1 Introduction

Nowadays polymer matrix nanocomposites are widely used in industrial applications because of their exceptional properties that can be tailored to specific requirements. Incorporating nanoparticles into the polymer matrices to improve the electrical (*1-4*), thermal (*5-9*) and mechanical (*5*, *7*, *10-15*) properties of the polymers have been readily investigated. The insulating nature of polymers is desirable for many applications. However in the fields such as oil, mine and chemical facilities, static charging can be dangerous. On the insulating polymer surface, static charge can induce fire or even cause explosion. Furthermore, in the electronic industry, the need of conductive or anti-static polymeric materials is growing everyday (*16*). In some aerospace components materials with improved conductivity should be used to achieve electrostatic discharge and electromagnetic-radio frequency interference protection. The use of carbon black with high filler loadings seems to be a solution for this problem. Using high volume fractions increases the cost and the weight of the final product and also degrades the mechanical properties of the composite and reduces the smoothness of the surface finish. Increasing filler volume fraction also increases the viscosity of the melt, which is critical in thin wall molding applications (*17*).

Carbon nanotubes (CNTs) are novel materials that have promising properties and can replace carbon blacks. Multiwalled carbon nanotubes (MWCNTs) are cheaper and thus they are preferred over single walled carbon nanotubes (SWCNTs) in industrial applications (*17*). Previous studies showed that using multiwalled carbon nanotubes in place of carbon black promotes to a lower percolation threshold and higher conductivity in bulk samples (*18*). Percolation threshold is defined as the critical concentration where the transition from an insulating to a conductive system occurs. Percolation is previously described by many statistical theories (*19*) which assumes random distribution of the conductive fillers but in reality these theories predict percolation thresholds orders of magnitude larger than found in experimental studies. Moreover percolation threshold differs greatly among the studies because these studies do not possibly consider the particle movement during the manufacturing steps. Particles can move via shear forces or electrical fields during processing which leads to very percolation thresholds (*20*). Achieving low percolation threshold is of industrial interest because it reduces the weight and the production cost by decreasing the filler concentration that is necessary to achieve the desired conductivity level.

During processing of these composites, materials are exposed to significant deformation that changes the microstructure and affects the properties of the final products. One of the main reasons of not having many commercial CNT/polymer composite products in the market is the difficulty to control the processing conditions and obtaining reproducible properties with carbon nanotubes. An agglomerated or dispersed microstructure could be achieved by changing the processing parameters. Initial dispersion of the nanotubes within the polymer matrix is crucial to improve the mechanical properties because remaining agglomerates could behave as defects (*21*). Although an agglomerated-network structure is not preferential for the mechanical properties, it is beneficial for the electrical conductivity in these composites. Therefore, in order to improve the material properties and manufacturing process, a clear understanding of how these materials react to the flow fields is required.

The purpose of this work is to understand the dependence of the electrical properties on the processing variables and material properties of CNT/polymer composites. While previous simulation studies have illustrated that fiber shape influences the electrical properties of CNT composites, they did not consider the effects of nanotube shape, composite microstructure and imposed shear flow together on the electrical properties of these composites. In this study, we employ fiber-level simulation method developed by Switzer and Klingenberg (*22*) to examine the effects of both material properties and imposed flow on the microstructure and electrical conductivity of CNT/polymer composites. The electrical conductivities of the composites are calculated using a resistor network algorithm developed by Tozzi (*23*). We show that fiber shape, aspect ratio, shear history and interparticle interactions influence the formation and dispersion of agglomerates in shear flow and determine the structure and conductivity of the composites. In order to explain the extremely low percolation thresholds obtained by applying moderate shear rates, simulation studies are crucial. Besides single carbon nanotubes cannot be observed during processing with commercial characterization methods. Therefore simulations are the only way to get insight the movement of the carbon nanotubes in polymer melts which determines the microstructures and properties of the final composites. In addition, simulations have the great advantage to work on the effects of each parameter separately. Throughout this study we give the results of previously performed experimental studies on the microstructure and electrical conductivity of CNT/polymer composites and we show that our model could closely reproduce the dynamics of composite microstructure formation and electrical conductivity behavior of these composites. Also we observe many new phenomena which would help us to understand and benefit more from these systems.

