

Electrical and mechanical properties of catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite materials

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January 18, 2023

Abstract

Carbon nanotubes are excellent candidates for the development of nano-reinforced polymer composite materials. However, assurance of homogeneous dispersion, interfacial compatibility between the carbon nanotube and the polymer, and exfoliation of the aggregates of carbon nanotubes, are required for the successful integration of carbon nanotubes into nanocomposites. The present study is focused primarily upon the electrical and mechanical properties of catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite materials. Particular emphasis is placed upon the effect of carbon loading on the electrical conductivity and the influence of temperature on the loss factor and modulus for the composite materials. The results indicate that the electrical properties of the composite would not be changed from those of the bulk polymer until the average distance between the carbon nanotubes is reduced such that either electron tunneling through the polymer or physical contacts may be formed. Among the challenges introduced in the fabrication of carbon nanotube-filled polymer composites is the necessity to creatively control and make use of surface interactions between carbon nanotubes and polymeric chains in order to obtain an adequate dispersion throughout the matrix without destroying the integrity of the carbon nanotubes. Frequency domain material properties are therefore limited to applications where strains are small and stress is approximately linear with strain and the strain rate. Frequency domain material properties become irrelevant if the material exhibits nonlinear elastic behavior or is subjected to large strains. Depending on the type of polymers in the matrix, above a certain temperature limit, degradation starts or cross-linking starts. The deformed elastic body possess an amount of potential energy equal to the initial amount of potential energy minus the amount of energy irreversibly dissipated. The modulus and loss factor variables of a damping material are highly dependent upon the temperature of the damping material and the vibration frequency. Because of their viscoelastic nature, the stress and strain in viscoelastic materials are not in phase, and, in fact, exhibit hysteresis. The resonant frequency is related to the modulus of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite.

Keywords: Composite materials; Electrical properties; Mechanical properties; Carbon nanotubes; Electrical conductivity; Loss modulus

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1. Introduction

Carbon is a nonmetallic chemical element in Group 14 of the periodic table. Although widely distributed in nature, carbon is not particularly plentiful. Elemental carbon exists in several forms, each of which has its own physical characteristics. Two of its well-defined forms, diamond and graphite, are crystalline in structure, but they differ in physical properties because the arrangements of the atoms in their structures are dissimilar [1, 2]. A third form, called fullerene, consists of a variety of molecules composed entirely of carbon [3, 4]. Spheroidal, closed-cage fullerenes are called buckminsterfullerenes, or buckyballs, and cylindrical fullerenes are called carbon nanotubes [5, 6]. A fourth form, called Q-carbon, is crystalline and magnetic [7, 8]. Yet another form, called amorphous carbon, has no crystalline structure. Other forms, such as carbon black, charcoal, lampblack, coal, and coke, are sometimes called amorphous, but X-ray examination has revealed that these substances do possess a low degree of crystallinity [9, 10]. Diamond and graphite occur naturally on Earth, and they also can be produced synthetically; they are chemically inert but do combine with oxygen at high temperatures, just as amorphous carbon does [1, 2]. Fullerene was serendipitously discovered in 1985 as a synthetic product in the course of laboratory experiments to simulate the chemistry in the atmosphere of giant stars [3, 4]. It was later found to occur naturally in tiny amounts on Earth and in meteorites [5, 6]. Q-carbon is also synthetic, but scientists have speculated that it could form within the hot environments of some planetary cores [7, 8]. At ordinary temperatures, carbon is very unreactive, it is difficult to oxidize, and it does not react with acids or alkalis. At high temperatures it combines with sulfur vapor to form carbon disulfide, with silicon and certain metals to form carbides, and with oxygen to form oxides, of which the most important are carbon monoxide and carbon dioxide. Because at high temperatures carbon combines readily with oxygen that is present in compounds with metals, large quantities of coke are used in metallurgical processes to reduce metal oxide ores.

Pure diamond is the hardest naturally occurring substance known and is a poor conductor of electricity [11]. Graphite, on the other hand, is a soft slippery solid that is a good conductor of both heat and electricity

[12]. Carbon as diamond is the most expensive and brilliant of all the natural gemstones and the hardest of the naturally occurring abrasives [11]. In microcrystalline and nearly amorphous form, graphite is used as a black pigment, as an adsorbent, as a fuel, as a filler for rubber, and, mixed with clay, as the lead of pencils [12]. Because it conducts electricity but does not melt, graphite is also used for electrodes in electric furnaces and dry cells as well as for making crucibles in which metals are melted [13]. Molecules of fullerene show promise in a range of applications, including high-tensile-strength materials, unique electronic and energy-storage devices, and safe encapsulation of flammable gases, such as hydrogen [14]. Q-carbon, which is created by rapidly cooling a sample of elemental carbon whose temperature has been raised to 4,000 K [15], is harder than diamond, and it can be used to manufacture diamond structures, such as diamond films and microneedles [16], within its matrix. Elemental carbon is nontoxic.

Each of the amorphous forms of carbon has its own specific character, and, hence, each has its own particular applications [17, 18]. All are products of oxidation and other forms of decomposition of organic compounds. Coal and coke, for example, are used extensively as fuels [19, 20]. Charcoal is used as an absorptive and filtering agent and as a fuel and was once widely used as an ingredient in gunpowder [21, 22]. Coals are elemental carbon mixed with varying amounts of carbon compounds. Coke and charcoal are nearly pure carbon. In addition to its uses in making inks and paints, carbon black is added to the rubber used in tires to improve its wearing qualities [23, 24]. Carbon, either elemental or combined, is usually determined quantitatively by conversion to carbon dioxide gas, which can then be absorbed by other chemicals to give either a weighable product or a solution with acidic properties that can be titrated.

When an element exists in more than one crystalline form, those forms are called allotropes; the two most common allotropes of carbon are diamond and graphite [25, 26]. The crystal structure of diamond is an infinite three-dimensional array of carbon atoms, each of which forms a structure in which each of the bonds makes equal angles with its neighbors. If the ends of the bonds are connected, the structure is that of a tetrahedron, a three-sided pyramid of four faces including the base. Every carbon atom is covalently bonded at the four corners of the tetrahedron to four other carbon atoms. The distance between carbon atoms along the bond is called the single-bond length. The space lattice of the diamond can be visualized as carbon atoms in puckered hexagonal rings that lie roughly in one plane, the natural cleavage plane of the crystal; and these sheets of hexagonal, puckered rings are stacked in such a way that the atoms in every fourth layer lie in the same position as those in the first layer. Such a crystal structure can be destroyed only by the rupture of many strong bonds. Thus, the extreme hardness, the high sublimation temperature, the presumed extremely high melting point extrapolated from known behavior, and the reduced chemical reactivity and insulating properties are all reasonable consequences of the crystal structure [27, 28]. Because of both the sense and the direction of the tetrahedral axis, four spatial orientations of carbon atoms exist, leading to two tetrahedral and two octahedral forms of diamond.

The crystal structure of graphite amounts to a parallel stacking of layers of carbon atoms. Within each layer the carbon atoms lie in fused hexagonal rings that extend infinitely in two dimensions. Each layer separates two identically oriented layers. Within each layer the carbon-carbon bond distance is intermediate between the single bond and double bond distances. All carbon-carbon bonds within a layer are the same. The interlayer distance is sufficiently large to preclude localized bonding between the layers; the bonding between layers is probably by van der Waals interaction, namely the result of attraction between electrons of one carbon atom and the nuclei of neighboring atoms. Ready cleavage, as compared with diamond, and electrical conductivity are consequences of the crystal structure of graphite [29, 30]. Other related properties are softness, smoothness, and slipperiness [31, 32]. A less common form of graphite, which occurs in nature, is based upon an ABCABCA... stacking, in which every fourth layer is the same. The amorphous varieties of carbon are based upon microcrystalline forms of graphite. The individual layers of carbon in graphite are called graphene, which was successfully isolated in single-layer form.

