

Electrical and thermal properties of epoxy matrix composite materials reinforced with multi-walled carbon nanotubes under different weight fraction conditions

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Abstract

The present study is focused primarily upon the electrical and thermal properties of epoxy matrix composite materials reinforced with multi-walled carbon nanotubes under different weight fraction conditions. Stable suspensions of carbon nanotubes are achieved in water with the use of surfactants, and non-covalent and covalent attachment of polymers. Scanning electron microscopy characterization is performed and electrical resistance is measured. Mechanical properties are studied and the loading rate is continuously adjusted to keep a constant representative strain rate. The Oliver-Pharr method is used to analyze partial load-unload data in order to calculate the indentation elastic modulus as a function of the indenter penetration. The present study aims to provide an improved method for the preparation of epoxy matrix composite materials reinforced with multi-walled carbon nanotubes with reduced volume resistivity and enhanced thermal conductivity. Particular emphasis is placed upon the effect of carbon nanotube weight fraction on the volume resistivity and thermal conductivity of the epoxy matrix composite materials reinforced with multi-walled carbon nanotubes. The results indicate that single-walled carbon nanotube structures can have smaller effective pore size than multi-walled carbon nanotube structures. Single-walled carbon nanotubes are harder to disperse and more difficult to functionalize than multi-walled carbon nanotubes. Heat resistance of carbon nanotubes varies depending on the diameter of carbon nanotubes and the quality of a graphene sheet constituting the wall of carbon nanotubes. As a G to D ratio of the carbon nanotube becomes higher, a degree of graphitization becomes higher. The single-walled carbon nanotube-reinforced fracture surfaces express substantial increases in the micron-level surface roughness. The multi-walled carbon nanotubes interact with the crack path and result in crack deflection and a more torturous fracture path. The percolation threshold for conductive particles embedded in an insulating polymer matrix is sensitive to the structure of the reinforcement, and the decrease in electrical resistivity with an increase in reinforcement content is attributed to the probability of reinforcement contact. Unlike electrical conductivity, where a sharp percolation threshold is achieved, the increase in thermal conductivity with increasing carbon nanotube concentration is nearly linear.

Keywords: Electrical properties; Thermal properties; Carbon nanotubes; Electrical conductivity; Thermal conductivity; Thermogravimetric analysis

1. Introduction

A composite material is a material which is produced from two or more constituent materials [1, 2]. These constituent materials have notably dissimilar chemical or physical properties and are merged to create a material with properties unlike the individual elements [3, 4]. Within the finished structure, the individual elements remain separate and distinct, distinguishing composites from mixtures and solid solutions. There are various reasons where new material can be favored. Typical examples include materials which are less expensive, lighter, stronger or more durable when compared with common

materials, as well as composite materials inspired from animals and natural sources with low carbon footprint [5, 6]. Composite materials are generally used for buildings, bridges, and structures [7, 8]. They are also being increasingly used in general automotive applications. The most advanced examples perform routinely on spacecraft and aircraft in demanding environments.

Fiber-reinforced polymers include carbon fiber reinforced polymer and glass-reinforced plastic. If classified by matrix then there are thermoplastic composites, short fiber thermoplastics, long fiber thermoplastics or long fiber-reinforced thermoplastics [9, 10]. There are numerous thermoset composites [11, 12]. Many advanced thermoset polymer matrix systems usually incorporate aramid fiber and carbon fiber in an epoxy resin matrix [13, 14]. Composite materials are created from individual materials. These individual materials are known as constituent materials, and there are two main categories of it. One is the matrix and the other reinforcement [15, 16]. A portion of each kind is needed at least. The reinforcement receives support from the matrix as the matrix surrounds the reinforcement and maintains its relative positions. The properties of the matrix are improved as the reinforcements impart their exceptional physical and mechanical properties [17, 18]. The mechanical properties become unavailable from the individual constituent materials by synergism [19, 20]. At the same time, the designer of the product or structure receives options to choose an optimum combination from the variety of matrix and strengthening materials.

To shape the engineered composites, it must be formed [21, 22]. The reinforcement is placed onto the mold surface or into the mold cavity. Before or after this, the matrix can be introduced to the reinforcement. The matrix undergoes a melding event which sets the part shape necessarily. This melding event can happen in several ways, depending upon the matrix nature, such as solidification from the melted state for a thermoplastic polymer matrix composite or chemical polymerization for a thermoset polymer matrix [23, 24]. Although the two phases are chemically equivalent, semi-crystalline polymers can be described both quantitatively and qualitatively as composite materials. The crystalline portion has a higher elastic modulus and provides reinforcement for the less stiff, amorphous phase. Different processing techniques can be employed to vary the percent crystallinity in these polymer matrix composite materials and thus the mechanical properties of these materials [25, 26]. In many cases these materials act like particle composites with randomly dispersed crystals known as spherulites. However, they can also be engineered to be anisotropic and act more like fiber reinforced composites [27, 28]. In the case of spider silk, the properties of the material can even be dependent on the size of the crystals, independent of the volume fraction. Ironically, single component polymeric materials are some of the most easily tunable composite materials known.

Usually, the composite's physical properties are not isotropic in nature. But they are typically anisotropic. For instance, the composite panel's stiffness will usually depend upon the orientation of the applied forces and moments [29, 30]. In general, particle reinforcement is strengthening the composites less than fiber reinforcement [31, 32]. It is used to enhance the stiffness of the composites while increasing the strength and the toughness [33, 34]. Because of their mechanical properties, they are used in applications in which wear resistance is required. For example, hardness of cement can be increased by reinforcing gravel particles, drastically [35, 36]. Particle reinforcement a highly advantageous method of tuning mechanical properties of materials since it is very easy implement while being low cost [37, 38]. In general, continuous fiber reinforcement is implemented by incorporating a fiber as the strong phase into a weak phase, matrix. The reason for the popularity of fiber usage is materials with extraordinary strength can be obtained in their fiber form [39, 40]. Non-metallic fibers are usually indicating a very high strength to density ratio compared to metal fibers because of the covalent nature of their bonds.