After this introduction, Chapter 2 provides the literature review which gives the necessary scientific background and literatures for understanding the properties of carbon nanotubes and CNT/polymer composites where we mainly focus on the electrical properties. Chapter 2 includes the percolation theory that concerns with the transport in inhomogeneous conductors which exhibits percolation threshold. The initial attempts to find out the relationship between the electrical percolation threshold and the excluded volume of the particles are also explained. Insulator to conductor transition in CNT/polymer composites was previously explained by these theories. A brief discussion on the electrical conduction mechanisms such as tunneling in CNT/polymer composites is given to provide a better understanding to these materials.

To estimate the final properties and microstructure of the composites after manufacturing process, understanding the fiber dynamics in suspensions is important. The previous attempts to describe the behaviors of fibers under flow fields are given in Chapter 3. Fiber-level simulation technique that is known to reproduce observed fiber suspension behavior under flow fields is also described in this chapter. This technique includes fiber flexibility and inter-fiber interactions such as friction and attractive/repulsive forces which makes simulations realistic. Using these simulations can help us to predict the formation and destruction of the aggregates under shear flow and henceforth help to understand the response of these materials to the processing conditions. The Monte Carlo method which was previously developed by Tozzi (*23*), used to generate randomly oriented well dispersed nanotube suspensions is also described in Chapter 3. By using this method, simulation results are compared with theoretical predictions of electrical conductivity and percolation thresholds to validate the simulations. Chapter 4 describes the resistor network algorithm which employs periodic boundary conditions and is used to predict electrical conductivity and percolation thresholds of sheared and randomly oriented CNT/polymer composites.

In Chapter 5, we investigate the combined effects of carbon nanotube properties such as aspect ratio, curvature, anisotropy and tunneling length on the electrical conductivities of CNT/polymer composites. We show that results for percolation thresholds in static systems agree with predictions and experimental measurements. In agreement with previous research we also find that lower percolation thresholds are obtained for less curved and high aspect ratio nanotubes. Increasing tunneling distance between the conductive fillers decreases the electrical percolation threshold of the composites. When the anisotropy of the system increases, the conductive network is formed at higher filler concentrations.

We investigate the effects of both material properties and imposed shear flow on the electrical percolation threshold of CNT/polymer composites in Chapter 6. We show that nanotube properties determine the final microstructure hence final properties of the composites. Percolation threshold in sheared suspensions are observed at lower volume fractions than both non-sheared suspensions and theoretical predictions. The effect of nanotube shape is found to be different for sheared and non-sheared suspensions. For sheared suspensions, increasing nanotube curvature resulted in a decrease in percolation threshold because of the agglomeration dynamics. Our prediction is that increasing nanotube curvature favors the formation of agglomerates in sheared suspensions which leads to formation of percolative networks.

The rate of imposed shear flow on microstructure and electrical conductivity is analyzed in Chapter 7. We also discuss the effect of agglomeration on electrical conductivity. Applying high shear rates cause de-agglomeration and alignment of the nanotubes in the flow direction with a decrease in composite conductivity. We show that upon shearing at constant shear rate, the system attains a state with substantially constant electrical conductivity, nanotube orientation and agglomerate size that are a function of the applied shear rate. The state reached for a given shear rate is independent of the initial state of orientation and agglomeration.

Finally, a brief review which gives general discussion on the study and summary of the key conclusions as well as recommendations for future work is given in Chapter 8.