The greater degree of compactness in the diamond structure as compared with graphite suggests that by the application of sufficient pressure on graphite it should be converted to diamond. At room temperature and atmospheric pressure, diamond is actually less stable than graphite. The rate of conversion of diamond to

graphite is so slow, however, that a diamond persists in its crystal form indefinitely [33, 34]. As temperature rises, the rate of conversion to graphite increases substantially, and at high temperatures it becomes thermodynamically favorable if the pressure is sufficiently high. At the same time, however, the rate of conversion decreases as the thermodynamic favorability increases. Thus, pure graphite does not yield diamond when heated under high pressure, and it appears that direct deformation of the graphite structure to the diamond structure in the solid state is not feasible. The occurrence of diamonds in iron-magnesium silicates in the volcanic structures called pipes and in iron-nickel and iron sulfide phases in meteorites suggests that they were formed by dissolution of carbon in those compounds and subsequent crystallization from them in the molten state at temperatures and pressures favorable to diamond stability [35, 36]. The successful synthesis of diamond is based upon this principle. The crystal structure of graphite is of a kind that permits the formation of many compounds, called lamellar or intercalation compounds, by penetration of molecules or ions [37, 38]. Graphitic oxide and graphitic fluoride are nonconducting lamellar substances not obtained in true molecular forms that can be reproduced, but their formulas do approximate, respectively, the compositions of carbon dioxide and carbon monofluoride.

The present study is focused primarily upon the electrical and mechanical properties of catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite materials. Development of carbon nanotube-based, and particularly multi-walled carbon nanotube-based, polymer nanocomposites is attractive because of the possibility of combining the extraordinary properties of carbon nanotubes with the lightweight character of polymers to develop unique, tailorable materials. On the basis of the extraordinary mechanical properties and the large aspect ratio associated with individual tubes, carbon nanotubes are excellent candidates for the development of nano-reinforced polymer composite materials. However, assurance of homogeneous dispersion, interfacial compatibility between the carbon nanotube and the polymer, and exfoliation of the aggregates of carbon nanotubes, are required for the successful integration of carbon nanotubes into nanocomposites. Carbon nanotubes, according to the present invention, include, but are not limited to, single-walled carbon nanotubes, multi-walled carbon nanotubes, double-walled carbon nanotubes, buckytubes, small-diameter carbon nanotubes, fullerene tubes, tubular fullerenes, graphite fibrils, carbon nanofibers, and combinations thereof. Such carbon nanotubes can be of a variety and range of lengths, diameters, number of tube walls, and chirality, and can be made by any known technique. The present study aims to provide a fundamental understanding of the electrical and mechanical properties of catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite materials. Particular emphasis is placed upon the effect of carbon loading on the electrical conductivity and the influence of temperature on the loss factor and modulus for the composite materials.

2. Methods

Carbon nanotubes, with their unique shapes and characteristics, are being considered for various applications. A carbon nanotube has a tubular shape of one-dimensional nature which can be grown through a nano metal particle catalyst. More specifically, carbon nanotubes can be synthesized by arc discharge or laser ablation of graphite. In addition, carbon nanotubes can be grown by a chemical vapor deposition technique. With the chemical vapor deposition technique, there are also variations including plasma enhanced and so forth. Carbon nanotubes can also be formed with a frame synthesis technique similar to that used to form fumed silica. In this technique, carbon atoms are first nucleated on the surface of the nano metal particles. Once supersaturation of carbon is reached, a tube of carbon will grow. Regardless of the form of synthesis, and generally speaking, the diameter of the tube will be comparable to the size of the nanoparticle. Depending on the method of synthesis, reaction condition, the metal nanoparticles, temperature and many other parameters, the carbon nanotube can have just one wall, characterized as a single walled carbon nanotube, it can have two walls, characterized as a double walled carbon nanotube, or can be a multi-walled carbon nanotube. The purity, chirality, length, and defect rate can vary. Very often, after the carbon nanotube synthesis, there can occur a mixture of tubes with a distribution of all of the above, some long, some short. Some of the carbon nanotubes will be metallic and some will be semiconducting.

One aspect of the present study is directed to mechanical functionalization of carbon fibers processed in situ

with molten polymers to create reactive bonding sites at the ends of the fibers. The reactive sites react with the polymer to chemically bond the carbon fibers to the polymer. This can be achieved with a variety of carbon fibers, including single or multi-walled carbon nanotubes and standard micron sized carbon fibers. It works well in conjunction with a variety of polymers that possess chemical groups having double bonds or various tertiary carbon bonds. Similar observations of good bonding at sites of broken covalent graphite and graphene bonds have been made while mechanically exfoliating graphite into graphene in situ with polymers. The fibers are broken or cut while in molten polymers during melt processing, and this can be achieved either by having a specially designed cutting tool in the melt processing equipment, or through high shear in the melt processing, or by a combination of the two. The opening up of new fiber ends by breaking or cutting the fibers while surrounded by liquid polymers introduces dangling bonds having unfilled valences which provide reactive sites on the fiber ends, which represent sites for strong bonding, such as covalent bonding, by the polymers having the attributes mentioned above. The resulting solid composites have improved mechanical properties upon cooling, and the optimal fiber length, and, subsequently, cost will be greatly reduced by this bonding. In one aspect, the present study provides a high efficiency mixing method to transform a polymer composite that contains carbon fibers into broken carbon fibers having reactive ends or edges, by compounding in a batch mixer or extruder that imparts repetitive, high shear strain rates. The method is low cost to produce a carbon fiber-reinforced polymer matrix composites that offers numerous property advantages, including increased specific stiffness and strength, enhanced electrical and thermal conductivity, and retention of optical transparency. Furthermore, these properties are tunable by modification of the process, *vide infra*. In some cases, an inert gas or vacuum may be used during processing. Other advantages of in situ carbon fiber breaking are that it avoids handling size reduced carbon fibers, and also avoids the need to disperse them uniformly in the polymer matrix phase. Superior mixing produces finer composite structures and very good particle distribution.

It should be understood that essentially any polymer inert to carbon fibers or nanotubes and capable of imparting sufficient shear strain to achieve the desired carbon fiber breakage may be used in the method of the present study. Mechanical functionalization of carbon fibers within a polymer matrix may be accomplished by a polymer processing technique that imparts repetitive high shear strain events to mechanically break the carbon fibers within the polymer matrix. A succession of shear strain events is defined as subjecting the molten polymer to an alternating series of higher and lower shear strain rates over essentially the same time intervals so that a pulsating series of higher and lower shear forces associated with the shear strain rate are applied to the carbon fibers in the molten polymer. Higher and lower shear strain rates are defined as a first higher, shear strain rate that is at least twice the magnitude of a second lower shear strain rate. After high-shear mixing, the mechanically size reduced carbon fibers are uniformly dispersed in the molten polymer, are randomly oriented, and have high aspect ratio. Graphite microparticles are also added to the molten polymer and are mechanically exfoliated into graphene via the succession of shear strain events. The amount of graphite added to the molten polymer can be an amount up to and including the amount of carbon fibers and nanotubes added. The shear strain rate within the polymer is controlled by the type of polymer and the processing parameters, including the geometry of the mixer, processing temperature, and speed in revolutions per minute. The required processing temperature and speed for a particular polymer is determinable from polymer rheology data given that, at a constant temperature, the shear strain rate is linearly dependent upon speed in revolutions per minute. Polymer rheology data collected for a particular polymer at three different temperatures provides a log shear stress versus log shear strain rate graph.