Fiber-reinforced plastic is a composite material made of a polymer matrix reinforced with fibers [41, 42]. The fibers are usually glass, carbon, aramid, or basalt. The polymer is usually an epoxy, vinyl

ester, or polyester thermosetting plastic, though phenol formaldehyde resins are still in use [43, 44]. Carbon fiber reinforced polymer, or carbon fiber reinforced plastic, or carbon fiber reinforced thermoplastic, is an extremely strong and light fiber-reinforced plastic which contains carbon fibers. Carbon fiber reinforced polymers can be expensive to produce, but are commonly used wherever high strength-to-weight ratio and stiffness are required, such as aerospace, superstructures of ships, automotive, civil engineering, and an increasing number of consumer and technical applications [45, 46]. The binding polymer is often a thermoset resin such as epoxy, but other thermoset or thermoplastic polymers, such as polyester, vinyl ester, or nylon, are sometimes used. The properties of the final carbon fiber reinforced polymer product can be affected by the type of additives introduced to the binding matrix [47, 48]. The most common additive is silica, but other additives such as rubber and carbon nanotubes can be used.

Carbon nanotubes are generally elongated hollow, tubular bodies with a linear graphene structure. They are typically only a few atoms in circumference and may be single-walled or multi-walled. Carbon nanotubes are recognized as possessing excellent mechanical, chemical, electrical, and thermal properties and have potential uses in a diverse number of applications [49, 50]. One use of carbon nanotubes has been to add them to polymer matrices as separate fillers or as reinforcing agents [51, 52]. However, the more recent development of attaching polymers to carbon nanotubes to form polymer-carbon nanotube composites offers exciting new potential uses [53, 54]. By chemically or physically linking the carbon nanotubes to the polymer chains, the resultant polymer-carbon nanotube composites benefit from the mechanical, thermal, and electrical properties of the carbon nanotubes to provide multifunctional new lightweight materials [55, 56]. Attempts to make such polymer-carbon nanotube composites include chemically modifying the ends or the side walls of carbon nanotubes with functional groups, which then react to form, or to link with, polymer chains [57, 58]. The process involves the functionalization of the sidewalls and the ends of carbon nanotubes with diazonium species using an electrochemical process [59, 60]. The functional group is then actively involved in a polymerization process which results in a polymer-carbon nanotube composite material in which the carbon nanotubes are chemically involved.

Carbon nanotubes have very anisotropic structures, and may be formed in various shapes such as single-walled, multi-walled, and rope shapes. The carbon nanotubes may have semiconducting or conducting characteristics depending on how they are coiled, different energy gaps depending on their chirality and diameters, and particular quantum effects due to quasi-one-dimensional structures. The present study is focused primarily upon the electrical and thermal properties of epoxy matrix composite materials reinforced with multi-walled carbon nanotubes under different weight fraction conditions. Stable suspensions of carbon nanotubes are achieved in water with the use of surfactants, and non-covalent and covalent attachment of polymers. Scanning electron microscopy characterization is performed and electrical resistance is measured. Mechanical properties are studied and the loading rate is continuously adjusted to keep a constant representative strain rate. The Oliver-Pharr method is used to analyze partial load-unload data in order to calculate the indentation elastic modulus as a function of the indenter penetration. The present study aims to provide an improved method for the preparation of epoxy matrix composite materials reinforced with multi-walled carbon nanotubes with reduced volume resistivity and enhanced thermal conductivity. Particular emphasis is placed upon the effect of carbon nanotube weight fraction on the volume resistivity and thermal conductivity of the epoxy matrix composite materials reinforced with multi-walled carbon nanotubes.

2. Methods

The method of preparation can encompass dissolving a polymer in a solvent while maintaining the temperature of the solvent at a level high enough to prevent precipitation of the polymer out of the

solvent; sonicating a plurality of carbon nanotubes in a solvent; mixing the dissolved polymer and the sonicated carbon nanotubes; and sonicating the mixture for a sufficient period of time to disperse the carbon nanotubes throughout the polymer to produce a subject nanocomposite in solvent. The composite is optionally further processed by spin coating the nanocomposite and solvent onto a substrate. The spin coating step evaporates the solvent so that the nanocomposite is deposited as a coating on the substrate. The solvent can also be removed by heating the nanocomposite under a vacuum, thereby removing the solvent. The nanocomposite can then be molded into a device or structure. Optionally, the solvents used to dissolve the polymer and to sonicate the carbon nanotubes are the same. Preferably, the solvent is cyclohexyl chloride.

Stable suspensions of carbon nanotubes are achieved in water with the use of surfactants, and non-covalent and covalent attachment of polymers. Covalent functionalization is a valuable approach to the preparation of carbon nanotube materials, as controlled compositions and reproducible properties may be obtained. The incorporation of carbon nanotubes into polymer matrices results in composites that exhibit increased thermal stability, modulus, strength, and electrical and optical properties. The polymer is dissolved in cyclohexyl chloride at 110 °C to make a solution. Carbon nanotubes are sonicated in N,N-dimethylformamide using a Branson Sonifer for one hour. The dispersion is placed in a vacuum oven at 80 °C to remove the solvent. The N,N-dimethylformamide treated carbon nanotubes are then dispersed in the polymer solution via sonication for 6 hours. The carbon nanotube-polymer mixture is placed in a warm beaker lined with TEFLON film, the solvent is allowed to evaporate at room temperature for 12 hours, and the composite is then placed in a vacuum oven at 80 °C to remove any residual solvent. The dried composite with carbon nanotubes is compression molded for analysis. Pieces are placed between KAPTON film and stainless-steel plates and pressed for 6 minutes at 6000 pounds of pressure at a temperature of 246 °C. A neat polymer is prepared in the same manner. After processing, the melt temperature for the neat and composite sample is measured.

The composites comprise carbon nanotubes that are incorporated into the matrix of a polymer. Advantageously, the carbon nanotubes can be single-walled, multi-walled, or a combination thereof. Advantageously, carbon nanotubes are 100 times stronger than steel, exhibit excellent electrical and mechanical strength, and are light in weight. Due to their weight, carbon nanotubes are thought to be ideal fillers in a polymer matrix in order to produce a composite with improved thermal properties, as well as with enhanced electrical and mechanical properties. The polymer utilized in the nanocomposites comprises a plurality of repeating hydrocarbon units that exhibits solubility in organic solvents. Preferably, the solvents are cyclohexane, cyclohexyl chloride, and cyclohexene. More preferably, the solvent is cyclohexyl chloride. The polymer composites are then characterized by measuring their physical, melt rheological, and electrical properties. Carbon nanotubes have a powerful effect on the melt rheology, increasing the low shear viscosity dramatically. Escalating the carbon nanotube concentration also increased the flexural and tensile moduli, decreased the elongation, and increased the electrical conductivity. Polymerization is generally preferred as the method of dispersing the carbon nanotubes. The electrical conductivity is in some cases quite high, approaching that of metal strips. In addition, the electrical conductivity is pressure sensitive.