These simulations give us insight about the structural and electrical conductivity changes during production processes, henceforth helping us to understand production processes and their effects on product properties. It has been experimentally demonstrated that under some conditions, ultra low percolation thresholds have been obtained (*2*) which are not properly described by models that do not account for flow. Such class of models therefore, cannot be used to design or control a large scale process, where a failed batch or production run would have a large cost in time and materials. For such applications, improved models are needed, that quantitatively describe the relation between conductivity and flow processing parameters.

2 Literature Survey

2.1 Carbon Nanotubes

Carbon nanotubes are produced by the catalyzing effect on the gaseous species from the thermal decomposition of hydrocarbons (*24*). In 1991, Iijima (*25*) imaged multiwalled carbon nanotubes using a transmission electron microscopy (TEM). This is the first experimental evidence of the existence of the carbon nanotubes (Figure 2.1). After this work CNT research has been expanded at an extreme speed.

Carbon nanotubes are rolled graphene sheets into cylinders to form tubes and the way the sheet is rolled determines the physical properties of the nanotube. The nanotubes can be tens of millimeters long but with small diameters as low as 0.7 nm (*26*).

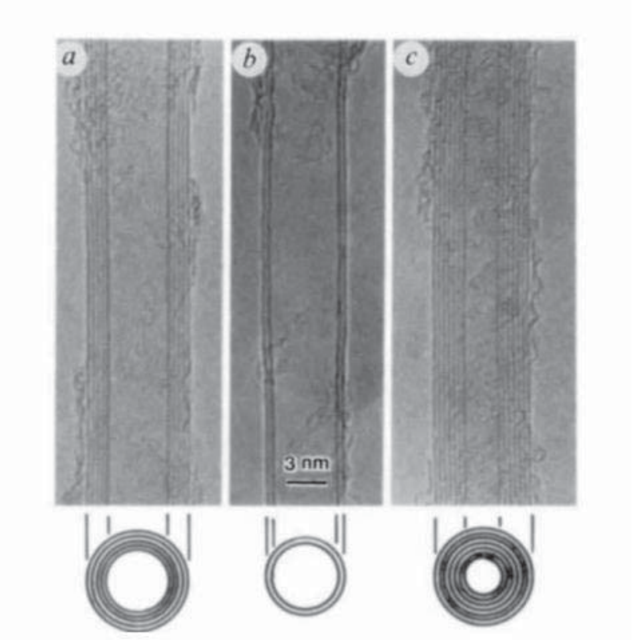

Figure 2.1. TEM observation of multiwalled nanotubes first reported by Iijima (*25*).

Tube walls are made up of a hexagonal lattice of carbon atoms and they are capped at their ends by a fullerene-like molecule (*27*). Nanotube structure can be specified by its chiral vector, $\vec{C_h}$ and chiral angle, θ based on the orientation of the tube axis with respect to the hexagonal lattice (Figure 2.2). The chiral vector can be described by;

$$\vec{C_h} = n\vec{a}_1 + m\vec{a}_2 \tag{2.1}$$

where n and m are integers, $\vec{a}_1$ and $\vec{a}_2$ are the two basis vectors of graphite with

$$a_1 = \frac{a\sqrt{3}}{2}x + \frac{a}{2}y \tag{2.2}$$

and

$$a_2 = \frac{a\sqrt{3}}{2}x - \frac{a}{2}y \tag{2.3}$$

where $a = 2.46\ \dot{A}$ and chiral angle is defined as;

