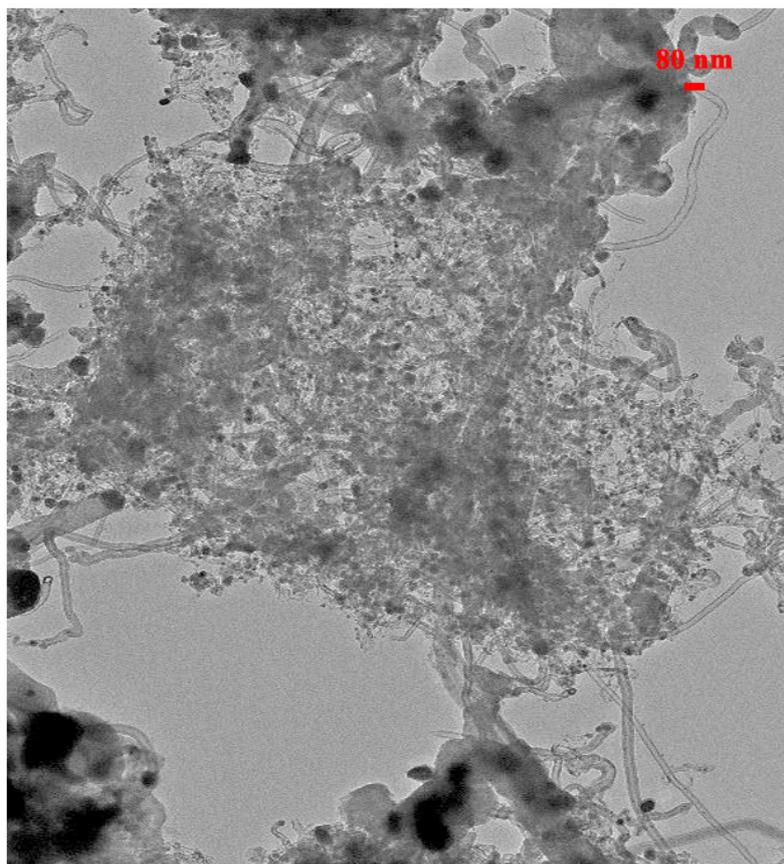


Figure 1. Low-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The high-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 2 for the production of fiber-reinforced polymer composites. The porous mat comprising graphene-carbon nanotubes is contacted with one or more condensation polymer precursors, and optionally a catalyst. Under polymerization conditions, the condensation polymer precursors undergo in situ polymerization to produce a condensation polymer which forms the polymer component of the graphene-carbon nanotube fiber-reinforced polymer composite. As the polymerization step is performed in the presence of the mat, the mat of entangled graphene-carbon nanotubes maintains its nanostructured sheet form and becomes embedded in the condensation polymer, and a nonporous graphene-carbon nanotube fiber-reinforced polymer composite is formed. The composite is nonporous as a result of the condensation polymer occupying the openings previously present between adjacent graphene-carbon nanotubes, or between adjacent ropelike structures of graphene-carbon nanotubes, within the mat. The condensation polymer precursors are polymerized in the presence of the mat under suitable polymerization conditions to form a nonporous fiber-reinforced polymer composite comprising a mat of graphene-carbon nanotubes embedded in the condensation polymer produced from the polymer precursors. Suitable polymerization conditions include sufficient pressure, temperature, time, and other process conditions for polymerization of the polymer precursors to occur. Suitable polymerization conditions can include addition of a catalyst. The poor dispersibility

of graphene-carbon nanotubes greatly affects the characteristics of the composites which they form with the polymer matrices into which they are introduced. There is observed in particular the appearance of nano-cracks, formed in aggregates of graphene-carbon nanotubes, which lead to the composite becoming fragile. Moreover, since graphene-carbon nanotubes are poorly dispersed, it is necessary to increase their amount in order to reach a given electrical and thermal conductivity, which has the effect of increasing the viscosity of the mixture for manufacturing the composite, leading to self-heating of this mixture which may result in degradation of the polymer and a reduction in productivity. Thermal properties refer to a material's response to applied heat. Non-limiting examples include thermal conductivity, thermal diffusivity, coefficient of thermal expansion, emissivity, specific heat, melting point, glass transition temperature, boiling point, flash point, triple point, heat of vaporization, heat of fusion, pyrophoricity, autoignition temperature, and vapor pressure.

