EFFECT OF DISPERSION OF SWCNTs ON THE VISCOELASTIC AND FINAL PROPERTIES OF EPOXY BASED NANOCOMPOSITES

by

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Abstract

The properties of polymer nanocomposites depend primarily on the dispersion of nanoparticles and the interaction between nanoparticles and the polymer matrix. Homogeneous dispersion and good interfacial adhesion can transfer mechanical loads effectively to carbon nanotubes (CNT) and significantly improve bulk properties. However, because of the extreme inertness of CNT, efforts to enhance the mechanical properties of CNT-polymer nanocomposites have met with only modest success.

The aim of this research is to understand the effect of the dispersion quality on the final properties (mechanical and thermo-mechanical) of single wall carbon nanotube/epoxy composites. Several dispersion techniques such as sonication, surfactant and chemical functionalization were chosen. The quality of the dispersion was evaluated through rheological studies. In addition the effect of the aspect ratio with different SWCNT concentration was examined by using experimental results and the Einstein analytical model. Using a combination of techniques (microscopy, thermal gravimetric analysis, rheology and dynamic mechanical analysis), an attempt was made to characterize the single wall carbon nanotube/epoxy systems.

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List of Abbreviations

SWCNT	Single Wall Carbon Nanotube
MWCNT	Multi Wall Carbon Nanotube
CNF	Carbon Nanofiber
MPa	Megapascal
GPa	Gigapascal
TPa	Terapascal
DSC	Differential Scanning Calorimetry
TGA	Thermal Gravimetric Analysis
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
AFM	Atomic Force Microscopy
DMA	Dynamic Mechanical Analysis
G’	Storage modulus
G”	Loss modulus
E’	Storage modulus
E’’	Loss modulus
T_g	Glass transition temperature

CHAPTER ONE

INTRODUCTION

1.1 LITERATURE REVIEW

1.1.1 NANOCOMPOSITES

Recent technological progress has created new challenges in the field of materials, composites in particular. Experimental work has generally shown that virtually most types and classes of nanocomposite materials lead to new and improved properties when compared to their macro-composite counterparts. Nanocomposites can be defined as a composite material in which at least one of the phases (mostly the filler) shows dimensions in the nanometer range. As the fillers size reach the nanometer level, the interactions at the interfaces become considerable large with respect to the size of the inclusion and thus the final properties show significant change.

Nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components (automotive parts), non-linear optical devices, batteries, nano-wires, sensors, bio-electronic, etc. Moreover, advanced technologies like bone cement, filter membranes, aerogels and solar gels are significant other applications for nanocomposites. Nowadays, nanocomposites offer new technology and business opportunities for different industries (Camargo et al. 2009, Hay et al. 2000).

Nanocomposites can be classified according to their matrix materials in three different categories; ceramic matrix nanocomposites, metal matrix nanocomposites and polymer matrix nanocomposites.

1.1.1.1 Ceramic matrix nanocomposites (CMNC)

Although typical ceramic composites have good wear resistance and high thermal and chemical stability, they are mainly brittle materials. In order to overcome this disadvantage, the incorporation of energy-dissipating components, such as nanowhiskers, fibers platelets, or particles into the ceramic matrix is a good way to increase the fracture toughness of these materials (Sternitzke et al. 1997). The most common methodologies for CMNCs preparations are spray pyrolysis, vapor techniques and chemical methods such as the sol-gel process. Potential applications for ceramic matrix nanocomposites are wear or friction surfaces, load-bearing structural parts, automotive, aerospace, power generation applications (engines, turbines), medical devices and implants.

1.1.1.2 Metal matrix nanocomposites (MMNC)

Metal matrix nanocomposites refer to materials consisting of a ductile metal or alloy matrix in which some nanosized reinforcement material is implanted. They are high strength and high modulus materials with substantial ductility and toughness (Tjong et al. 2000). They are suitable for uses in aerospace and automotive industries. The most common techniques for MMNCs are mechanical alloying, vertex process, spray deposition liquid metal infiltration, rapid solidification, and chemical processes such as sol-gel and colloidal (Padhi et al. 2008).