$$cos\theta = \frac{2n+m}{2\sqrt{n^2+m^2+nm}} \tag{2.4}$$

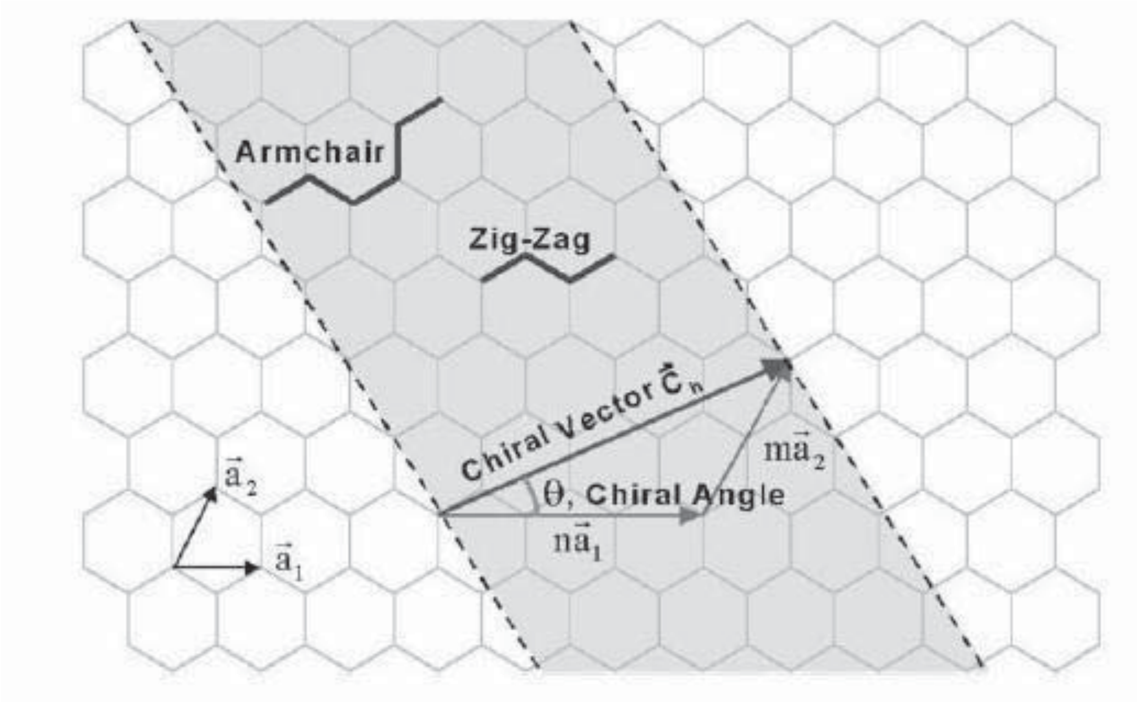

Figure 2.2. A hexagonal graphite sheet is rolled to form a carbon nanotube (*28*).

The arrangement of the carbon atoms changes the electronic structure of the carbon nanotubes. The chiral angle separate carbon nanotubes into three different classes by their electronic properties; armchair ($n = m,\ \theta = 30°$), zigzag ($m = 0,\ n > 0,\ \theta = 0°$) and chiral ($0 < |m| < n,\ 0 < \theta < 30°$). Armchair carbon nanotubes are metallic and zig-zag and chiral nanotubes can be semi-metallic or semiconductors (*29*). Rolling a sheet of graphene to obtain three different carbon nanotube types is given in Figure 2.3.

Parameters such as the carbon nanotube diameter are related to chiral vector and can be determined from n and m;

$$D = \frac{|C_h|}{\pi} = \frac{a_{cc}\sqrt{3(n^2 + m^2 + nm)}}{\pi} \tag{2.5}$$

where

$$1.41\ \dot{A} \leq a_{cc} \leq 1.44\ \dot{A}$$

where for graphite C-C bond length is 1.41 $\dot{A}$ and for C_{60} it is 1.44 $\dot{A}$ (*24*).