Such acid derivatized carbon nanotubes can be added to and subsequently copolymerized with precursors of polymers including but not limited to monomeric precursors to polyamides, polyesters, polyimides, or polyurethanes [61, 62]. For example, the acid derivatized carbon nanotubes can be contacted with a diacid and a diamine and the resultant pre-polymer product polymerized to form a carbon nanotube-polymer composite, or the acid derivatized carbon nanotubes can be contacted with a diacid or a diester, and a diol and the resultant pre-polymer product polymerized to form a carbon nanotube-polymer composite [63, 64]. Following contact of the acid derivatized carbon nanotubes with the polymer precursors, the pre-polymer product of such contact may be filtered, washed, and dried [65,

66]. For example, this procedure would be appropriate for treatment of the salt precipitate when using polyamide precursors [67, 68]. In addition, for the formation of other pre-polymer products, water or alcohol may be removed such as in the formation of pre-polymers.

One of the problems with blending any filler into a molten polymer is the difficulty of dispersing the individual particles into the polymer matrix. High shear mixing is usually employed for this purpose, but certain fillers, such as carbon nanotubes, offer a special problem because they require dispersal at the angstrom or nanometer level, and they have a particularly strong Van der-Waals affinity for each other. These characteristics make it especially difficult to effectively disperse clusters of carbon nanotubes, and then keep them dispersed in the polymer matrix. Indeed, the quality of dispersion is usually the limiting factor when engineering these composites. To measure the electrical resistance across these composites, a circular disk of 0.6-inch diameter and 0.06-inch thickness is first compression molded. The measurement is carried out by heating the polymer to 180 °C in a 2 inch by 2 inches by 0.05-inch mold, applying about 600 pounds per square inch pressure to the mold, waiting 6 minutes, then cooling under pressure for another 8 minutes to 60 °C, where the hardened plaque is removed. The circular disk is then cut from this larger plaque. To each side of this disk is then smeared a small amount of micronized silver paste. The brass disk is then pressed against the silver paste on each side of the disk, and the two metal plates with sample sandwiched between are then pressed together by means of a strong spring-loaded wood-gluing clamp. These two brass plates, which are soldered to a wire, are then connected to a voltmeter.

Electrical resistance, measured in ohms, is then taken as the two metal disks are being pressed together. Sometimes the force is varied to obtain maximum contact, and duplicates are obtained to achieve a consistent result. A blank determination is also made in which the composite is omitted, to determine the electrical resistance of the other parts of the circuit. This electrical resistance is small, usually 0.2 ohms at most, compared to sample measurements of many orders of magnitude larger. The electrical resistance measured in this way is then converted into a standard resistivity by multiplying by the area of the disk and dividing by the path length. Electrical conductivity as a function of pressure is determined by placing a sample of the composite between two metal plates, which are then inserted in a hydraulic press between insulating barriers. Electrical resistance between the plates is then monitored as the force exerted by the press is increased.

Scanning electron microscopy characterization is performed on a JEOL 7401-F with energies greater than approximately 6 keV in secondary electron imaging mode with a working distance of 2-8 mm. Electrical conductivity is measured using the four-probe method with metal electrodes attached to the ends of cylindrical samples. The amount of current transmitted through the sample during measurement is 80 mA, and the voltage drop along the sample is measured over distances of 2 to 6 mm. Seven or more measurements are taken on each sample, and results are averaged. Mechanical properties are studied by indentation in an MTS XP Nanoindenter with a Berkovich diamond tip. A series of both continuous and partial load-unload indents is carried out in laboratory air at room temperature. The loading rate is continuously adjusted to keep a constant representative strain rate. For every cycle, the unloading rate is kept constant and equal to the maximum loading rate of the cycle. The Oliver-Pharr method is used to analyze partial load-unload data in order to calculate the indentation elastic modulus as a function of the indenter penetration.

3. Results and discussion

The scanning electron micrographs of the multi-walled carbon nanotubes are illustrated in Figure 1 for the preparation of epoxy matrix composite materials. 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. The morphology of the aggregate is controlled by the choice of catalyst support. Spherical supports grow multi-walled carbon nanotubes in all directions leading to the formation of bird nest aggregates. Combed yarn and open nest aggregates are prepared using supports having one or more readily cleavable planar surfaces. Single walled carbon nanotubes typically have smaller diameter than most multi walled carbon nanotubes. Thus, structures created from single walled carbon nanotubes will have significantly greater specific surface area and lower density than structures created from multi-walled carbon nanotubes. Surface area can be a critical performance parameter for many applications that use carbon nanotubes structures.