A polymer-carbon nanotube composite differs from a conventional carbon-fiber composite in that there is a much higher interface area between reinforcing carbon and polymer matrix phases. It has been proposed that introducing a uniform distribution of carbon nanotubes into a polymer matrix should yield property enhancements that go beyond that of a simple rule of mixtures [39, 40]. The challenge is to take full advantage of the exceptional properties of carbon nanotubes in the composite material. Carbon nanotubes are considered to be ideal reinforcing material for polymer matrices because of their high aspect ratio, low density, remarkable mechanical properties, and good electrical and thermal conductivity [41, 42]. One of the matrices that has been studied is commercially important epoxy [43, 44]. However, property improvements

have not been significant to date, apparently due to poor interfacial carbon nanotube-polymer bonding and severe carbon nanotube agglomeration [45, 46]. These obstacles have now been overcome by utilizing a new processing route that involves high-shear mixing in a molten polymer to induce de-agglomeration and dispersal of carbon nanotubes, while enhancing adhesive bonding and covalent bonding by creating new sites on the carbon nanotubes to which the polymer chains can bond. An attempt is also being made to increase impact energy absorption by forming a biphasic composite, comprising a high fraction of strong carbon nanotube-reinforced epoxy particles uniformly dispersed in a tough epoxy matrix. A carbon nanotube consists of a sheet of hexagonal-bonded carbon atoms rolled up to form a tube. A single-walled carbon nanotube comprises a single layer of this tubular structure of carbon atoms. However, the structure of a multi-walled carbon nanotube is still open to some debate. In one model, a multi-walled carbon nanotube is imagined to be a single graphene sheet rolled up into a scroll. In another model, a multi-walled carbon nanotube is considered to be made of co-axial layers of helically-aligned carbon hexagons, with matching at the joint lines, leading to a nested-shell structure. In yet another model, a combination of scroll-like and nested-shell structures has been proposed.

A small percentage of carbon nanotubes can improve the robustness of the material without significantly compromising the elastomeric properties. Increases in mechanical strength properties reduce blade edge tears and substantially extend blade life due to edge wear. Low percentage additions of carbon nanotubes can also significantly increase electrical and thermal conductivity. Enhanced electrical conductivity can dissipate charge accumulation at the blade edge due to rubbing against the photoreceptor and air breakdown from the accumulation of charged toner at the blade edge. Enhanced thermal conductivity can aid heat dissipation due to friction at the blade-photoreceptor interface. Polymer properties such as electrical conductivity can be enhanced by incorporating therein a combination of carbon fibers or carbon nanotubes. Additionally, carbon nanotubes can prevent delamination and provide structural stability in polymer composites. Because carbon nanotubes have uniquely high strength to mass ratio, intrinsic light weight, thermal conductivity, electrical conductivity, and chemical functionality, and can prevent delamination and provide structural stability in polymer composites, they can impart these properties to polymers when effectively combined therewith. Though 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. Carbon nanotubes can be functionalized via covalent or non-covalent bonding, to either the ends of the nanotubes or to the sidewalls. Covalent functionalization often requires beginning with modified tubes, such as fluorinated nanotubes, or with purified tubes where defect sites in the carbon nanotubes are produced by oxidation. Because these modifications often result in the disruption of the bonds along the tubes themselves, covalent functionalization can degrade the mechanical and electrical properties of the nanotubes and, thus, is not ideal for all applications. 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. This type of functionalization results in higher degrees of functionalization as the entire length of the carbon nanotube can be functionalized rather than just the ends and specific active sites. Like end-functionalization, non-covalent functionalization also opens up the possibility for tailoring the functionalization via the choice of molecule. For the purpose of polymerizing the carbon nanotube to a polymer resin or epoxy, in one embodiment, a polymerizable ligand comprising a polyaromatic molecule with an appropriate polymerizable group such as a vinyl, styryl, or amino group can be non-covalently bonded to the carbon nanotubes.

It is known that increases in elastic modulus and strength of epoxy-carbon nanotube composite resulted from making small additions of carbon nanotubes to polymer matrices. While Van der Waals bonding dominates interactions between carbon nanotubes and polymers, adhesion in some carbon nanotube composites also occurs via covalent bonds, which plays a role in reinforcement of carbon nanotube composites. Measurements by atomic force microscopy of the pull-out force necessary to remove a given length of an individual multi-walled carbon nanotube embedded in copolymers demonstrate covalent bonding between the outer layer of a multi-walled carbon nanotube and the polymer matrix. 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 carbon nanotube having the same magnitude as the radius of gyration of the polymer chain. Because of the tendency of carbon nanotubes to agglomerate, difficulty of aligning them in the matrix and often poor load transfer, attempts are made to produce composites using different polymer matrix phases. The present study provides remarkable improvements in stiffness and strength of a carbon nanotube-reinforced epoxy composite. The composites are characterized by an increase in impact energy absorption. Processing parameters which achieve superior mechanical properties and performance are provided herein.

Incremental additions of carbon nanotubes to the molten epoxy are necessary to produce a composite that contains a high fraction of carbon nanotubes. It takes about one hour 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 carbon nanotubes and epoxy polymer matrix. After completion of the mixing process, the composite material is extracted from the barrel at the mixing temperature. Upon cooling to ambient temperature, the material became hard and brittle. This is further evidence for chemical bonding between dispersed carbon nanotubes and epoxy matrix. Larger samples of carbon nanotube-reinforced epoxy can be prepared using an integrated high shear mixing and injection molding apparatus. American Society for Testing and Materials standard test bars can be fabricated and evaluated for mechanical properties. Preliminary tests performed on small samples indicate significant improvements in stiffness and strength.

3. Results and discussion

The high-resolution transmission electron micrographs are illustrated in Figure 1 for the catalytically-grown multi-walled carbon nanotube material. A typical particle consists of loosely-agglomerated multi-walled carbon nanotubes, most of which are about 30-40 nm in diameter and more than one micron in length. Therefore, the multi-walled carbon nanotubes have high aspect ratios. In several cases, the multi-walled carbon nanotubes have white-contrasting tips, which are transition-metal catalyst particles. Hence, it is apparent that the multi-walled carbon nanotubes are produced by the particle-at-the-tip growth mechanism. Generally, multi-walled carbon nanotubes are used for applications in plastic composites. Multi-walled carbon nanotubes, however, can have inferior electrical properties due to amorphous carbon or defects on the surface formed during synthesis. Accordingly, a composite including the same may not have the desired electrical property. Thus, it can be important to improve the crystallinity of the surface of the carbon nanotubes. One method re-aligns the hexagon structure of carbon atoms using a high temperature treatment to improve surface crystallinity of carbon nanotubes. This method, however, increases manufacturing cost because an additional process is required after carbon nanotube synthesis. It can also be difficult to select synthesis conditions for the high heat treatment. In addition, productivity can be impaired. Carbon nanotubes are nanomaterials that individually include properties of high modulus, tensile strength, aspect ratio, and electrical and thermal conductivity. The fabrication of carbon nanotube filaments can be based on wet spinning methods, which require dispersing carbon nanotubes in a solution for further spinning processes. The chemical dispersion process generally leads to a low usage of carbon nanotubes, and the spun filament usually contains surfactants or polymer molecules which reduce the strength and the thermal and electrical properties of the filament. Dry spinning methods can be used to prepare carbon nanotube filaments composed of pure carbon nanotubes from as-grown super-aligned carbon nanotube arrays. The dry spinning method that directly spins carbon nanotube filaments from super-aligned carbon nanotube arrays has attracted attention because the dry spinning method is simple and controllable to produce continuous carbon nanotube filaments. The dry spinning method is enabled by the van der Waals forces between carbon nanotubes that provide a cohesive force that enables the carbon nanotubes to readily stick to one another. While the van der Waals forces may be disadvantageous to applications such as composite films where a high degree of dispersion is preferred, the van der Waals forces can prove useful in the preparation of carbon nanotube filaments, threads, and ribbons. However, while the van der Waals forces are relatively strong in an orientation that adheres the carbon nanotubes to one another the van der Waals forces are comparatively weak in an orientation of carbon nanotube alignment. Therefore, filaments made from carbon nanotubes typically exhibit tensile strength that is orders of magnitude less than the tensile strength of the individual carbon nanotubes. Accordingly, improvements in the strength of thread made from carbon nanotubes is