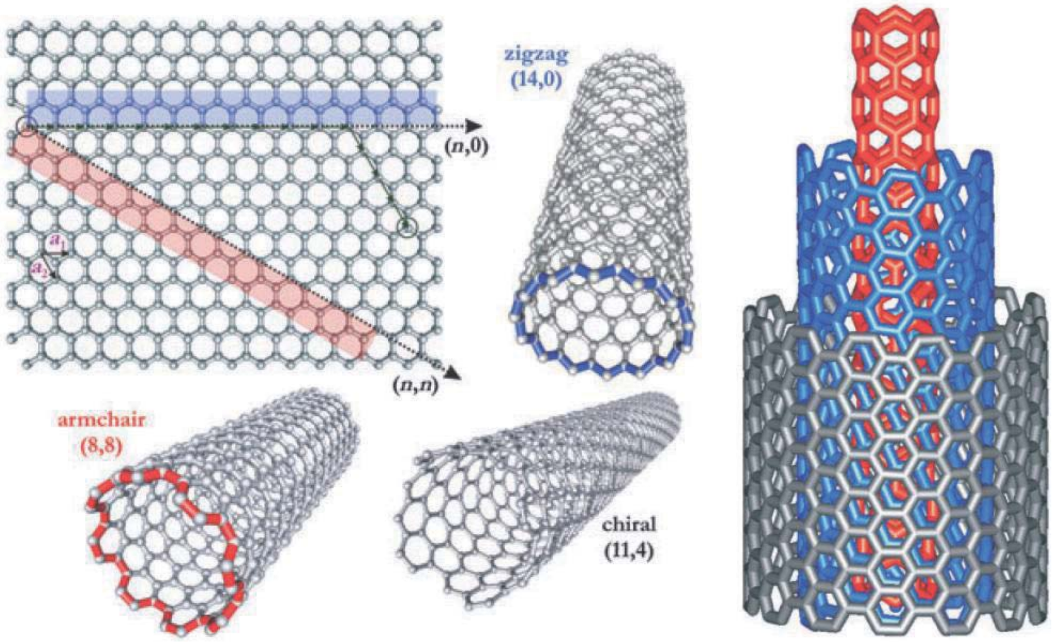

Figure 2.3. Rolling a sheet of graphene to obtain three different carbon nanotube types. Structure of a multiwalled carbon nanotube (*27*).

There are mainly two types of carbon nanotubes, so called “single-walled carbon nanotubes (SWCNT)” and “multi-walled carbon nanotubes (MWCNT)”. SWCNTs are hollow single cylinders of a graphene sheet which are defined by their diameter and chirality. SWCNTs can be either metallic or semiconductive (*30*). MWCNTs posses two or more concentric single wall tubes with diameters ranges from $10\,nm$ up to $100\,nm$. By using electron and x-ray diffraction studies, Saito et al. (*31*) measured the mean value of the interlayer spacing between the graphitic sheets in nanotubes as $0.344\,nm$. The graphitic shells are held together by secondary van der Waals forces.

Carbon nanotubes exhibit a large surface atom to bulk atom ratio. Percentage of surface atoms decreases with increasing number of shells (100% for SWCNTs). Therefore the theoretical specific surface area (SSA) of the SWCNTs is very high up to $1315\,m^2/g$ (*32*). This value mostly depends on the wall number of MWCNTs (for a MWCNT 35 nm in diameter with 40 walls, Peigney et al. (*32*) calculated the SSA as $50\,m^2/g$). This high SSA of the carbon nanotubes is one of the main reasons for the high tendency to agglomerate in a liquid media (*33*).

High aspect ratio (300-1000) of the nanotubes is a very important characteristic because of its use as nanoscale fillers to produce composite materials with improved properties (*34*). Because of their excellent mechanical, electrical and thermal properties, they are considered as fillers for advanced applications. Both SWCNTs and MWCNTs show unique properties and can be used in composite materials.

2.2 Properties of Carbon Nanotubes

Carbon nanotubes exhibit extremely high elastic modulus ($1\,TPa$) which is 10-100 times stronger than steel and comparable to diamond (*35*). They have also superior thermal and electrical properties. Their electrical conductivities are $10^5 - 10^7\ S/m$ and they are thermally stable up to $2800\ °C$ in vacuum and their thermal conductivity is greater than diamond (*28*) and can be as high as $6000\ W/mK$ (*34*).