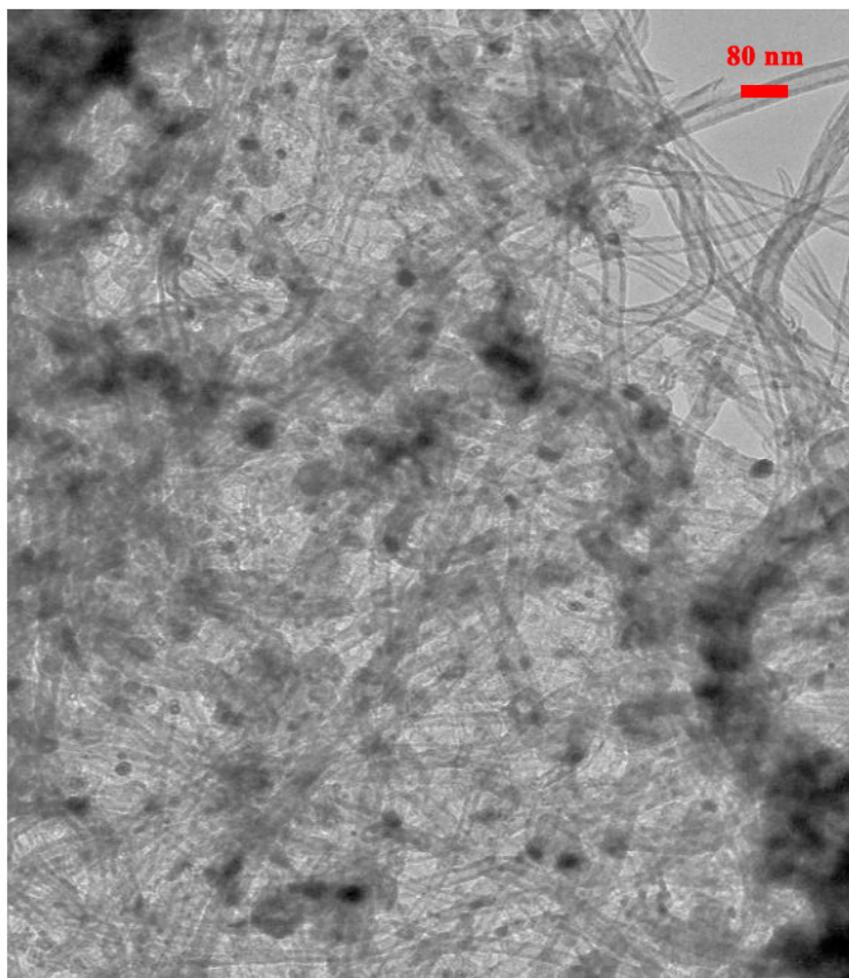


Figure 2. High-resolution transmission electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The effect of the weight fraction of the graphene-carbon nanotube hybrid material on the modulus of elasticity is illustrated in Figure 3 for the fiber-reinforced polymer composite. Intense research has been focused on polymer nanocomposites because of their potential to dramatically enhance properties relative to neat polymer and to yield multifunctional materials [53, 54]. Carbon nanotubes have been extensively studied as nanofillers because of their low density, high aspect ratio, and excellent mechanical, electrical, and thermal properties [55, 56]. However, major challenges remain in the development of polymer-carbon nanotube nanocomposites, especially as related to carbon nanotube dispersion via industrially scalable, environmentally friendly methods and understanding the relationship between dispersion and optimum properties [57, 58]. Several strategies have been studied

to achieve well-dispersed polymer-carbon nanotube nanocomposites, including melt mixing, polymer-carbon nanotube blending in solvent, and in situ polymerization [59, 60]. Use of melt mixing alone often leads to limited carbon nanotube dispersion in polymer. Blending polymer and in situ polymerization methods can lead to better dispersion, but the former is not environmentally friendly and both methods have limited applicability and scalability. One or more mechanical or physical properties of the graphene-carbon nanotube fiber-reinforced polymer composite are enhanced, including but not limited to increased Young's modulus and increased yield strength, electrical conductivity, thermal stability and crystallization rate, as compared to the corresponding neat polymer. For example, the modulus of elasticity of the composite is enhanced as compared to the corresponding neat polymer. The method of preparing the composite comprises providing a polymer component and a graphene-carbon nanotube mixture; applying a mechanical energy thereto through solid-state shear pulverization in the presence of cooling at least partially sufficient to maintain such a polymer component in a solid state, such pulverization at least sufficient to provide a pulverization product comprising a graphene-carbon nanotube component at least partially homogeneously dispersed therein; and melt-mixing such a pulverization product, to provide a graphene-carbon nanotube fiber-reinforced polymer composite. Crystallization kinetic effect can be selected from increased rate of isothermal crystallization and decreased distribution of crystallization time. Solid-state shear pulverization and melt-mixing can be at least partially sufficiently to affect a mechanical and physical property of such a mixture, such a property as can be selected from Young's modulus, yield strength, electrical conductivity, and thermal stability. Dispersion can be characterized by field-emission scanning electron microscopy and the absence of agglomeration at micron-length scales under microscopy conditions.