1.1.1.3 Polymer matrix nanocomposites (PMNC)

Polymers are the most widely used materials for composites because of their lightweight, low cost, and good chemical resistance. Using a polymer as the matrix facilitates processing and structural integrity while the fillers add different functionalities. On the other hand, they have some disadvantages such as low modulus and strength compared to metals and ceramics. Therefore, an effective method for property enhancement is the addition of nanoreinforcements to the polymer matrix. For instance, polymers have been filled with several synthetic or natural compounds in order to increase heat and impact resistance, flame retardancy and mechanical strength. (Fischer , 2003).

In recent years, the use of nanofillers as reinforcement of a polymer matrix has been gaining in popularity in industrial and academic research. These materials have been used as alternatives to conventional polymers or polymer blends. In mechanical terms, because of their enormous surface area to volume ratio and high aspect ratio (length to diameter),nanocomposites differ from conventional composite materials. The nanofillers' interfacial area (103-104 m^2/ml) is typically orders of magnitude greater than conventional composite materials (30 m^2/ml) (Chawla, 1998). Thus, the mechanical properties of the final composite are significantly affected by the strong interactions created at the matrix-filler interface. Ajayan et al.(2000) reported that local chemistry, degree of thermoset curing, polymer chain mobility, polymer chain conformation, degree of crystallinity and final physical and mechanical properties of the polymer nanocomposites can vary significantly and continuously from the interface of the reinforcement to the bulk of the matrix. Therefore, a relatively small amount of nanoscale reinforcement (1-5wt %) can have significant effect on the macro-scale properties of the composites (Schadler et al. 1998, Lu et al. 1997). Haggenmueller et al. observed ~100% increase in elastic modulus for single wall carbon nanotube (SWCNT)/poly(methyl methacrylate) (PMMA) nanocomposites. Park et al. obtained 10 decade enhancement in electrical conductivity at a nanotube loading of only 0.1 vol % for SWNT/Polyimide nanocomposites (Du et al. 2004). Many methods have been described in the literature for the fabrication of polymer nanocomposite materials (Fischer et al. 2003, Thostenson et al. 2001), such as, intercalation of the polymer (Shen et al. 2002) (clay with high density polyethylene (HDPE) or polyvinylalcohol (PVA) etc.); in-situ intercalative polymerization (montmorillonate with epoxy or polyurethane) (Yao et al. 2002); melt intercalation (montmorillonote with polystyrene) (Vaia et al. 1997), direct mixture of polymer and particulates (CNTs with epoxy) (Sandler et al. 1999), template synthesis (hectorite with polyacrylonitrile (PAN)) (Watkins et al. 1995), and in-situ polymerization (poly(ethylene terephthalate) with calcium carbonate (Roslaniec et al. 2003)) and sol-gel process (polyimide with silica (SiO_2) (Liu et al. 2002).

1.1.2 CARBON NANOTUBES

Carbon nanotubes, which were first discovered by Sumo Iijima in 1991, are comprised of sheets of carbon in a hexagonal lattice that are rolled into a cylinder (Iijima 1991). Since their discovery, carbon nanotubes have been gaining popularity in research area due to their unprecedented physical and chemical properties (Kennedy 2008).

Nanotubes are members of the fullerene structural family, which also includes the spherical bucky-balls that were discovered by Smalley and coworkers at Rice University (Kroto et al. 1985). Carbon nanotubes are long, slender fullerenes with walls composed of hexagonal carbon and capped ends. Their name is derived from their size, since the diameter of a nanotube is on the order of few nanometers (approximately 1/50,000th of the width of a human hair).