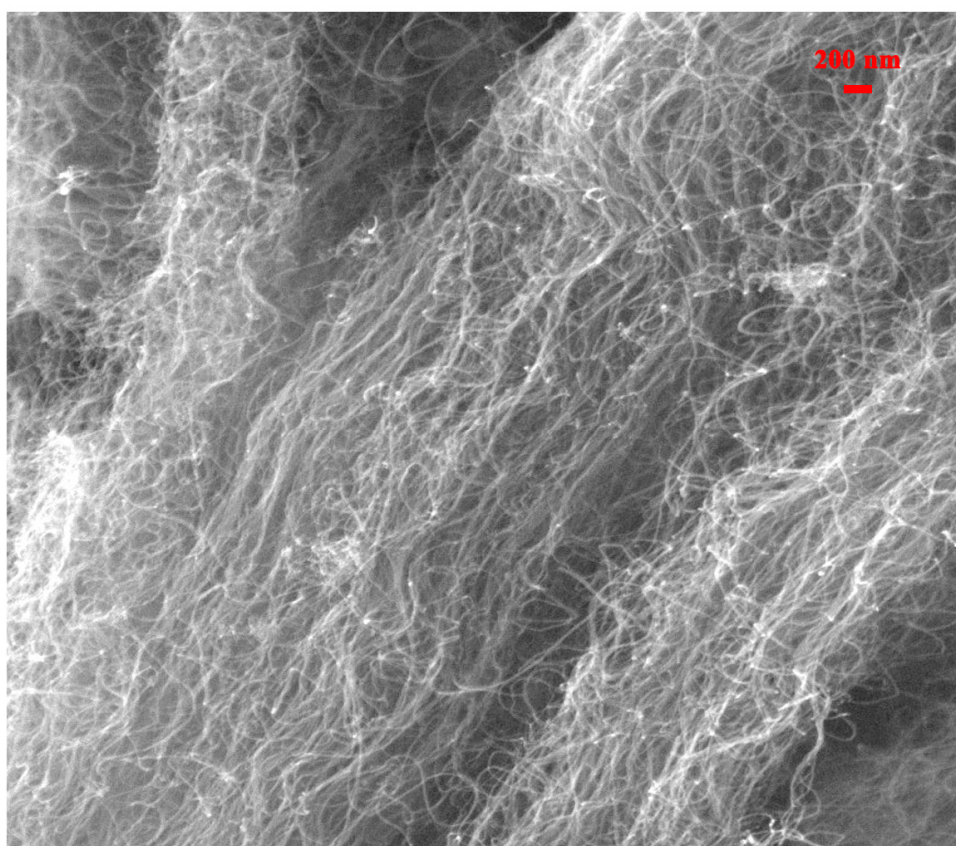


Figure 1. Scanning electron micrographs of the multi-walled carbon nanotubes for the preparation of epoxy matrix composite materials.

The transmission electron micrographs of the multi-walled carbon nanotubes are illustrated in Figure 2 for the preparation of epoxy matrix composite materials. Multi-walled carbon nanotubes as used herein refers to carbon nanotubes which are substantially cylindrical, graphitic nanotubes of substantially constant diameter and comprise cylindrical graphitic sheets or layers whose c-axes are substantially perpendicular to the cylindrical axis. Single-walled carbon nanotube structures can have smaller effective pore size than multi-walled carbon nanotube structures. Having smaller effective pore size may be beneficial in many applications, and undesirable in other circumstances. For example, smaller pores result in catalyst supports having higher specific surface. Conversely, smaller pores are subject to diffusion limitations and plugging. Thus, the advantages of smaller pore size need to be balanced against other considerations. Parameters, like total porosity and pore size distribution, become important qualifiers of effective pore size. Generally, single-walled carbon nanotubes are more expensive and less pure than multi-walled carbon nanotubes, and are harder to disperse and more

difficult to functionalize. As such, multi-walled carbon nanotube structures are easier to prepare. Multi-walled carbon nanotubes are attracting increasing interest as constituents of novel nanoscale materials and device structures. Defect-free multi-walled carbon nanotubes are expected to have remarkable mechanical, electronic, and magnetic properties that will be tunable by varying the diameter, number of concentric shells, and chirality of the tube. The multi-walled carbon nanotubes aggregated into ropes in which many tubes are held together by van der Waals forces. The multi-walled carbon nanotubes produced are remarkably uniform in diameter.

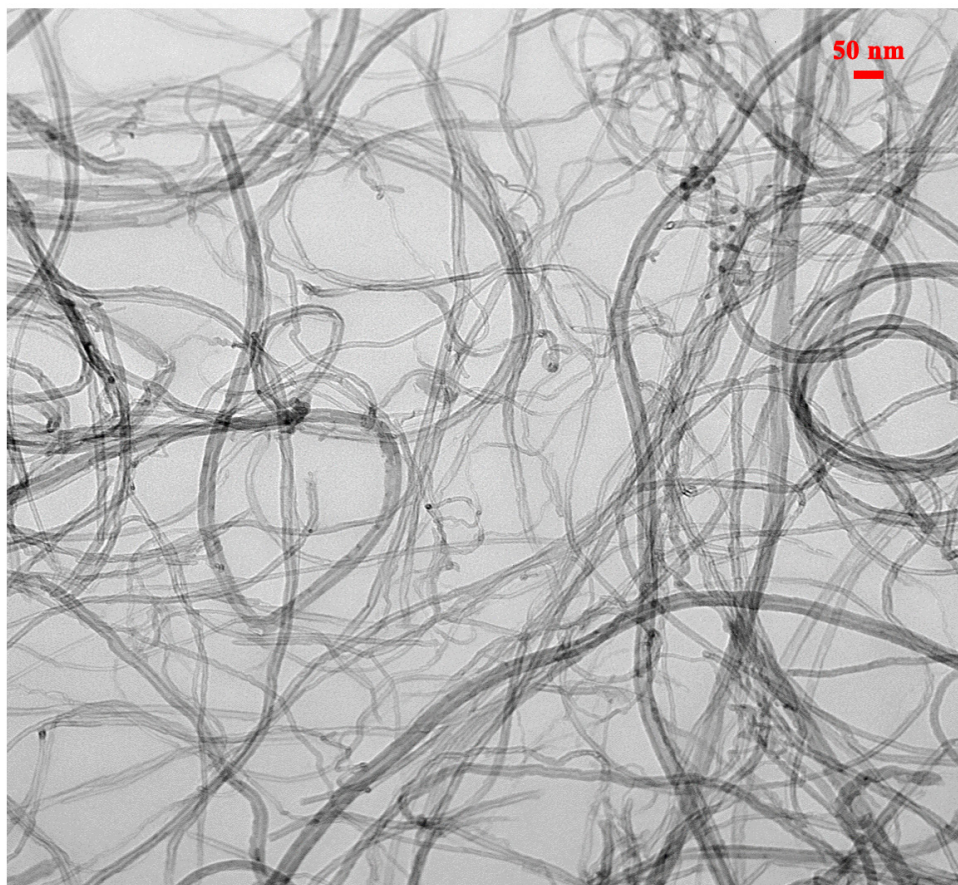


Figure 2. Transmission electron micrographs of the multi-walled carbon nanotubes for the preparation of epoxy matrix composite materials.

The thermogravimetric analysis results and derivative thermogravimetric analysis results of the multi-walled carbon nanotubes are presented in Figure 3 for the preparation of epoxy matrix composite materials. In thermogravimetric analysis of multi-walled carbon nanotubes which are usually commercially available, there is one combustion peak at a temperature of about 600 °C. This is because carbon impurities are attached to carbon nanotubes. An apparent purity of carbon nanotubes appears high, but this does not indicate the state of carbon nanotubes having a high purity, an attention must be paid. Further, it is thought that heat resistance of carbon nanotubes varies depending on the diameter of carbon nanotubes and the quality of a graphene sheet constituting the wall of carbon nanotubes, and in the prior technique, it is difficult to realize high resistance with multi-walled carbon nanotubes having a small outer diameter. At this time, carbon nanotubes are preferably in the state where they are attached to a catalyst body. Then, after a catalyst body is removed, thermogravimetric analysis is performed, the resulting weight reduction curve is differentiated with a time to obtain a differential thermogravimetric curve, and a heating temperature is determined as follows, based on a graph obtained by plotting, letting an x-axis to be a temperature and a y-axis to be the differential thermogravimetric curve, and carbon nanotubes are heated. That is, a sample is heated to an inflection point at which a peak is

changed from a low temperature combustion peak to a high temperature combustion peak, of two combustion peaks which are on a high temperature side and on a low temperature side in the differential thermogravimetric curve under the oxygen atmosphere and, at the time point at which a temperature reaches the temperature, heating is stopped, and oxygen is replaced with a nitrogen gas.