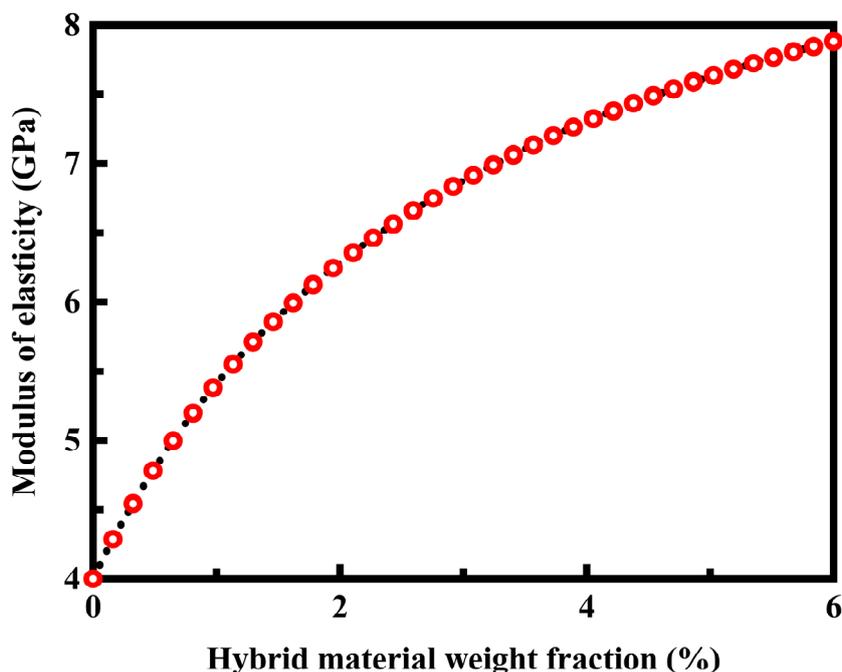


Figure 3. Effect of the weight fraction of the graphene-carbon nanotube hybrid material on the modulus of elasticity for the fiber-reinforced polymer composite.

The effect of the weight fraction of the graphene-carbon nanotube hybrid material on the hardness is illustrated in Figure 4 for the fiber-reinforced polymer composite. Regarding the enhancement of mechanical properties, superior dispersion relates to the maximization of Young's modulus, which may be expected if the graphene-carbon nanotubes are dispersed homogeneously at the level of individual graphene and carbon nanotubes. However, as can relate to other considerations, when enhanced electrical conductivity is the goal, the development of a contiguous, cellular graphene-carbon nanotube structure yielding electrical percolation can result in greater property enhancement than a relatively

homogeneous graphene-carbon nanotube dispersion. The hybrid material exhibits great improvements in hardness and yield strength and major deteriorations in strain at break. A modest degree of chemical attachment between the derivatized graphene-carbon nanotubes and the polymer matrix could be tolerated, while retaining the thermoplastic properties. Physical blending of the graphene-carbon nanotubes with the polymer can be enhanced by the derivatization process. For instance, a polymer composite material containing pure graphene-carbon nanotubes may be desired so that the polymer would have certain enhanced conductive properties; however, the pure and underivatized graphene-carbon nanotubes may not sufficiently disperse in the polymer. By derivatizing the graphene-carbon nanotubes with a particular moiety, the derivatized graphene-carbon nanotubes could then be dispersed adequately. In this manner, the conductivity of the material can be recovered. Polymer properties are enhanced by incorporating therein a combination of graphene or carbon nanotubes. Additionally, graphene-carbon nanotubes prevent delamination and provide structural stability in polymer composites. Because graphene-carbon nanotubes have uniquely high strength to mass ratio, intrinsic light weight, thermal conductivity, electrical conductivity, and chemical functionality, and prevent delamination and provide structural stability in polymer composites, they can impart these properties to polymers when effectively combined therewith. Incremental additions of graphene-carbon nanotubes to the polymer matrix are necessary to produce a composite that contains a high fraction of graphene-carbon nanotubes. It is important to ensure that mixing parameters remain as stable as possible. The rapid increase in melt viscosity during mixing is attributed to chemical bonding between dispersed graphene-carbon nanotubes and the polymer matrix. After completion of the mixing process, the composite material, now having a rubber-like consistency, is extracted from the barrel at the mixing temperature. Larger samples of the fiber-reinforced polymer composite can be prepared using an integrated high shear mixing and injection molding apparatus. ASTM standard test bars can be fabricated and evaluated for mechanical properties. Preliminary tests performed on small samples indicate significant improvements in stiffness and strength. Typically, fiber-reinforced thermoplastic composites suffer from lower impact resistance than the polymer alone. Additionally, the high-shear mixing process can efficiently disperse the graphene-carbon nanotube agglomerates, forming a uniform distribution of graphene-carbon nanotubes in the polymer matrix.