desired. It should now be understood that carbon nanotube filaments that are braided into a thread exhibit tensile strength properties that exceed the tensile strength properties of the carbon nanotube filaments themselves. The improvement in tensile strength properties is attributed to the frequency of intersections per length of the individual carbon nanotubes that are formed into the carbon nanotube filament. To increase the frequency of intersections in a thread, thinner carbon nanotube filaments may be braided with a high pick frequency. Further, to prevent breakage of the thinner carbon nanotube filaments in a machine braiding operation, low-tension carriers that pay out the carbon nanotube filaments may be used.

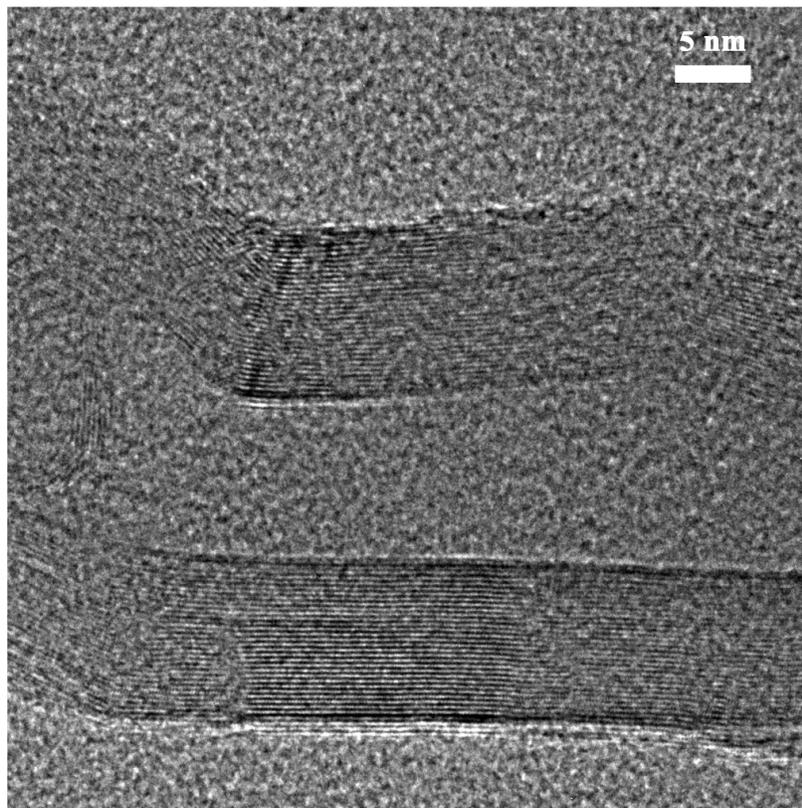


Figure 1. High resolution transmission electron micrographs of the catalytically-grown multi-walled carbon nanotube material.

The scanning electron micrographs are illustrated in Figure 2 for the catalytically-grown multi-walled carbon nanotube material used as a filler. Multi-walled carbon nanotubes include concentric nanotubes with an inter-wall spacing of about 0.34 nm and outside diameters on the order of about 10 to about 100 nm. Multi-walled carbon nanotubes have gained increasing interest in various industrial and technological applications because of the development of techniques to produce bulk quantities of high-quality carbon nanotubes with uniform diameters, number of walls, and atomic structure. A key technological challenge is growing high-quality single-walled carbon nanotubes in large quantities. Although chemical vapor deposition provides the highest quality single-walled carbon nanotubes, large quantity forest growth is hampered by the presence of double and multi-walled carbon nanotubes. The ratio of single-walled to multi-walled carbon nanotubes can vary greatly from one process to another and is difficult to control. Several methods of synthesizing fullerenes have developed from the condensation of vaporized carbon at high temperature. Fullerenes may be prepared by carbon arc methods using vaporized carbon at high temperature. Carbon nanotubes have

also been produced as one of the deposits on the cathode in carbon arc processes. An important way to synthesize carbon nanotubes is by catalytic decomposition of a carbon-containing gas by nanometer-scale metal particles supported on a substrate. The carbon feedstock molecules dissociate on the metal particle surface and the resulting carbon atoms combine to form carbon nanotubes. The method typically produces imperfect multi-walled carbon nanotubes. One example of this method involves the disproportionation of carbon monoxide to form single-walled carbon nanotubes and carbon dioxide catalyzed by transition metal catalyst particles comprising molybdenum, iron, nickel, cobalt, or mixtures thereof residing on a support, such as alumina. Although the method can use inexpensive feedstocks and moderate temperatures, the yield of single-walled carbon nanotubes can be low, with large amounts of other forms of carbon, such as amorphous carbon and multi-walled carbon nanotubes present in the product. The method often results in tangled carbon nanotubes and also requires the removal of the support material for many applications.