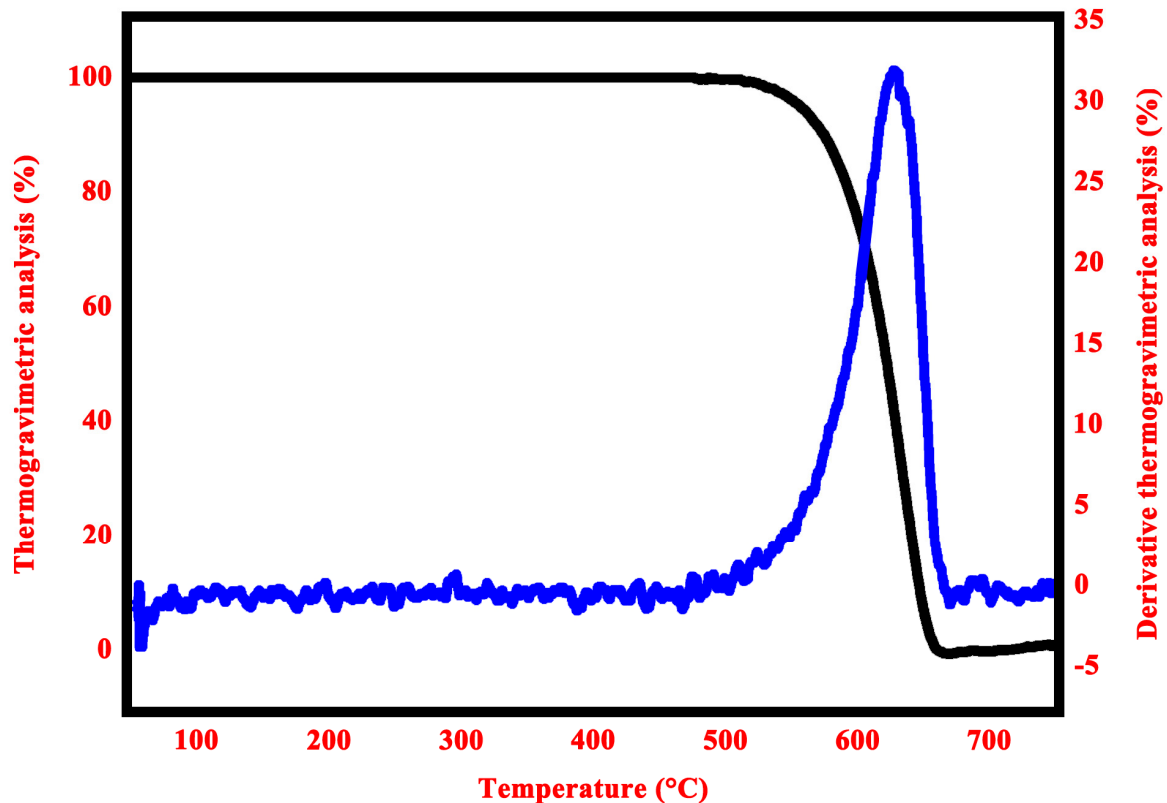


Figure 3. Thermogravimetric analysis and derivative thermogravimetric analysis of the multi-walled carbon nanotubes for the preparation of epoxy matrix composite materials.

The Raman spectra of the multi-walled carbon nanotubes are illustrated in Figure 4 for the preparation of epoxy matrix composite materials. Although Raman spectroscopy is a powerful analytical method for molecular analysis, Raman spectra are often plagued with intense fluorescence backgrounds resulting from impurities or from the population of a sample's excited states. Algorithm-based methods attempt to mathematically estimate a baseline and then subtract the estimated baseline from the Raman spectrum to give a fluorescence free spectrum. Algorithm-based methods suffer from the requirement that they cannot be applied to all types of fluorescence without either significant degradation in performance or significant user intervention to adjust sensitive algorithm parameters. One reason for this disadvantage is the varied nature of fluorescence backgrounds. Another reason is due to the complexity of the fitting algorithms. A carbon nanotube has a shape in which flat graphite is wound in a cylindrical shape. The carbon nanotube may be a carbon nanotube into which a single-walled carbon nanotube is incorporated. Single-walled carbon nanotubes have a structure in which one layer of graphite is wound. A multi-walled carbon nanotube has a structure in which two or three or more layers of graphite are wound. Furthermore, a side wall of the carbon nanotube may not have a graphite structure. For example, a carbon nanotube having a side wall having an amorphous structure can be used as the carbon nanotube. The G to D ratio is 1.5 to 5.0, wherein G represents the maximum peak intensity in the range from 1560 to 1600 per centimeter and D represents the maximum peak intensity in the range from 1310 to 1350 Per centimeter in the Raman spectra. There are various laser wavelengths used in Raman spectroscopy, but in the present specification, 532 nm and 632 nm are used. A Raman shift observed near 1590 per centimeter in the Raman spectrum is called a G band derived from graphite, and a Raman shift observed near 1350 per centimeter is called a D band derived

from a defect of amorphous carbon or graphite. As a G to D ratio of the carbon nanotube becomes higher, a degree of graphitization becomes higher.