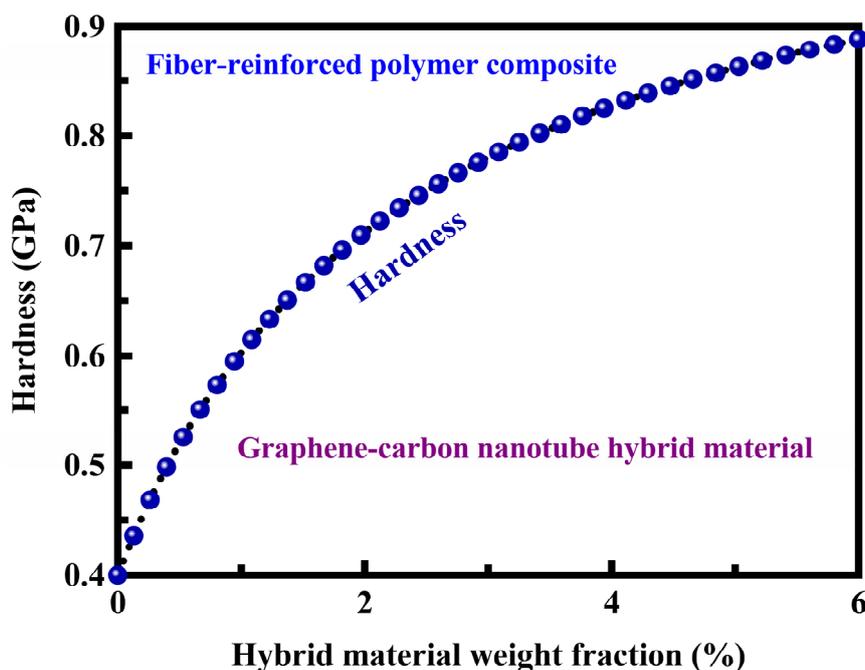


Figure 4. Effect of the weight fraction of the graphene-carbon nanotube hybrid material on the hardness for the fiber-reinforced polymer composite.

The low-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 5 for the production of fiber-reinforced polymer composites. Graphene is the term for a modification of carbon having a two-dimensional structure in which each carbon atom is surrounded by three further carbon atoms so as to form a honeycomb-like pattern. In this respect, graphene may be regarded as a single graphite layer. However, the term graphene also includes thin stacks of single graphite layers which owing to their small thickness have physical properties which differ substantially from those of graphite bulk material. Each graphene platelet has a length and a width parallel to the graphite plane and a thickness perpendicular to the graphite plane. The largest dimension is here referred to as the length, the smallest dimension as the thickness and the last dimension as the width. The carbon nanotubes and the graphene platelets are advantageously dispersed separately or together in an aqueous medium and the dispersions obtained are subsequently combined. The dispersing step can be carried out with the aid of ultrasound and jet dispersers. Material property refers to the response of a material to an external stimulus [61, 62]. Non-limiting examples of material properties include mechanical properties, electrical properties, magnetic properties, thermal properties, chemical properties, and acoustical properties. Mechanical properties refer to the response of a material to an applied load or force [63, 64]. Non-limiting examples of mechanical properties include Young's modulus, specific modulus, strength, for example, tensile, compressive, shear, yield, bearing, and creep, ductility, Poisson's ratio, hardness, impact toughness, resilience, fatigue limit, and fracture toughness. Thermal properties refer to a material's response to applied heat. Non-limiting examples include thermal conductivity, thermal diffusivity, coefficient of thermal expansion, emissivity, specific heat, melting point, glass transition temperature, boiling point, flash point, triple point, heat of vaporization, heat of fusion, pyrophoricity, autoignition temperature, and vapor pressure. Electrical properties refer to the response of a material to an applied electric or electromagnetic field. Non-limiting examples include electrical conductivity, electrical resistivity, permittivity, dielectric constant, dielectric strength, and piezoelectric constant. Composite or composite material refer to a material composed of two or more materials, where each material possesses a distinct phase at a length scale of interest and a distinct interface is present between each of the two or more materials [65, 66]. Reinforced composite refers to a composite including at least two phases, a matrix phase that is continuous and that surrounds at least a portion of a dispersed phase [67, 68]. The composite is formed from a free mixture of graphene, carbon nanotube, and porous carbon. The graphene self-aligns in a plurality of sheets approximately parallel to a substrate upon which the mixture is deposited, while at least a portion of the carbon nanotubes are aligned at a defined angle to the graphene sheets. The carbon nanotubes exhibit no preferred orientation and are approximately random. Concurrently, the plurality of graphene sheets is oriented approximately horizontally, that is approximately parallel to the substrate surface. Depositing a layer of graphene over the cleaned layer of carbon nanotube film to form a carbon nanotube-graphene hybrid film includes transferring chemical vapor deposition grown graphene using several known transfer processes, such as polymer assisted transfer. The graphene films can also be directly obtained from bulk graphite through a scotch tape transfer process. Graphene can also be deposited through solution in the form of dissolved graphene oxide. This can be accomplished through spraying the solution or spinning graphene oxide flakes suspending in a solvent over the substrate containing carbon nanotubes, and graphene oxide flakes can later be reduced to graphene through gas or solution phase reducing treatments. The polymer interacts with solvents. The combination of the Van der Waals inhibition and polymer-solvent interaction causes the wrapped carbon nanotubes to be much more readily suspended at high concentrations in solvents. This enables creation of high-concentration carbon nanotube solutions and suspensions, which in turn substantially enables manipulation of carbon nanotubes into the bulk material. The novel electrical properties are isotropic in compositions where the carbon nanotubes are essentially randomly oriented with one another, such as in an electrically-insulating matrix.