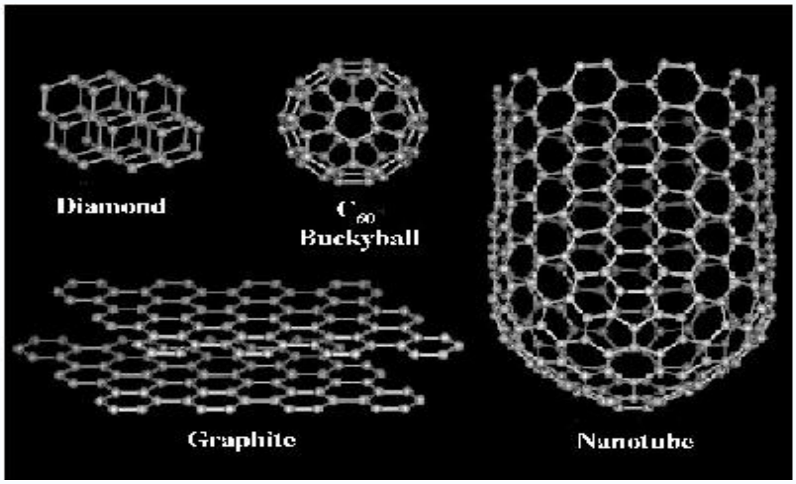

Figure 1.1: Allotropes of carbon (Hoagland 2005)

Three types of carbon nanotubes exist; they are multi-wall (MWCNT), double-wall (DWCNT) and single wall carbon nanotubes (SWCNT) (Figure 1.2). Multi-wall carbon nanotubes consist of a central tube of nanometric diameter surrounded by graphitic cylinders separated by approximately 0.34 nm. MWCNTs can have diameters ranging from 2 to 100nm and lengths of microns. DWCNTs have two graphene sheets rolled up to form a cylinder. Single wall carbon nanotubes have only one central tube. Their diameter is approximately 1 nm and their length is up to few centimeters (Rao et al., 2005). The density of a SWCNT is approximately 1.33-1.40 g/cm^3 and its elastic modulus is around 1.2 TPa.

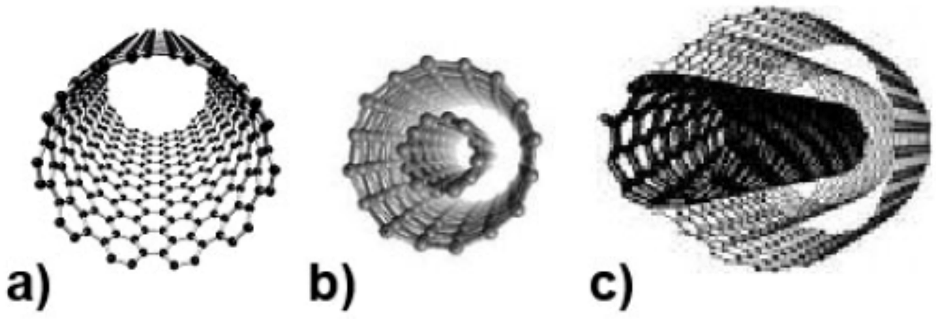

Figure 1.2: Schematic of a) SWCNT, b) DWCNT, c) MWCNT

(reproduced from http://www.wtec.org/loyola/nano/04_03.htm)

Because of the carbon-carbon bond symmetry of the cylindrical tube, CNTs have a discreet number of orientations which are called chirality. Chirality is the way of rolling graphene into a tube and is defined by a circumferential vector (chiral vector (n and m)). Figure 1.3 shows how a hexagonal sheet of graphene is rolled to form a carbon nanotube. If n and m are equal (n=m), then it is an arm chair circumference (arm chair CNT). If (n,m)=(n,0) or (0,m) then it is a zig zag circumference (zig zag nanotubes). All armchair SWCNTs are metallic where as SWCNTs with n-m= 3i (i being an integer different than 0) are semi-metallic and n-m≠ 3i are semiconductors (Figure 1.4). For MWCNT, the chirality is more complicated since each tube that forms the nanotube may possess a different chirality.