The comparison between the theoretical properties of carbon nanotubes and some commercial high-performance fibers are listed in Table 2.1 (*36*);

Table 2.1. Typical properties of CNT, Carbon fiber, Spectra and Kevlar 49 (*36*, *37*).

	Carbon Nanotube (MWCNT)	Carbon Fiber	Spectra®	Kevlar 49®
Tensile Strength (GPa)	11-63 GPa	4-7	3.1	3.6-4.1
Tensile Modulus (GPa)	0.9-1.9 TPa	150-950	105	130
Density (g/cm^3)	1.4	1.7-2.2	0.97	1.44
Electrical Conductivity (S/m)	~10^6	500 (*38*)		

More detail regarding electrical properties of carbon nanotubes is given below.

Electrical transport through the SWCNTs has been extensively studied in the past years and many applications based on their exceptional electronic properties have been proposed for the future's nanoscale devices. The transport properties of carbon nanotubes depend on the electronic band structure which is composed of 1-dimensional (1D) subbands (*26*). By rolling the graphene sheet, electronic wave functions are modified giving a rise to the 1D subbands (*24*). SWCNTs are nearly perfect systems for 1D conductors. When compared with other 1D conductors, SWCNTs exhibit several advantages such as being atomically uniform and well defined as well as having large spacing between their 1D subbands showing that the 1D nature is conserved even at the room temperature and above. Also, compared to the molecular wires, SWCNTs exhibit a robust and chemically inert structure (*39*).

SWCNTs can be classified into 3 classes according to their bandgaps:

- SWCNTs with small band gap are partially conducting ($E_g < 100\ meV$). These type of nanotubes exhibit a strong dependence on the temperature (*33*).

- Metallic SWCNTs with $E_g = 0$. These types of nanotubes are rare because of the perturbations existing in all SWCNTs which increase the band gap (*40*). However they do not show a Peierls instability like the other 1D materials. Even at low temperatures they do not undergo a metal-to-insulator transition (*41*). Reduced electron scattering provide metallic SWCNTs a high current density ($109\ A/cm^2$) up to 3 orders of magnitude higher than copper (*24*).
- Semiconducting SWCNTs with $E_g = \frac{0.7eV}{d_{CNT}}(mm)$ (*40*). The band gap is inversely proportional to the tube diameter (*24*). When gate voltage is zero, current can pass through carbon nanotubes and conductance is by unoccupied valence states. Increasing the gate voltage changes the conductor type from p-type to n-type (*42*).

Since there is a confinement effect on the tube circumferences, MWCNTs behave like quantum wires. They are composed of many SWCNT shells having different band gaps provides their metallic nature (*30*). Also, nanotubes are ballistic conductors because their resistances depend on the number of available conduction channels and the transmission contacts. Electrons can travel along the nanotube without any scattering because scales are normally smaller than the scattering lengths (*43*). In ballistic transport, electrons do not experience any scattering or resistance. Hence, no energy is dissipated along the nanotube and large currents can be conducted without energy loss. Therefore the expected quantized conductance of a metallic nanotube is $4e^2/h$ (*40*).

For the semiconducting nanotubes, conduction is diffusive and after neglecting the coherence effects, resistance of a tube can be written as;

$$R_{tube} = \left(\frac{h}{4e^2}\right)\left(\frac{L}{l}\right) \tag{2.6}$$

where L is the tube length, l is the electron mean-free path and $L >> l$ (*40*).