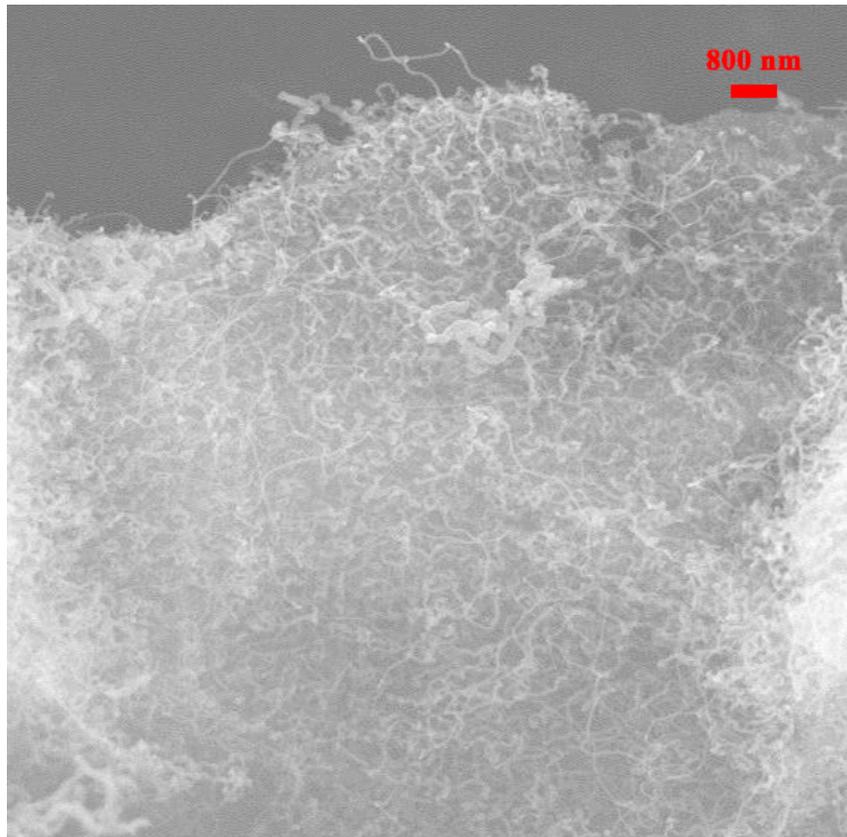


Figure 5. Low-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The high-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material are illustrated in Figure 6 for the production of fiber-reinforced polymer composites. A key difficulty of using graphene-carbon nanotubes in many applications is their poor adhesion to the substrate which can give rise to reliability issues and also compromise good electrical contacts. In chemical vapor deposition of both graphene and carbon nanotube, a metal catalyst is used which is susceptible to environmental poisoning, such as oxidation, prior to the growth process and hence degrades the material properties. The poisoned catalyst may further poison underneath materials. Furthermore, many in-situ graphene and carbon nanotubes-based device fabrication processes involve patterning where etching is performed. In a buried catalyst arrangement, the catalyst is also attacked by etchants during the etching process. Protection of the catalyst film from etchants attack, process poisoning, and growth of reliably attached material with the substrate is highly favorable for the applications of graphene-carbon nanotubes in various areas. The techniques may include chemically doping the cleaned carbon nanotube-graphene hybrid film to increase conductivity. A carbon nanotube film can be a mixture of semiconducting and metallic carbon nanotubes. The doping permanently increases the charge concentration in semiconducting carbon nanotubes present in the film, thereby decreasing the sheet resistance of the network. The doping step also increases the electrical performance of the film. Doping the nanotube-graphene hybrid film can include using a solution doping technique. Carbon nanotubes can be doped in solution before getting deposited over the substrate. Similarly, solution suspended graphene oxide flakes can be doped before getting deposited over carbon nanotubes. The dopants can be acid solutions such as nitric acid and sulfuric acid, or the dopants can be metal-organic compounds which can form charge-transfer complexes with the bonded carbon atoms in carbon nanotube and graphene. The resultant structure can appear as nanotubes scattered over or under a single or multiple large area graphene sheet reducing the sheet resistance of graphene. Doping is preferably conducted in solution phase, although gas phase doping is also feasible.