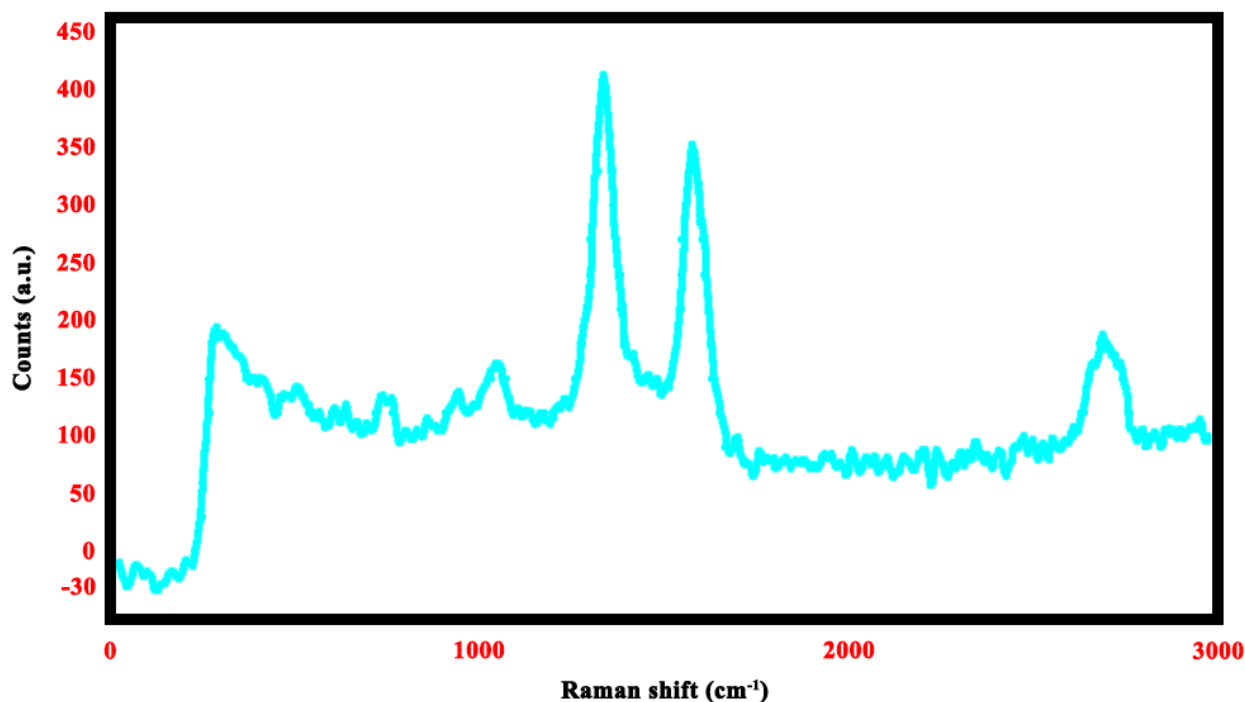


Figure 4. Raman spectra of the multi-walled carbon nanotubes for the preparation of epoxy matrix composite materials.

The scanning electron micrographs of the epoxy matrix composite materials are illustrated in Figure 5 which are reinforced with single-walled carbon nanotubes. The fracture surface is relatively smooth and absent of any structural features. The single-walled carbon nanotube-reinforced fracture surfaces express substantial increases in the micron-level surface roughness. This increase in surface roughness is the likely reason that the nanocomposites express enhanced fracture toughness. In the resultant polymer carbon nanotube composites, the carbon nanotubes are an integral part of polymer chains rather than separate fillers within a polymer matrix. Polymer-carbon nanotube composites where the carbon nanotube is chemically associated with the polymer has the advantage that load can be transferred to the nanotubes which provides enhanced mechanical properties to the composite and also helps prevent separation between the polymer surface and the carbon nanotubes. The thermal and electrical properties of the carbon nanotubes can also be exploited in this way. The at least one oxygen moiety of the carbon nanotubes are reacted with a suitable molecule to form a carbon nanotube macromer before being reacted with the at least one monomer to attach polymer chains to the sidewalls of the carbon nanotubes. The reaction between the carbon nanotube-molecule complex and the at least one monomer may be activated or initiated through the application of energy in the form of heat or by the presence of a suitable chemical initiator. However, individual carbon nanotubes tend to agglomerate, which tends to complicate subsequent processing. For example, agglomeration of individual carbon nanotubes tends to clog nozzles used in fused deposition modeling. More specifically, fused deposition modeling works by laying down material in layers from a polymer filament to form the shape of the article having final or near-final dimensions. However, as individual carbon nanotubes tend to agglomerate, processing becomes complicated due to clogging of a nozzle used to lay down the layers of a polymer incorporated with individual carbon nanotubes. Also, individual carbon nanotubes may become airborne, raising concerns with handling of the carbon nanotubes. The dimensions of the carbon nanotube sheetlets are not limited and may depend upon the application of the carbon nanotube enhanced polymer. If the dimensions of the carbon nanotube sheetlets are too small, then concerns with

handling of the carbon nanotubes may be raised. A width of the carbon nanotube sheetlets is not limited and may depend upon the application of the carbon nanotube enhanced polymer.

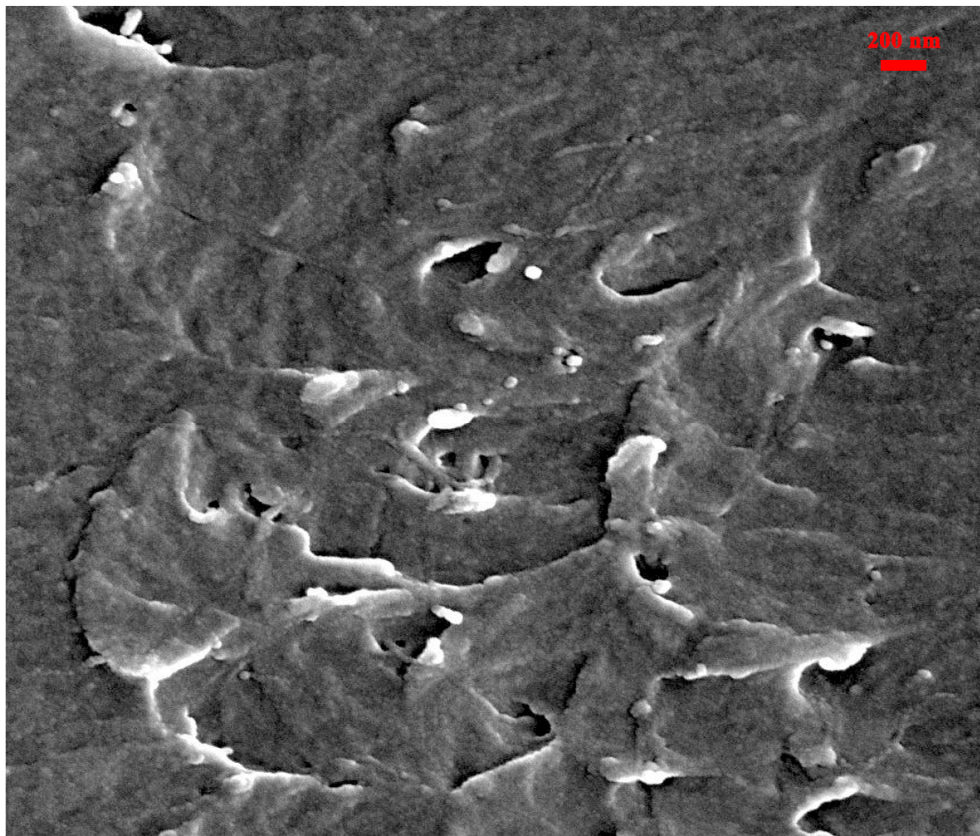


Figure 5. Scanning electron micrographs of the epoxy matrix composite materials reinforced with single-walled carbon nanotubes.