The environmental effects or even disordered structure of the carbon nanotubes can influence the electronic and optical properties of the tubes (*24*, *33*). Localized defects in the lattices, fluctuations in electrostatic potential and mechanical deformations can modify the band gap of the nanotubes (*40*). Applying mechanical stretching (*42, 44*), axial magnetic field (*42*), internal defects such as atomic vacancies (*45, 46*), impurities (*47-52*) or even agglomeration (*24*) were proved to change the band structure of the nanotubes. Branden et al. (*53*) showed the effect of silicon impurities on the electronic properties of carbon nanotubes by reporting density functional theory calculations. Added Si atoms opened the band gap of metallic carbon nanotubes ranging between $0.10\,eV$ to $0.47\,eV$. In their study Cartoxia et al. (*54*) determined that BN-pair addition turned the metallic tubes to semiconducting. It is not easy to generalize the effects of disorder because of the coexistence of the disorder sources and variability of the nanotube properties. Detailed information can be found in (*40*).

Some potential applications of carbon nanotubes are: vacuum microelectronics, hydrogen storage, nanoprobes and sensors, templates and electron emission devices such as cathode-ray lighting elements, flat panel display and gas-discharge tubes (*55*).

2.3 Polymer Based CNT-Filled Materials

Carbon nanotubes are considered as ultimate reinforcing materials due to their superior electrical, mechanical and thermal properties. Carbon nanotubes are widely used to reinforce polymer (*4, 56-59*), ceramic (*58, 60-65*) and metal (*66-69*) matrices.

As discussed in (*36*) some previously reported polymer matrices for carbon nanotube fillers are; semicrystalline (*70, 71*) and amorphous (*72, 73*) thermoplastics, thermosetting (*2, 18, 74*) resins, water soluble polymer (*75*), liquid crystalline polymer (*76*) and conjugated polymers (*77, 78*). Carbon nanotubes were previously used to improve the polymeric materials' properties such as tensile modulus (*79, 80*), tensile strength (*81*), torsional modulus (*82*), compressive strength (*83*), fatigue behavior (*84*), toughness (*83*), glass transition temperature (*85, 86*), electrical conductivity (*1, 2*), thermal conductivity (*5, 6*), solvent resistance (*87*) and optical properties (*88, 89*).

Polymers are widely used in numerous fields because of their advantages over other materials such as lightness, low-cost, chemical resistance and easy processing (*30*). Carbon nanotubes has found many applications in military (*90*) and space (*91*). In military applications, carbon nanotube composites can be used as structural composites/adhesives, coatings and smart materials. Reducing the total weight of component by manufacturing one-piece sections from composites and incorporating health monitoring-systems (*92*, *93*) can be stated as the greatest opportunities for military and aerospace applications. Besides, carbon nanotube composites have also been used as coatings for radar absorption or radar transparency. Biosensors, thermal protection via ablation and protective military uniforms are other potential applications of carbon nanotube composites (*90*).

Incorporating carbon nanotubes into polymers increases the electrical conductivity of the materials while leaving other properties and behaviors unaffected (*24*). They can transform an insulating matrix to a conductive composite at very low volume fractions because of their high aspect ratio (*3*). Electrostatic discharge (preventing fire or explosion hazards in combustible environments or perturbations in electronics), electrostatic painting (preventing charged paint droplets from being repelled) and electromagnetic interference shielding are the main interesting areas regarding the electrical conductivity (*24*).

Polymeric coatings with sufficient electrical conductivity to discharge the electricity are needed for space structures. Energetic particles can penetrate inside the surface layers causing an electrostatic charging in the insulating materials on a space structure. Hence discharging is crucial to prevent the fatal damage on the electronic parts (*91*). Required surface conductivity to provide the electrostatic discharge is $10^{-6}\ S$ (*94*).

Figure 2.4 shows the experimental results of electrical conductivity of the SWCNT/Polystyrene composites as a function of filler concentration together with the required electrical conductivity values for different applications (*95*).