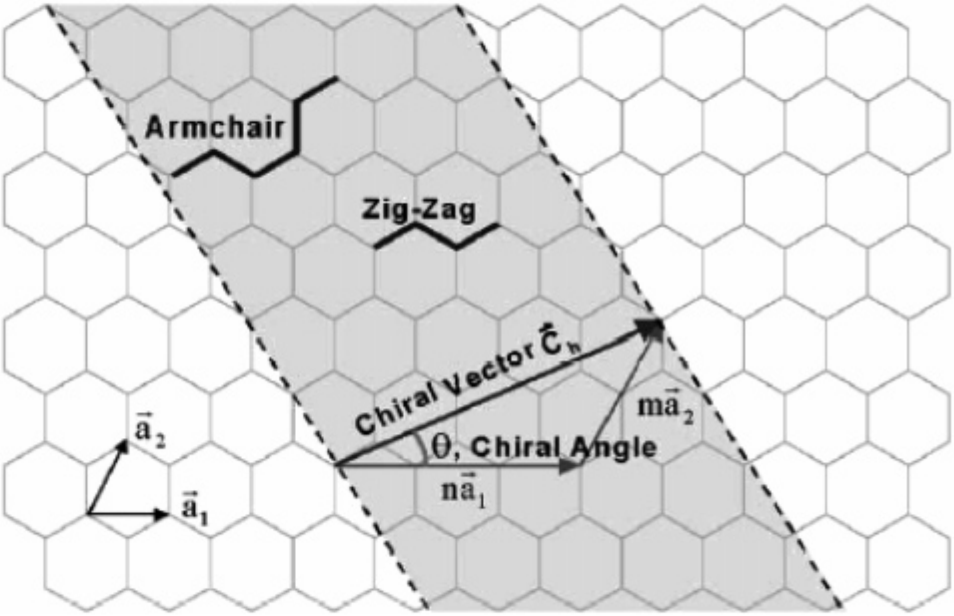

Figure 1.3: Schematic of chirality on graphene sheet (Moniruzzaman and Winey 2006)

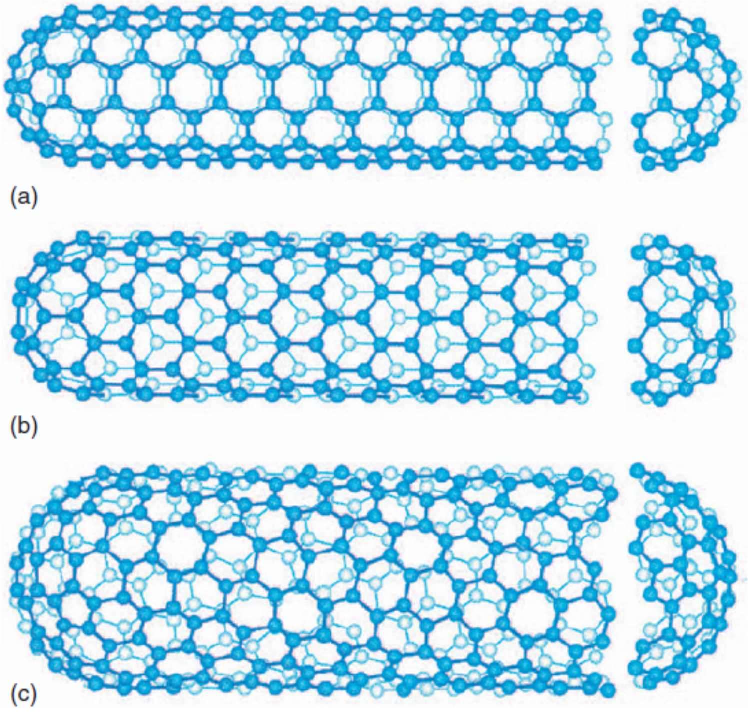

Figure 1.4: Chirality of CNTs a) Arm-chair b) Zig-zag c) Chiral (Khare et al. 2005)

Carbon nanotubes exhibit exceptional properties that are a consequence of the covalent sp^2 bonds formed between the individual carbon atoms. They are one of the best performance fillers that have low density (1.3 to 1.4 g·cm^{-3}). Their mechanical properties have been reported by different research groups. The first measurements were made by Treacy et al. with MWCNT which were produced by arc discharge method. While measuring the amplitude of the intrinsic thermal vibration with transmission electron microscopy (TEM), Treacy and others found that the Young's modulus ranged from 0.41-4.15 TPa (Treacy et al., 1996). The first direct measurement was made by Wong et al. in 1997 using atomic force microscopy (AFM) where the Young's modulus of single wall nanotubes was found to be 1.28 TPa. Additionally, the strength of the carbon nanotubes was estimated at around 14 GPa (Wong et al., 1997). Yu et al. performed stress-strain measurements for individual MWCNTs inside an electron microscope. They reported modulus values of 0.27-0.95 TPa, fracture strain of 12%, strengths in the range 11-63 GPa and toughness of 1240 J/g (Yu et al., 2000).