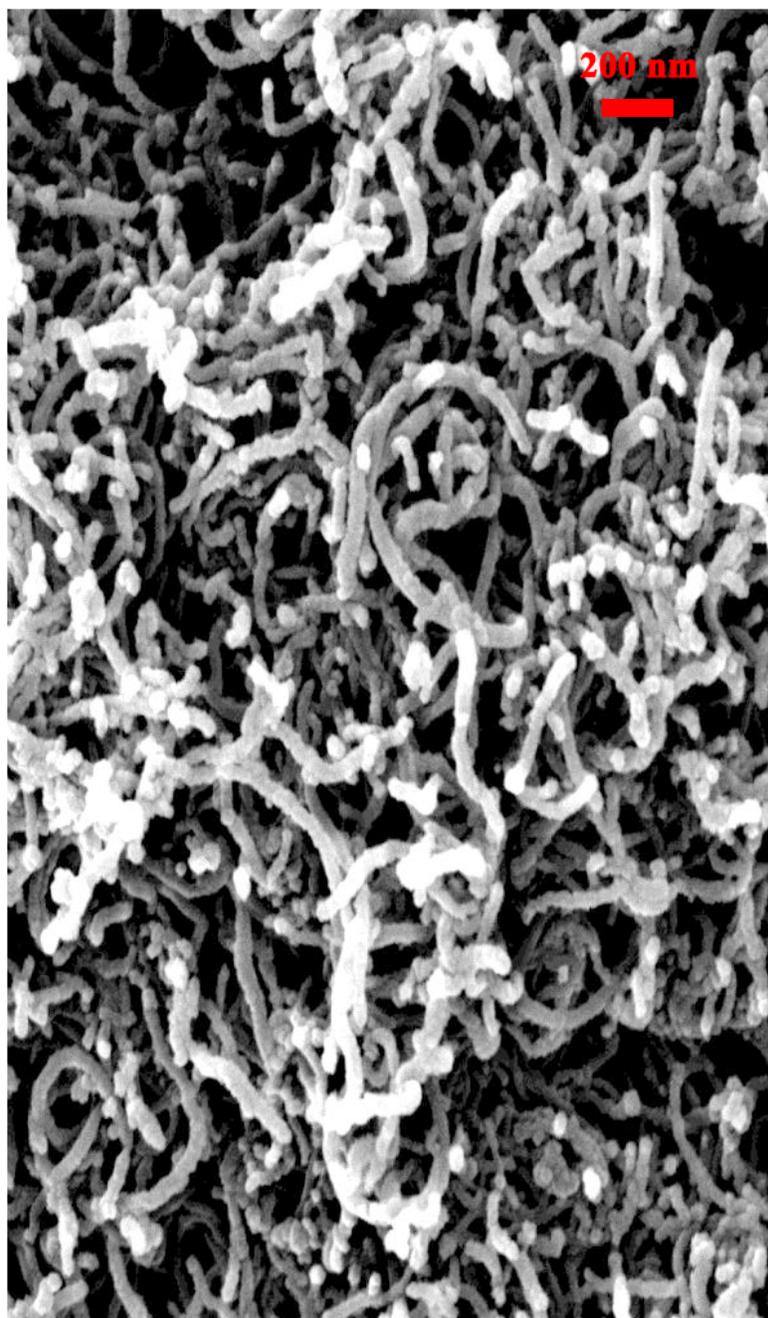


Figure 2. Scanning electron micrographs of the catalytically-grown multi-walled carbon nanotube material used as a filler.

The scanning electron micrographs are illustrated in Figure 3 for the graphitic carbon nanofibers that represent a class of nanostructured carbon fibers having atomic structures uniquely different from that of carbon nanotubes. Interest in developing carbon nanostructures appropriately surface-derivatized for diverse ap-

plications remains high [47, 48]. Considerable progress has been made in controlling the dispersibility and wettability properties of single-walled or multi-walled carbon nanotubes through either covalent or non-covalent surface derivatization [49, 50]. Herringbone graphitic carbon nanofibers possess canted graphene sheets, also described as geodesic-like conical graphene sheets, stacked in a nested fashion along the long fiber axis. Graphitic carbon nanofibers of this type can be prepared having average diameters from 25 nm-200 nm and lengths on the micron scale. The graphitic atomic structure of herringbone graphitic carbon nanofibers gives a carbon nanofiber long-axis surface comprised of carbon edge sites, usually passivated by hydrogen atoms. The surface-functionalization of herringbone graphitic carbon nanofibers with reactive linker molecules using surface oxidation and carboxyl group coupling chemistry occurs without degradation of the structural integrity of the graphitic carbon nanofiber backbone and affords surface-derivatized graphitic carbon nanofibers having a high surface density of functional groups. Covalent binding of such linker molecules to either polymer resins or ceramic condensation oligomers gives graphitic carbon nanofiber-polymer or graphitic carbon nanofiber-ceramics hybrid materials. A particularly interesting class of carbon nanotubes are the vertically aligned carbon nanofibers. Vertically aligned carbon nanofibers are multi-walled carbon nanotubes that are typically grown in a direct current plasma, yielding nanofibers that are aligned vertically from the surface. The resulting nanofiber forests have interesting properties because in addition to providing edge planes along the nanofiber walls, the interstices between the fibers are straight and relatively large, providing a high degree of accessibility to analytes. The presence of well-defined interstices is important because very small pores cannot support electrical double-layers and diffusion limitations can reduce the effective surface area. Vertically aligned carbon nanofibers are a promising high surface area, nanoscale carbon material. Vertically aligned carbon nanofibers have similar electrochemical and mechanical properties as other nanoscale carbon materials. The advantage of vertically aligned carbon nanofibers is the ability to control their physical dimensions allowing for large, accessible surface areas. Thus, vertically aligned carbon nanofibers are an ideal platform for modifications leading to increased surface area, such as covalent functionalization with molecular layers and decoration with metal coatings. Although aligned carbon nanotube arrays have drawn significant research interest, there exists a potential drawback for their implementation in applications. Conventionally-prepared carbon nanotube arrays are prepared by depositing a thin, insulating oxide layer upon a substrate, followed by deposition of a catalyst layer upon the oxide layer. The oxide layer supports the catalyst, maintains its activity and promotes the growth of carbon nanotubes. The general requirement of an intervening oxide layer between the substrate and the catalyst prevents the carbon nanotubes from becoming bonded directly to the substrate. Although simple techniques have been developed to transfer aligned carbon nanotubes from a growth substrate to a desired substrate, direct growth on a desired substrate would be a far more efficient process. Furthermore, the oxide layer is not compatible with a number of substrates, so there is a process limitation on the types of substrates upon which carbon nanotubes can be grown. As a result, for a number of interesting substrates, direct carbon nanotube growth is not possible by conventional growth processes. For example, direct growth of dense arrays of carbon nanotubes on a carbon surface or a conducting surface such as, for example, a metal is not possible by conventional growth methods. Carbon fibers are a substrate of particular interest due to their well-established use in the aerospace and polymer composite industries. Direct growth of carbon nanotubes on carbon surfaces according to conventional growth methods typically results in low carbon nanotube yields, sparse growth and potential damage to the carbon surface by the catalyst. Alignment generally enhances the electrical, thermal and mechanical properties of the carbon nanotubes relative to their unaligned counterparts. Aligned carbon nanotube arrays are conventionally prepared by coating a growth substrate with a thin insulating layer of alumina, followed by coating of the alumina layer with a thin iron catalyst layer. Upon reduction of the iron catalyst layer, the iron typically breaks apart to form point sources of high-density nucleation sites operable for forming carbon nanotubes in the presence of a feedstock gas. In this well-established growth technique, the catalyst is supported by the alumina layer and resides at the base of the growing carbon nanotube array next to the substrate. The catalyst particles absorb carbon from the gas phase and provide it at the particle interface to form the growing carbon nanotubes. As a result, bonding to the substrate occurs through the metal catalyst particle. This type of carbon-metal bond is air sensitive and breaks upon exposure to air. Therefore, conventionally-prepared carbon nanotube arrays are easily detached from their growth substrate.

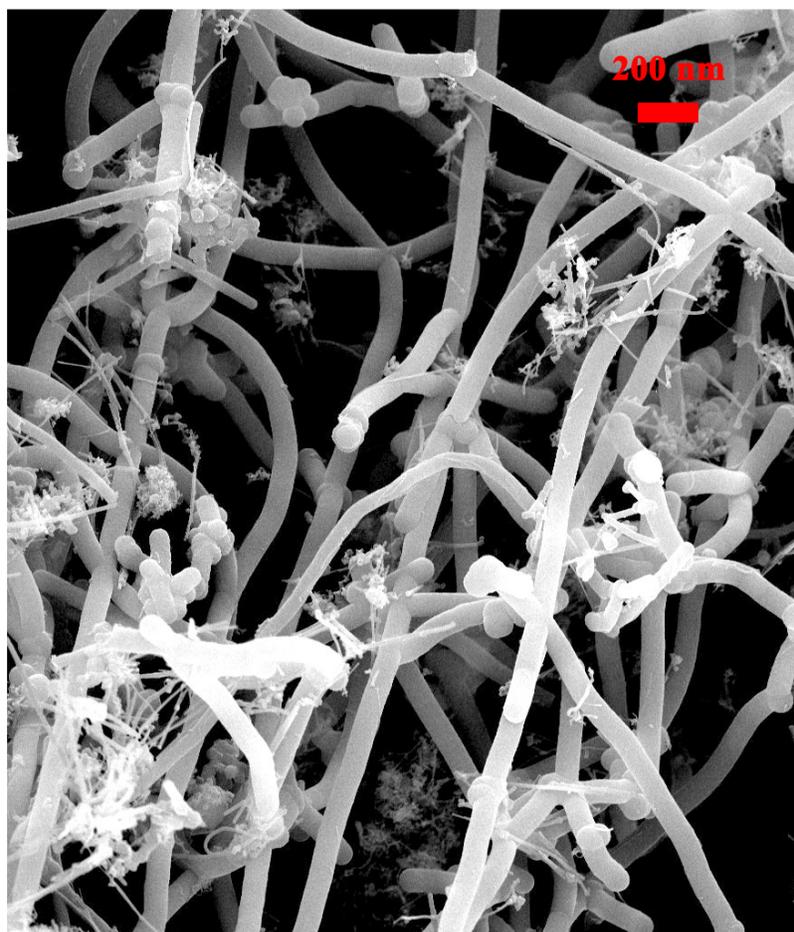


Figure 3. Scanning electron micrographs of the graphitic carbon nanofibers that represent a class of nanostructured carbon fibers having atomic structures uniquely different from that of carbon nanotubes.