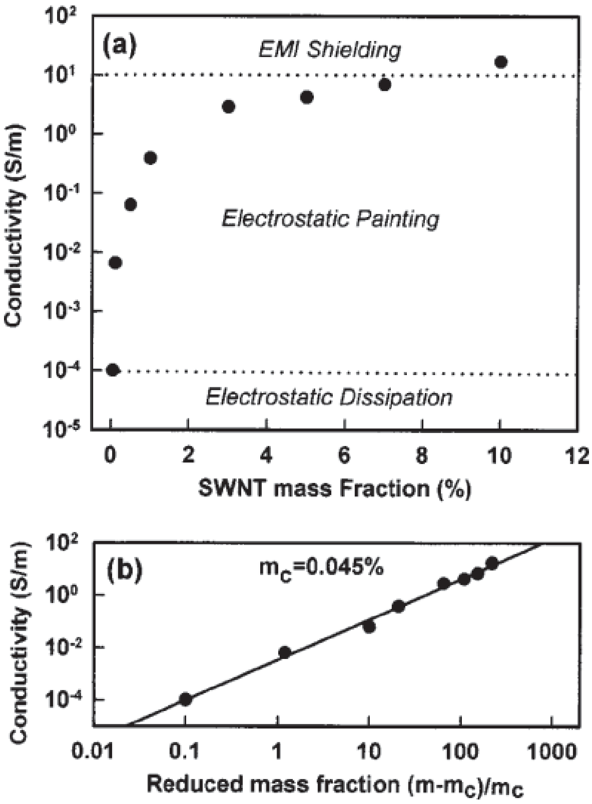

Figure 2.4. Electrical conductivity of single walled carbon nanotube/polystyrene composites as a function of filler loading together with the required electrical conductivity values for different applications (*95*).

2.4 Fabrication of CNT/Polymer Composites

Direct Mixing: Carbon nanotubes are dispersed into the thermosetting resins by mechanical mixing or sonication. Then the resin is cured to obtain the CNT/polymer composite (*13*).

Melt Processing: This process is used when the insoluble polymers (in any solvent) are considered. Polymers that melt upon heating (thermoplastic polymers) can be melted to form liquids and nanotubes are added to this melt and mixed together. Achieving high concentration and homogenous dispersion is difficult because of the high viscosities of the mixtures. Shear mixing, extrusion and injection molding are some of the melt processing methods (*96*).

In Situ Polymerization: Monomers are used as starting materials and are directly adhered to the nanotube walls. It is mostly used for thermally unstable and insoluble polymers that cannot be processed by melt processing (*30*). Park et al. (*97*) ultrasonicated the medium prior to in situ polymerization to obtain well dispersed nanotubes.

Solution Method: Carbon nanotubes are added to the thermoplastic polymer-solvent solution. The solvent is firstly used to dissolve the polymer but at the end of the process it should be evaporated. Then the thermoplastic solidifies and composite is formed (*98*). Agglomeration of the nanotubes during the solvent evaporation could be a potential problem of this method (*96*).

2.5 Percolation Theory

Percolation theory is used to describe the disordered systems. For example transport in composites can be explained by this theory. Consider a lattice, where a large array of squares exists. Some of the squares are filled and the others are empty. We can assume that filled sites are electrical conductors and empty sites are insulators. Then electrical current can flow only between the neighboring electrical conductors (*99*). A cluster is defined as a group of occupied neighbor squares.

At low concentrations, p, most of the sites are insulators and conductors are isolated or form small clusters which are not connected to the opposite edges. Therefore a current cannot flow across the edges and we have zero conductivity. On the other hand, at large p, the conductor sites can form a conducting path between opposite edges and electrical current can flow. The conductivity and the fraction of connected sites increase linearly with concentration. At some point in between, a threshold concentration p_c should exist where the connected clusters percolate for the first time through the lattice. This concentration is called the percolation threshold (*99*) and represents the minimum volume fraction that a continuous conductive network exists in the lattice (*30*).

Consider a section of bond cluster at percolation threshold. If a voltage is applied to the ends of the cluster, some of the bonds will lead nowhere and they will not carry any current. These bonds are called “dead ends” and will not contribute to the conductivity (Figure 2.5). When these bonds are erased, “backbone” will be obtained and all the bonds of the backbone will