Overney et al. calculated the Young's modulus of SWCNT to be 1.5 TPa similar to graphene (Overney et al. 1997, Lu et al. 1997). The measurement made by Salvetat et. al. using AFM method showed a tensile modulus of 1 TPa for small diameter bundles. Intertube slippage within bundles is a serious limitation for SWCNTs mechanical properties, since effective modulus and strength for bundles are far below to the expected values. (Salvetat et al. 1999). Additionally, the tubes can undergo plastic deformation under excessive tensile strain. This deformation begins at strains of approximately 5% and increases the maximum strain which the tubes undergo before fracture by releasing strain energy (Qian et al. 2002). CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional or bending stress (Yao et al. 1998).

The electric current carrying capacity is estimated to be around 10^9 amp/cm^2 (Song et al. 2005). The thermal conductivity of SWCNT is predicted to be 6000W/mK at room temperature (Penumadu et al. 2003). Additionally, they are stable up to 2800 ºC in vacuum and 750 ºC in air. (Thostenson et al. 2005)

1.1.2.1 Synthesis

Nanocomposites found great attention in the research and industry areas; however, they are still not well-industrialized materials. The main reason is that the synthesis of carbon nanotubes and purification processes increased the cost of these materials. In order to reduce costs associated with the production of these nanofillers, different fabrication methods have been explored. Some of these methods are arc discharge, laser ablation and chemical vapor deposition.

The arc method was first used for the production of C60 fullerenes, and single and multi-walled nanotubes are also produced by this process. A high current electric arc passes through graphite electrodes separated by approximately 1mm in the presence of metal catalyst particles. This is the easiest technique to produce CNTs; however, the tubes have a high amount of impurities which requires further purification steps. Additionally, the sample yield achieved with this method is not high, 30 percent by weight. . It is possible to produce nanotubes with lengths of up to 50 micrometers with few structural defects (Wilson et al., 2002).

Dr. Richard Smalley and co-workers at Rice University were the first to synthesize CNTs using a laser ablation method (Kroto et al. 1985). They used composite graphite and metal catalyst particles to create multi-wall carbon nanotubes and single-wall carbon nanotubes. The laser ablation method yields around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition. Laser vaporization of graphite rods with a 50:50 catalyst mixture of Cobalt and Nickel at 1200°C in flowing argon is usually used to prepare CNTs. This process is followed by a heat treatment in a vacuum at 1000ºC to remove fullerenes and impurities.

Arc-discharge and laser vaporization are currently used for obtaining small quantities of high quality CNTs. However, both methods suffer from industrial level production and also high amounts of impurities. Extra purification processes are required, which increases the associated costs of these techniques.

Carbon vapor deposition method (CVD) has been used for producing carbon fibers and filaments for over 20 years. CVD is more suitable for controlling the length and structure of produced nanotubes and is also conducive for achieving high quantities, which make nanotubes available for industrial fabrication. In CVD technique, a gaseous carbon source such as hydrocarbon is decomposed catalytically, and the nanotubes are deposited on a substrate or grow from a substrate which is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination of them. The diameters of the nanotubes are related to the size of the metal catalyst particles that are used. The diameter of the carbon nanotubes can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer. The substrate is heated to approximately 700°C. To initiate the growth of nanotubes, two gases are bled into the reactor: a process gas (such as ammonia, nitrogen or hydrogen) and a hydrocarbon source. Nanotubes grow at the sites of the metal catalyst; the hydrocarbon gas source is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. This process requires a lower preparation temperature and simpler equipment (Poulsen et al., 2000). Using this methodology, well-aligned or entangled SWCNTs and MWCNTs can be produced in high quantities.