For solution processes, organic solvents such as dichlorobenzene, dichloromethane, ethanol, acetonitrile, chloroform, methanol, butanol, among others, are suitable. Doping can be accomplished via charge transfer from the dopants to the nano-components, for example, interaction of the lone electron pairs of doping molecules with the quantum confined orbitals of semiconductor nanowires and nanocrystals which affects the concentration of carriers involved in charge transport.

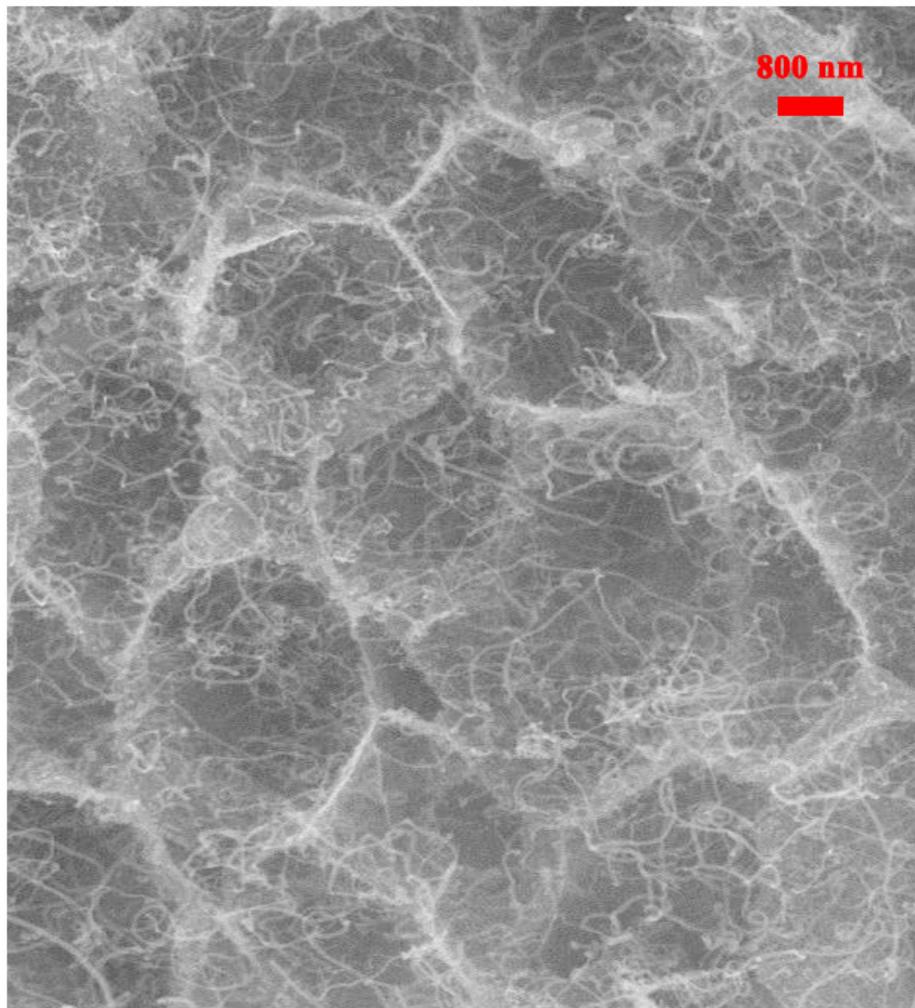


Figure 6. High-resolution scanning electron micrographs of the graphene-carbon nanotube hybrid material for the production of fiber-reinforced polymer composites.

The stress-strain responses of tensile deformation are illustrated in Figure 7 for the graphene-carbon nanotube fiber-reinforced polymer composite system. Carbon nanotubes can be functionalized via covalent or non-covalent bonding, to either the ends of the carbon nanotubes or to the sidewalls [69, 70]. Covalent functionalization often requires beginning with modified carbon nanotubes, such as fluorinated carbon nanotubes [71, 72], or with purified carbon nanotubes where defect sites in the carbon nanotubes are produced by oxidation [73, 74]. Because these modifications often result in the disruption of the bonds along the carbon nanotubes themselves [75, 76], covalent functionalization can degrade the mechanical and electrical properties of the carbon nanotubes [77, 78] and, thus, is not ideal for all applications. Though graphene and carbon nanotubes have extraordinary mechanical properties, their ability to strengthen polymers and epoxies is limited by the strength of interfacial bonding. As a result, when incorporated into polymeric resin without cross-linking or functionalization, they lack the ability to transfer loads across the structure. Generally, single-walled carbon nanotubes are preferred over multi-walled carbon nanotubes for use in these applications because they have fewer defects and are therefore stronger and more conductive than multi-walled