The scanning electron micrographs are illustrated in Figure 4 for the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. Carbon nanotubes differ physically and chemically from continuous carbon fibers which are commercially available as reinforcement materials, and from other forms of carbon such as standard graphite and carbon black. Standard graphite, because of its structure, can undergo oxidation to almost complete saturation. Moreover, carbon black is amorphous carbon generally in the form of spheroidal particles having a graphene structure, carbon layers around a disordered nucleus. The differences make graphite and carbon black poor predictors of carbon nanotube chemistry. Carbon nanotubes exist in a variety of forms and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces [51, 52]. Such vermicular carbon deposits have been observed almost since the advent of electron microscopy [53, 54]. Carbon nanotubes are known to have extraordinary tensile strength, including high strain to failure and relatively high tensile modulus [55, 56]. Carbon nanotubes may also be highly resistant to fatigue, radiation damage, and heat [57, 58]. To this end, the addition of carbon nanotubes to composites can increase tensile strength and stiffness. Unfortunately, adding even a small amount of carbon nanotubes to, for instance, a resin matrix to subsequently generate the desired composite can increase the viscosity of the matrix significantly. Moreover, continuous carbon nanotubes are not yet readily available, so as to permit the creation of a substantially continuous carbon nanotube

composite, or a substantially continuous composite reinforced with the continuous carbon nanotubes. The availability of either or both composites can allow for a variety of interesting commercial applications. Accordingly, it would be advantageous to provide a substantially continuous composite material reinforced with substantially continuous carbon nanotubes, such that the composite material can be provided with a low density while having high modulus and strength. In addition, it would be advantageous to provide a method for manufacturing such composite materials.



Figure 4. Scanning electron micrographs of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite.

The effect of volumetric carbon loading on the electrical conductivity is illustrated in Figure 5 for the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. The results are suggestive of a typical percolation system wherein the electrical properties of the composite would not be changed from those of the bulk polymer until the average distance between the carbon nanotubes is reduced such that either electron tunneling through the polymer or physical contacts may be formed. Polymer compositions are being increasingly used in a wide range of areas that have traditionally employed the use of other materials, such as metals [59, 60]. Polymers possess a number of desirable physical properties, are light weight, and inexpensive [61, 62]. In addition, many polymer materials may be formed into a number of various shapes and forms and exhibit significant flexibility in the forms that they assume, and may be

used as coatings, dispersions, extrusion and molding resins, pastes, powders, and the like [63, 64]. There are various applications for which it would be desirable to use polymer compositions, which require materials with electrical conductivity [65, 66]. However, a significant number of polymeric materials fail to be intrinsically electrically or thermally conductive enough for many of these applications [67, 68]. Most composites are made with the understanding that there will be only weak secondary bonds that exist between the fibers and polymer [69, 70]. This makes it necessary for very high aspect ratios of fibers to be used in order to get reasonable stress transfer, or else the fibers will slip upon load. Some commercial applications of carbon fiber-reinforced polymer matrix composites include aircraft and aerospace systems, automotive systems and vehicles, electronics, government defense and security, pressure vessels, and reactor chambers, among others [71, 72]. Progress in the development of low-cost methods to effectively produce carbon fiber-reinforced polymer matrix composites remains very slow [73, 74]. Currently, some of the challenges that exist affecting the development of carbon fiber-reinforced polymer matrix composites viable for use in real world applications include the expense of the materials and the impracticality of the presently used chemical and mechanical manipulations for large-scale commercial production [75, 76]. It would thus be desirable for a low-cost method to produce a carbon fiber-reinforced polymer matrix composite suitable for large-scale commercial production that offers many property advantages, including increased specific stiffness and strength, enhanced electrical and thermal conductivity, and retention of optical transparency [77, 78]. Among the challenges introduced in the fabrication of carbon nanotube-filled polymer composites is the necessity to creatively control and make use of surface interactions between carbon nanotubes and polymeric chains in order to obtain an adequate dispersion throughout the matrix without destroying the integrity of the carbon nanotubes.

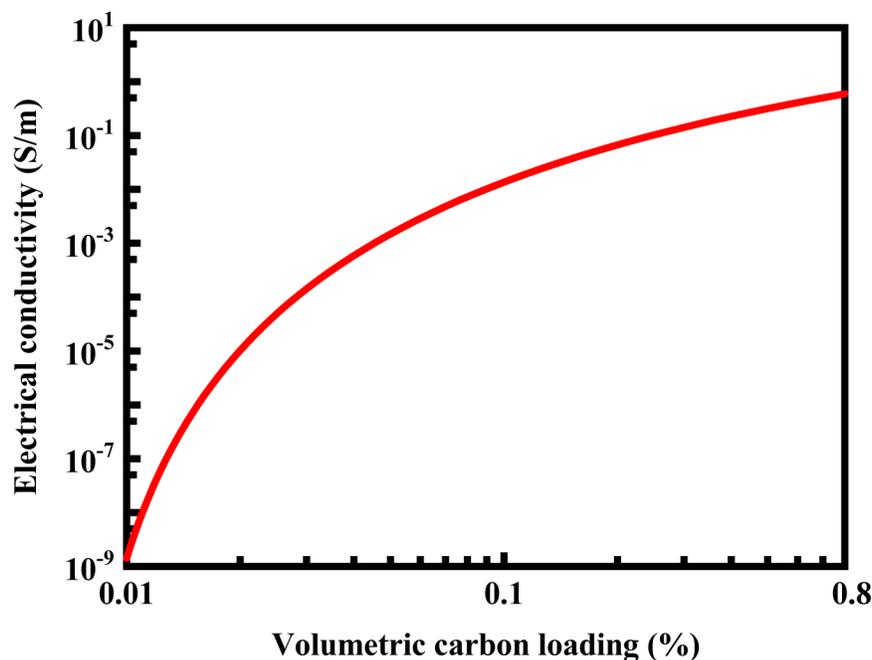


Figure 5. Effect of volumetric carbon loading on the electrical conductivity of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite.