1.1.3 CHALLENGES

Recently, extensive research has been carried out on the incorporation of different types of carbon nanotubes as reinforcements into polymeric materials to produce high performance composites with high mechanical strength, electrical and thermal conductivity (Cui et al., 2003). However, there are some challenges to create high performance carbon nanotube composites.

Due to the sp^2 bonds and the high intermolecular attraction between the bundles, the dispersion of these fillers in the host matrix and organic solvents is usually an issue. CNTs tend to agglomerate and are difficult to disperse in the host polymer. In most of the early work, untreated CNTs or only purified CNTs were used and no significant mechanical improvement was observed. At present, it is well recognized that in order to maximize the final performance of materials, a uniform dispersion of CNTs into the polymer matrix and good interfacial adhesion are two critical issues in the fabrication of CNT-polymer nanocomposites. The non-covalent functionalization approach of CNTs has been demonstrated to be capable of improving the dispersion of CNTs in epoxy resin. On the other hand, the covalent bonding between CNTs and polymers appear to be a very useful technique in order to achieve the maximum interfacial shear strength (Cheng et al., 2007).

Many of the applications of CNT composites are limited by the current cost of CNTs. While production costs are expected to fall in the future with increasing demand, costs associated with CNT processing such as purification, dispersing and functionalization will remain a substantial part of the end cost of CNTs nanocomposites.

1.1.4 DISPERSION

The key challenge for nanocomposite materials is to obtain a homogenous dispersion of nanotubes in the polymer matrix. Because of their small size, the attractive interactions between nanotubes are very strong and this strong interaction causes agglomeration of CNTs. Especially, SWCNTs aggregate to form bundles that are very difficult to disperse and these bundles are entangled with one another.

Several methods have been developed to prepare uniformly dispersed nanotube reinforced composites. These include the use of surfactants (Gong et al., 2000, Vaisman et al., 2006), high shear mixing (Gojny et al., 2004, Andrews et al., 2002), sonication (Qian et al., 2000), in situ polymerization of monomers in the presence of carbon nanotubes (Velasco-Santos et al., 2003), and chemical functionalization of the outside wall of the tubes (Dyke et al., 2004, Chen et al., 2006).

1.1.4.1 Ultra-Sonication

Sonication is a simple technique that uses high-intensity acoustic energy to mix and disperse materials. During sonication, nanotube entanglements are reduced. However, this technique damages and degrades the structure of the fillers which in turn could eventually reduce the length of the nanotubes. The sonication effect has been evaluated by Suave et al. They observed that the tensile strength of CNTs systems increased after sonication at high amplitude for a short period of time (20min). They also found that the best results were observed for low power sonication (165 W) performed over a longer period of time (40min) (Suave et al., 2009).

1.1.4.2 Surfactant-assisted functionalization

Surfactants are amphiphilic compounds that have a hydrophilic (polar head) and a hydrophobic (tail group) parts that are jointed by a short hydrocarbon chains. They can be classified as cationic, anionic, nonionic or zwitterionic (Geng et al., 2008).

Surfactants have been extensively used in processing stable colloidal dispersions since they are adsorbed at the interface of super-molecular structures. Chemical characteristics of the particles, surfactant molecules and the type of the solvent are key parameters for adsorption of surfactants onto inorganic and organic surfaces.

The adsorption of a surfactant on the CNT's surface lowers the surface tension of the CNT. This prevents the formation of aggregates (Figure 1.5). Furthermore, due to the presence of electrostatic repulsive forces promoted by the surfactant treatment, CNTs overcome the Van der Waals attractions which are responsible for the agglomerations (Geng et al., 2008). J. Liu et al. observed more than a 30 % increase in elastic modulus for non-ionic surfactant-assisted carbon nanotubes (Liu et al., 2000). Y. Geng et al. also observed significant improvements in mechanical properties, thermo-mechanical properties, and electrical conductivity of MWCNT/epoxy systems (Geng et al., 2008).