The scanning electron micrographs of the epoxy matrix composite materials are illustrated in Figure 6 which are reinforced with multi-walled carbon nanotubes. The use and development of carbon nanotubes has expanded [69, 70]. These materials are valuable in next generation industries including the fields of electronics and chemistry [71, 72]. The further development of carbon nanotube technology allows organized structures or intertwined randomly oriented bundles of carbon nanotubes to be formed [73, 74]. Techniques have been developed to controllably build organized architectures of carbon nanotubes having predetermined orientations, such as vertically aligned carbon nanotubes [75, 76]. Although such structures may be useful for a variety of purposes, the structures by themselves may be limited in terms of function and application [77, 78]. The structure is a combination of dispersed multi-walled carbon nanotubes and micron-scale agglomerates. On the fracture surface, multi-walled carbon nanotubes are pulled-out of the matrix, indicating that there is likely energy dissipation from interfacial debonding and pullout of the multi-walled carbon nanotubes. Outside the area where multi-walled carbon nanotubes are locally agglomerated the fracture surface is quite smooth, similar to that of the unreinforced epoxy. Where the multi-walled carbon nanotubes are present it is clear that there is an increase in surface roughness. In the areas where multi-walled carbon nanotubes are agglomerated, tail-like structures are formed. These features indicate that the multi-walled carbon nanotubes interact with the crack path and result in crack deflection and a more torturous fracture path. Some multi-walled carbon nanotube pullout as well as texturing of the fracture surface, but the formation of the larger-scale tail structures is not present. A possible reason for the overall higher fracture toughness for the structure that contains both dispersed and agglomerated features may be a result of larger agglomerates being able to more effectively interact with the crack front.



Figure 6. Scanning electron micrographs of the epoxy matrix composite materials reinforced with multi-walled carbon nanotubes.

The effect of carbon nanotube weight fraction on the volume resistivity of the epoxy matrix composite materials is illustrated in Figure 7 which are reinforced with multi-walled carbon nanotubes. For the highly dispersed structure and the partially agglomerated structure, the electrical percolation threshold occurs at a very low concentration. The percolation threshold for conductive particles embedded in an insulating polymer matrix is sensitive to the structure of the reinforcement, and the decrease in electrical resistivity with an increase in reinforcement content is attributed to the probability of reinforcement contact. For carbon nanotube composites that have large carbon nanotube aspect ratios, extremely low percolation thresholds can be achieved. The low percolation threshold of the polymer matrix nanocomposites indicates that the relatively large aspect ratios of the carbon nanotubes are likely maintained during processing and the multi-walled carbon nanotubes form a percolating network throughout the polymer matrix. Electrical properties are sensitive to local statistical perturbations in the microstructure that create a conducting path for transport. For the partially agglomerated structure the mean values of electrical resistivity are higher than for the more highly dispersed structure, particularly at lower fractions of multi-walled carbon nanotubes. Because of local agglomeration of carbon nanotubes, the statistical fraction of carbon nanotubes participating in conductive percolation is lower, resulting in higher volume resistivity. A homogeneous dispersion of the carbon nanotubes in a polymer matrix results in an improved stiffness, strength, and conductivity of the final polymer nano-composites. The process provides carbon nanotubes reinforced polymers having a percolation threshold at significantly lower loading of the carbon nanotubes compared to other mixing techniques. With percolation threshold is meant the amount of carbon nanotube needed to retrieve a significant increase in the electrical conductivity of the polymer nano-composites. However, there is a continuous need to improve the conductivity of polymers or to lower the percolation threshold of polymer nano-composites without being confronted with the above disadvantages.

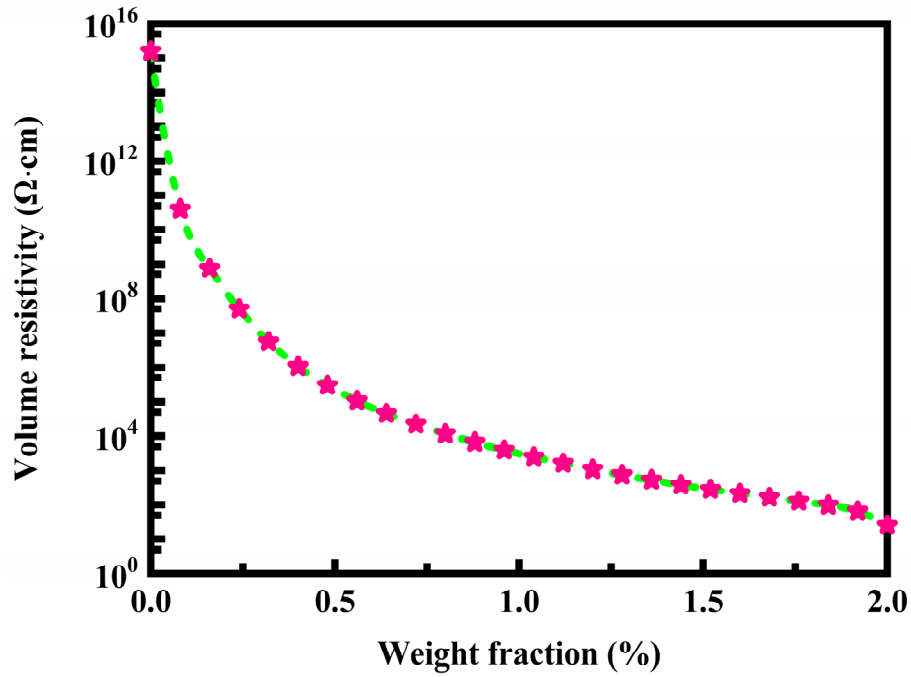


Figure 7. Volume resistivity of the epoxy matrix composite materials reinforced with multi-walled carbon nanotubes under different weight fraction conditions.