The typical tensile stress-strain curves are presented in Figure 6 for the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. Dynamic material properties for elastomers are often specified for structural response in the frequency rather than the time domain. Vibration experiments are used to find complex modulus in the frequency domain and this data is often used to design shock absorbers and base isolation bearings. However, the concept of a complex modulus is based on linear viscoelastic material behavior, namely material for which stress is directly proportional to strain and strain rate. Frequency

domain material properties are therefore limited to applications where strains are small and stress is approximately linear with strain and the strain rate. Frequency domain material properties become irrelevant if the material exhibits nonlinear elastic behavior or is subjected to large strains. Under tension, elastomers are not only nonlinear elastic but also hyper-elastic. Clearly, new dynamic material properties are needed to characterize elastomeric structures undergoing high strain rates and nonlinear, hyper-elastic behavior. Thus, there exist a need to develop a tensile impact apparatus that is designed to give dynamic stress-strain curves of a rubber specimen undergoing tensile impact loading. Particularly, there is a need for an apparatus that is capable of achieving strains sufficient to fracture virtually any elastomer sample. The data provided by the tensile impact apparatus would enable one to predict tensile fracture of rubber components under shock or impact loads. Generally, for all type of matrixes, and especially for the thermosets, the lower the viscosity of the precursor of the polymeric matrix, the lower the resulting chemical and physical final properties of the solidified matrix. The solidified matrixes with the highest physical and chemical properties usually also have the highest viscosity in the liquid precursor state, with the resulting restrictions in terms of their processability. In some cases, it is possible to reduce the global viscosity of the precursor polymer composition used to impregnate the substrate by using solvents. The drawback is due to the fact that the solvents need to be eliminated from the final composite, before the cross-linking of the precursor starts. For the processes which do not use solvents at all, the necessary viscosity for the processability of the precursor is achieved by a temperature increase. Nevertheless, the temperature cannot be increased for the hand lay-up process or can only slightly be increased for all other processes. Depending on the type of polymers in the matrix, above a certain temperature limit, degradation starts or cross-linking starts, thereby reducing the impregnation time window.

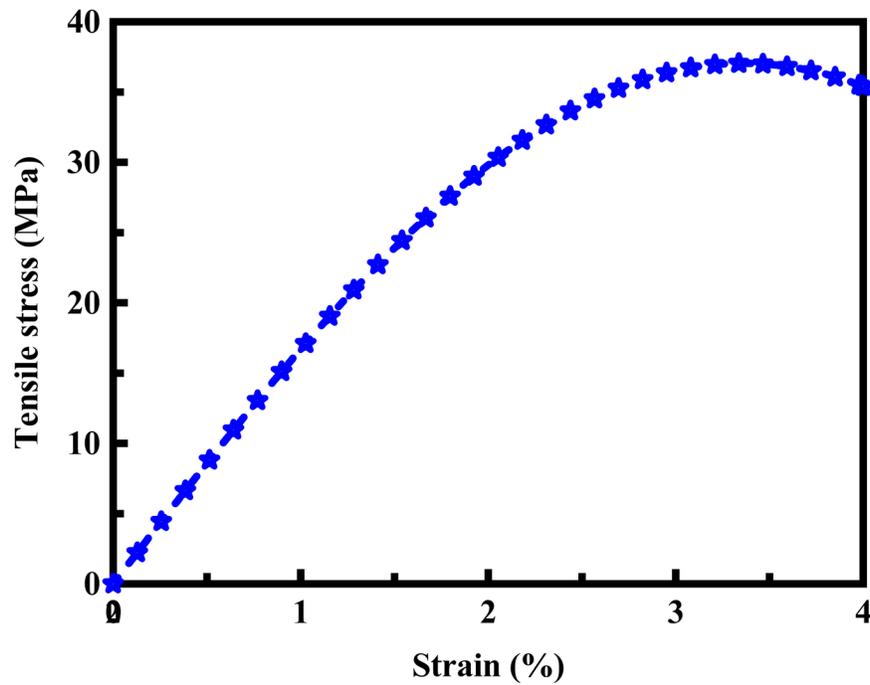


Figure 6. Typical tensile stress-strain curves of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite.

The effect of temperature on the loss factor is illustrated in Figure 7 for the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. Carbon nanotubes are the subject of intense theoretical and technological interest in materials science because of their extreme characteristics. Their theoretically-predicted and experimentally-measured mechanical properties, including high strength, high stiffness, tough-

ness, and low density, should make them ideal strengthening material in advanced fiber-reinforced composites. Carbon nanotubes are produced in primarily two configurations; single-walled carbon nanotubes and multi-walled carbon nanotubes, and can be twisted or woven into carbon nanotube fibers. Parallel-aligned carbon nanotube fibers form hexagonal closest packed fibers because of the van der Waals forces of attraction between the individual carbon nanotubes. Vibration is a physical phenomenon characterized by oscillatory deformation of an elastic body about a position of equilibrium. The basic physical concepts involved in vibratory motion are fairly simple. Deformation of an elastic body in a first direction by the application of an external force provides the elastic body with an initial amount of mechanical energy in the form of potential energy. Removal of the external force results in movement of the deformed elastic body from the high-energy deformed position towards the low-energy equilibrium position. Movement of the elastic body from the deformed position to the equilibrium position intrinsically results in the irreversible dissipation of a portion of the mechanical energy and conversion of the remaining mechanical energy from potential energy to kinetic energy. The thus converted kinetic energy causes the elastic body to move past the equilibrium position and result in deformation of the elastic body in a second direction. Deformation of the elastic body in the second direction intrinsically results in the irreversible dissipation of a second portion of the mechanical energy and reversion of the remaining mechanical energy from kinetic energy back into potential energy. Movement of the elastic body reverses when the kinetic energy is completely converted to potential energy. The thus deformed elastic body possess an amount of potential energy equal to the initial amount of potential energy minus the amount of energy irreversibly dissipated. Oscillation of the elastic body about the equilibrium position continues until the cumulative amounts of energy irreversibly dissipated equals the amount of mechanical energy originally provided to the elastic body. Vibration of a deformed elastic body can be perpetuated by periodically adding sufficient mechanical energy to the vibrating body to compensate for the energy lost through intrinsic dissipation. The irreversible dissipation of mechanical energy from a vibrating elastic body is an intrinsic phenomenon commonly referred to as damping. Damping is believed to result from a variety of energy loss mechanisms such as the conversion of mechanical energy to heat through internal friction within the elastic body, the conversion of mechanical energy to heat through friction caused by the rubbing of one component of the elastic body against another, the transfer of mechanical energy from the vibrating elastic body to adjacent structural components, the transfer of mechanical energy from the vibrating elastic body to the environment through acoustic radiation, the conversion of mechanical energy to heat through a viscous response either inherent in the system or subsequently added to the system. The energy dissipation mechanisms themselves are very complex and dependent upon a great number of factors including specifically, but not exclusively: the composition of the elastic body, the crystallinity of the elastic body, the geometry of the elastic body, the temperature of the elastic body, the initial strain placed upon the elastic body, the amount of any preload placed upon the elastic body, the interrelationship between the elastic body and other bodies, the amplitude and frequency of the vibration, and the amount of viscous response. Due to the variety of dissipative mechanisms and the internal complexity of those mechanism, it is extremely difficult to accurately predict the damping effect of a given material. The damping behavior of a material is dependent upon the modulus and loss factor of the material. Hence, knowledge of the modulus and loss factor of a material permits an assessment of the damping behavior of a material. The modulus and loss factor variables of a damping material are highly dependent upon the temperature of the damping material and the vibration frequency. Advent of the reduced temperature nomograph constitutes a tremendous advancement over the previously employed method of determining modulus and loss factor based upon separate temperature and frequency graphs. However, even with the increased simplicity offered by reduced-temperature nomographs, many individuals, particularly those with a limited scientific background, still find it difficult to determine the modulus and loss factor of a material.