carbon nanotubes of similar diameter. Defects are less likely to occur in single-walled carbon nanotubes than in multi-walled carbon nanotubes because multi-walled carbon nanotubes can survive occasional defects by forming bridges between unsaturated carbon valences, while single-walled carbon nanotubes have no neighboring walls to compensate for defects. Single-walled carbon nanotubes exhibit exceptional chemical and physical properties that have opened a vast number of potential applications. However, the availability of these new single-walled carbon nanotubes in quantities and forms necessary for practical technology is still problematic. Large scale processes for the production of high-quality single-walled carbon nanotubes are still needed, and suitable forms of the single-walled carbon nanotubes for application to various technologies are still needed. The fibers are broken in the presence of molten polymers during melt processing. Fiber breakage can be accomplished either by having a specially designed cutting tool in the melt processing equipment, or through high shear during melt processing, or by a combination of the two. The opening up of new fiber ends by breaking the fibers while surrounded by liquid polymers introduces dangling bonds, or reactive free radicals, on the fiber ends that represent sites for strong bonding by the polymers with the graphene-carbon nanotube hybrid material. The resulting solid composites have improved mechanical properties.

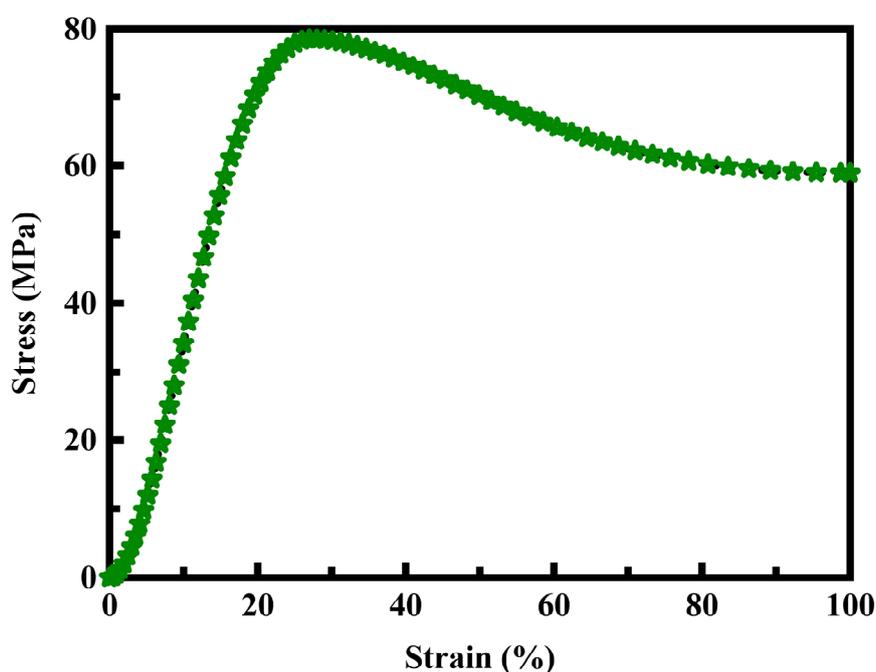


Figure 7. Stress-strain responses of the tensile deformation of the graphene-carbon nanotube fiber-reinforced polymer composite system.

The effect of strain on the bond order parameters of the tensile deformation is illustrated in Figure 8 for the graphene-carbon nanotube fiber-reinforced polymer composite system. Non-covalent functionalization to the sidewalls of carbon nanotubes can be attained by exploiting the van der Waals and pi-pi bonding between the pi electrons of the carbon nanotubes and that of a polyaromatic molecule, for example, a polyaromatic hydrocarbon [79, 80]. This type of functionalization results in higher degrees of functionalization as the entire length of the carbon nanotubes can be functionalized rather than just the ends and specific active sites [81, 82]. Like end-functionalization, non-covalent functionalization also opens up the possibility for tailoring the functionalization via the choice of molecule [83, 84]. The methods may be used to create light weight, high strength structures [85, 86]. This results in improving the mechanical properties of the interface between the carbon nanotubes and the polymer thereby imparting many of the valuable properties of carbon nanotubes into the polymer matrix resulting in a significantly improved polymer-carbon nanotube composite [87, 88]. Carbon nanotubes are ideal reinforcing material for polymer matrices because of their high aspect ratio, low