The effect of carbon nanotube weight fraction on the thermal conductivity of the epoxy matrix composite materials is illustrated in Figure 8 which are reinforced with multi-walled carbon nanotubes. The amount of carbon nanotube sheetlets may be defined by a weight percentage loading of the carbon nanotubes [79, 80]. If the weight percentage loading of the carbon nanotubes is too low, then the thermal conductivity to be imparted to the carbon nanotube enhanced polymer is limited [81, 82]. If the weight percentage loading of the carbon nanotubes is too high, then mechanical properties of the carbon nanotube enhanced polymer may be reduced. The carbon nanotube sheetlets may be made by any suitable method. For example, the carbon nanotube sheetlets may be made from a carbon nanotube sheet, the carbon nanotube sheet including a network of intertwined carbon nanotubes, in which the carbon nanotube sheet is subjected to cutting or grinding into a plurality of carbon nanotube sheetlets [83, 84]. In the case mixing the plurality of carbon nanotube sheetlets with a polymer, the present methods mitigating handling concerns associated with previous attempts to incorporate individual carbon nanotubes into polymers [85, 86]. Specifically, previous attempts have raised handling concerns due to the small size of the individual carbon nanotubes and potential for individual carbon nanotubes to become airborne [87, 88]. The presently described methods for manufacturing carbon nanotube enhanced polymer addresses these issues by providing carbon nanotube sheetlets, which each include a network of intertwined carbon nanotubes, thus mitigating handling concerns associated with individual carbon nanotubes. In the case of including the embedding the plurality of carbon nanotube sheetlets within a polymer matrix, the step of embedding the plurality of carbon nanotube sheetlets within the polymer matrix may include mixing the plurality of carbon nanotube sheetlets with a polymer powder. At the highest carbon nanotube concentration, the thermal conductivity increases greatly over that of the unreinforced epoxy. Unlike electrical conductivity, where a sharp percolation threshold is achieved, the increase in thermal conductivity with increasing carbon nanotube concentration is nearly linear. There is no statistical difference between the more highly dispersed and the agglomerated nanocomposites. Interfaces in carbon nanotube-polymer composites as well as concentration of defects in the multi-walled carbon nanotubes affect the thermal conductivity. The influence of the nanoscale structure of the carbon nanotubes, the structure of the nanocomposite, and properties of the carbon nanotube-matrix interface will affect the bulk thermal conductivity.

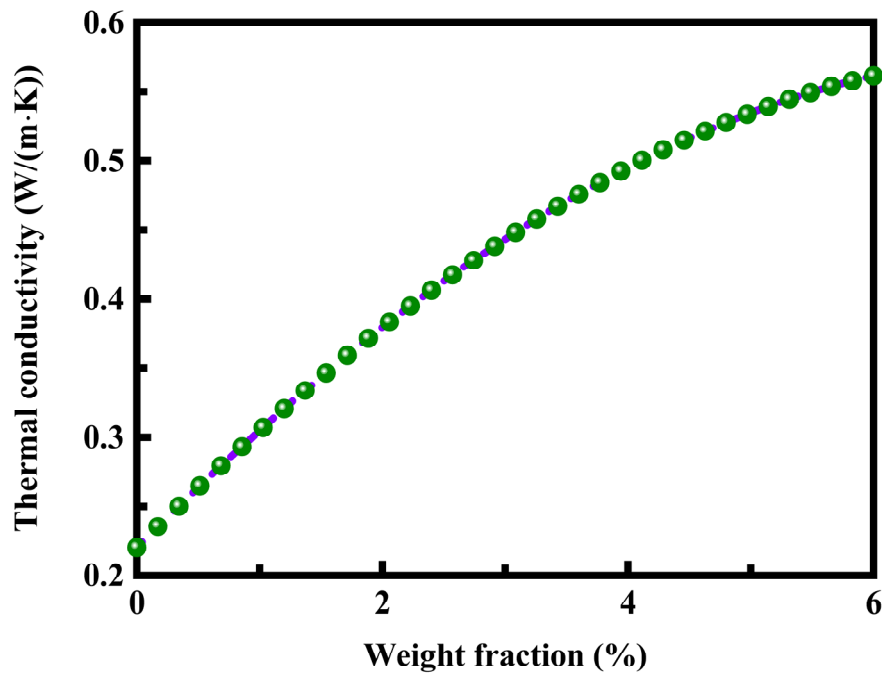


Figure 8. Thermal conductivity of the epoxy matrix composite materials reinforced with multi-walled carbon nanotubes under different weight fraction conditions.

4. Conclusions

Scanning electron microscopy characterization is performed and electrical resistance is measured. Mechanical properties are studied and the loading rate is continuously adjusted to keep a constant representative strain rate. The Oliver-Pharr method is used to analyze partial load-unload data in order to calculate the indentation elastic modulus as a function of the indenter penetration. Particular emphasis is placed upon the effect of carbon nanotube weight fraction on the volume resistivity and thermal conductivity of the epoxy matrix composite materials reinforced with multi-walled carbon nanotubes. The major conclusions are summarized as follows:

- Single-walled carbon nanotube structures can have smaller effective pore size than multi-walled carbon nanotube structures.
- Single-walled carbon nanotubes are harder to disperse and more difficult to functionalize than multi-walled carbon nanotubes.
- Heat resistance of carbon nanotubes varies depending on the diameter of carbon nanotubes and the quality of a graphene sheet constituting the wall of carbon nanotubes.
- As a G to D ratio of the carbon nanotube becomes higher wherein G and D represent the maximum peak intensity, a degree of graphitization becomes higher.
- The single-walled carbon nanotube-reinforced fracture surfaces express substantial increases in the micron-level surface roughness.
- The multi-walled carbon nanotubes interact with the crack path and result in crack deflection and a more torturous fracture path.
- The percolation threshold for conductive particles embedded in an insulating polymer matrix is sensitive to the structure of the reinforcement, and the decrease in electrical resistivity with an increase in reinforcement content is attributed to the probability of reinforcement contact.
- Unlike electrical conductivity, where a sharp percolation threshold is achieved, the increase in thermal conductivity with increasing carbon nanotube concentration is nearly linear.

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