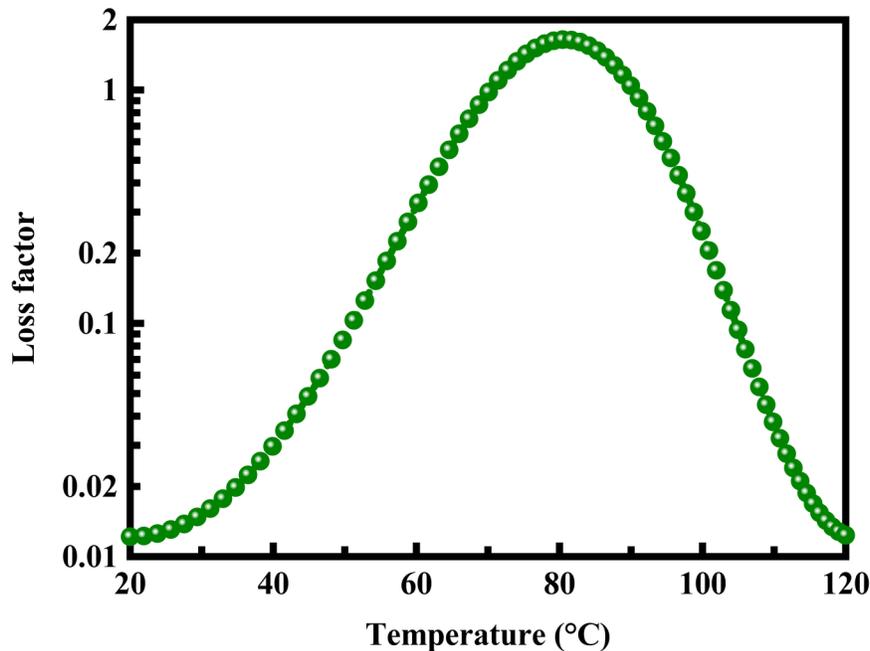


Figure 7. Loss factor of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite at different temperatures.

The effect of temperature on the loss modulus is illustrated in Figure 8 for the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. Virtually all synthetic materials in existence are viscoelastic, namely their behavior under mechanical stress lies somewhere between that of a purely viscous liquid and that of a perfectly elastic spring. Few materials behave like a perfect spring or a pure liquid. Rather, the mechanical behavior of these materials is generally time and temperature dependent and has led to such tests as creep, stress relaxation, tear, and impact resistance. One of the more important properties of materials sought is the materials' behavior under dynamic conditions. To explore this, a material's response to a cyclical stress as a function of temperature, time or frequency is determined. If the viscoelastic solid is deformed and then released, a portion of the stored deformation energy will be returned at a rate which is a fundamental property of the material. That is, the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite goes into damped oscillation. A portion of the deformation energy is dissipated in other forms. The greater the dissipation, the faster the oscillation dies away. If the dissipated energy is restored, the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite will vibrate at its natural frequency. The resonant frequency is related to the modulus of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. Energy dissipation relates to such properties as impact resistance, brittleness, and noise abatement. Because of their viscoelastic nature, the stress and strain in viscoelastic materials are not in phase, and, in fact, exhibit hysteresis. If a plot is made of this relationship, the area enclosed by the plot corresponds to the energy dissipated during each cycle of deformation of the material. In order to accurately describe this phenomenon, a complex modulus is often used to characterize the material. The real part of the modulus corresponds to the amount of energy that is stored in the strain and can be related to the spring constant, the complex part corresponds to the energy dissipation or loss and can be related to the damping coefficient used in second order differential equations to define vibrating systems. All of these systems place the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite under test into vibration or oscillation utilizing mechanical systems. These mechanical systems vibrate at a resonant frequency determined primarily by the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite. A drive transducer is used to maintain the system in oscillation, a displacement transducer is used to sense the displacement of the mechanical system, and a drive amplifier is used to energize the drive

transducer sufficiently to maintain the system oscillating at resonance at a constant amplitude. While many of these systems attempt to measure the elastic modulus, the loss modulus is typically measured only on a relative basis by sensing the power input to the system that is required to maintain a constant oscillation amplitude. Unfortunately, this does not provide a calibrated result in commonly accepted units. Other methods of determining the loss modulus are by obtaining the logarithmic decrement by free decay of the system. Unfortunately, this requires substantial additional instrumentation. Another method of determining loss modulus is to use the second order relationship that exists between oscillation frequency and amplitude. This approach, while satisfactory, does not always provide the results of the quality that might be desired.

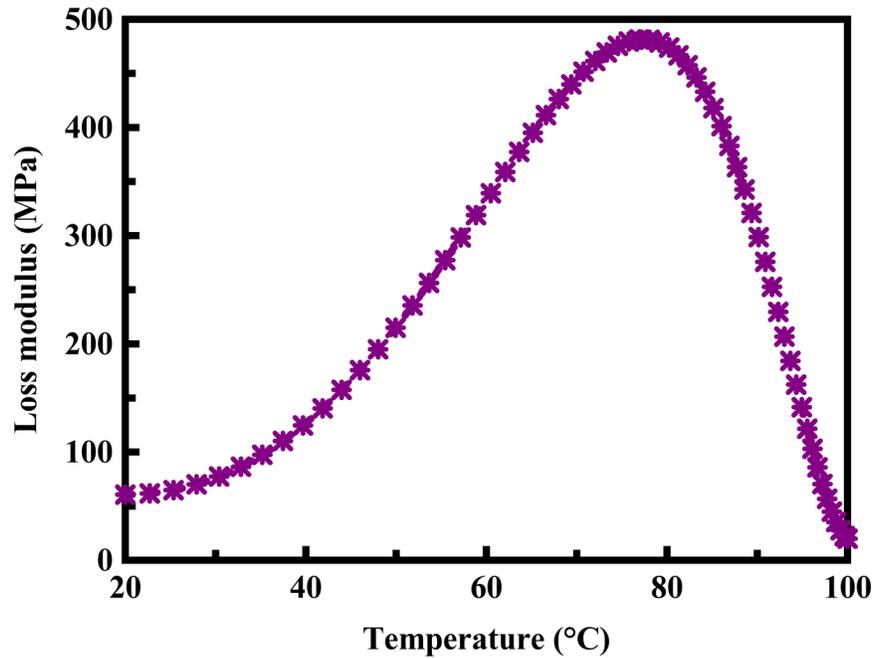


Figure 8. Loss modulus of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite at different temperatures.

4. Conclusions

The lattice thermal conductivity of graphene at different temperatures and frequencies and in different crystallite sizes is evaluated in the framework of a microscopic model that incorporates both acoustic and optical modes with phonon dispersion relations. The linearized phonon-Boltzmann transport equation is solved iteratively in the frame of three-phonon interactions. The major conclusions are summarized as follows:

- The electrical properties of the composite would not be changed from those of the bulk polymer until the average distance between the carbon nanotubes is reduced such that either electron tunneling through the polymer or physical contacts may be formed.
- Among the challenges introduced in the fabrication of carbon nanotube-filled polymer composites is the necessity to creatively control and make use of surface interactions between carbon nanotubes and polymeric chains in order to obtain an adequate dispersion throughout the matrix without destroying the integrity of the carbon nanotubes.
- Frequency domain material properties are therefore limited to applications where strains are small and stress is approximately linear with strain and the strain rate. Frequency domain material properties become irrelevant if the material exhibits nonlinear elastic behavior or is subjected to large strains.

- Depending on the type of polymers in the matrix, above a certain temperature limit, degradation starts or cross-linking starts, thereby reducing the impregnation time window.
- The deformed elastic body possess an amount of potential energy equal to the initial amount of potential energy minus the amount of energy irreversibly dissipated.
- The modulus and loss factor variables of a damping material are highly dependent upon the temperature of the damping material and the vibration frequency.
- Because of their viscoelastic nature, the stress and strain in viscoelastic materials are not in phase, and, in fact, exhibit hysteresis.
- The resonant frequency is related to the modulus of the catalytically-grown multi-walled carbon nanotube-reinforced epoxy composite.

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