density, remarkable mechanical properties, and good electrical and thermal conductivity. The graphene-carbon nanotube fiber-reinforced polymer composite differs from a conventional carbon-fiber composite in that there is a much higher interface area between reinforcing carbon and polymer matrix phases. Introducing a uniform distribution of graphene-carbon nanotubes into a polymer matrix should yield property enhancements that go beyond that of a simple rule of mixtures. The challenge is to take full advantage of the exceptional properties of graphene-carbon nanotubes in the composite material. However, property improvements are not significant to date, apparently due to poor interfacial graphene-carbon nanotube-polymer bonding and severe graphene-carbon nanotube agglomeration. These obstacles can be overcome by utilizing a new processing route that involves high-shear mixing in a molten polymer to induce de-agglomeration and dispersal of graphene-carbon nanotubes, while enhancing adhesive bonding and covalent bonding by creating new sites on the graphene-carbon nanotubes to which the polymer chains can bond. The polymer matrix in the near vicinity to the interface behaves differently than the polymer in the bulk, which is attributed to the outer diameter of a graphene-carbon nanotube having the same magnitude as the radius of gyration of the polymer chain.

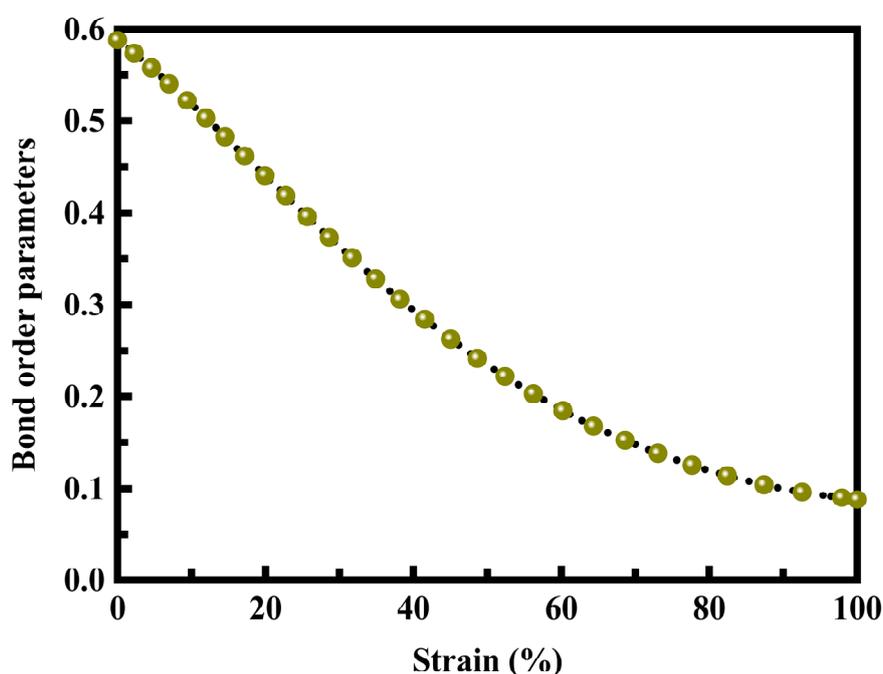


Figure 8. Effect of strain on the bond order parameters of the tensile deformation of the graphene-carbon nanotube fiber-reinforced polymer composite system.

#### 4. Conclusions

The present study is focused primarily upon the mechanical properties of fiber-reinforced polymer composites containing graphene-carbon nanotube hybrid materials. The graphene-carbon nanotube fiber-reinforced polymer composites utilize nanotechnology enhancements to provide advantageous durability and structural stability improvements over conventional fiber-reinforced polymer composites not containing graphene or carbon nanotubes. The effect of the hybrid material weight fraction on the modulus of elasticity and hardness is evaluated, stress-strain responses of the composite tensile deformation are illustrated, and the effect of strain on the bond order parameters is investigated for the fiber-reinforced polymer composite. The major conclusions are summarized as follows:

- Graphene-carbon nanotube multi-stack three-dimensional architectures can overcome the limitations and restricted performance typically encountered with carbon-based materials by using the combined strategies of three-dimensional architecture and low-dimensional carbon nanomaterial characteristics.

- The poor dispersibility of graphene-carbon nanotubes greatly affects the characteristics of the composites which they form with the polymer matrices into which they are introduced.
- The modulus of elasticity of the composite is enhanced as compared to the neat polymer.
- The hybrid material exhibits great improvements in hardness and yield strength and major deteriorations in strain at break.
- The carbon nanotubes exhibit no preferred orientation and are approximately random.
- The doping permanently increases the charge concentration in semiconducting carbon nanotubes present in the film, thereby decreasing the sheet resistance of the network.
- Though graphene and carbon nanotubes have extraordinary mechanical properties, their ability to strengthen polymers and epoxies is limited by the strength of interfacial bonding.
- The graphene-carbon nanotube fiber-reinforced polymer composite differs from a conventional carbon-fiber composite in that there is a much higher interface area between reinforcing carbon and polymer matrix phases.

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