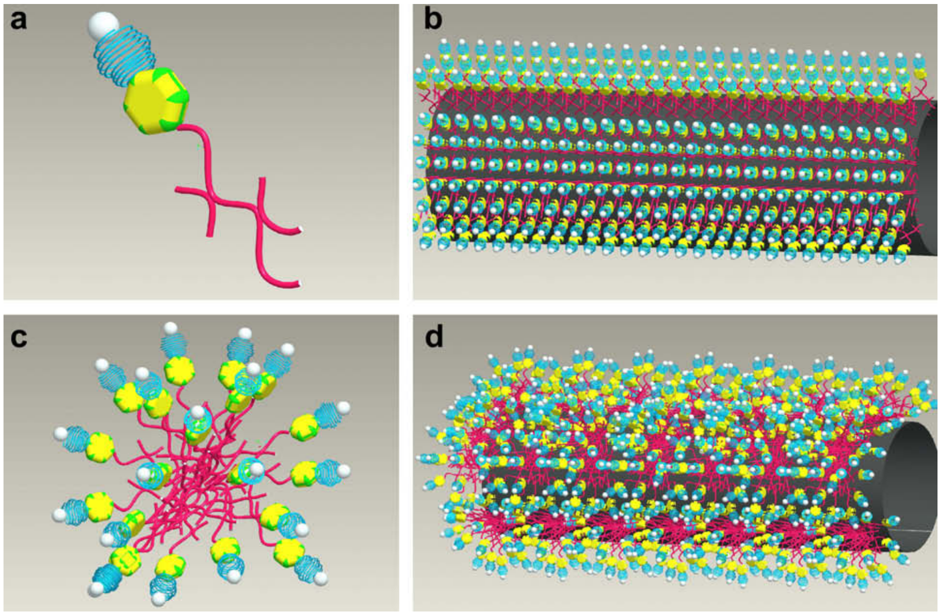

Figure 1.5: a) Non-ionic surfactant molecule b) CNT wrapped by surfactant molecule c) a surfactant micelle d) CNT wrapped by surfactant micelles (reproduced from Geng et al. 2008)

1.1.4.3 Covalent Functionalization

Covalent functionalization and surface chemistry of carbon nanotubes are important aspects for nanocomposite materials. Since carbon nanotubes have a relatively smooth graphene surface, interfacial bonding between a polymer matrix and carbon nanotubes is weak. As previously mentioned, nanotubes are typically held together as bundles in a polymer matrix which causes poor nanotube dispersion. The covalent functionalization of carbon nanotubes is expected to aid in dispersion, which improves the final properties of nanocomposites. However, during the functionalization process, the interaction between CNTs and the organic chemical used for the grafting process causes some defects on the nanotube surface. Chemical functionalization methods are not attractive for applications requiring high conductivity since defects on the nanotube surface decrease the electrical conductivity and tensile strength of nanotubes (Gojny et al., 2004).

1.1.5 APPLICATIONS

Nanocomposites present many benefits such as increased mechanical properties, high thermal and chemical stability, etc. However, the usage of nanocomposites in industry is not as high as expected, but the number of application areas has been growing in recent years. There are possible applications such as aerospace structural panels, sporting goods, and ultra-lightweight thin-walled space structures (Mallick 1993, Rao et al., 2005, Thostenson et al., 2005).

The automotive sector is one of the leading application areas for nanocomposite materials. Nanocomposites may be potentially utilized as mirror housings on various vehicle types, door handles, engine covers and intake manifolds and timing belt covers. Additionally, safety issues and environmental policies push manufacturers to find new materials that meet expectations. CNT-based nanocomposites are now available for different car models. For example Audi, Evobus and Diamler Chrysler automobiles have nano-coatings on their car's parts. Moreover, fuel cells, porous filters and energy conversion components are other popular applications. Additionally, light weight bodies made of polymer based nanocomposites are another significant area for the car industry.

Other application areas are microelectronics, dental applications, optical devices, composite membranes for gas separation applications, abrasion resistant coatings, beverage container applications, power tool housing, mobile phones, food packaging applications, etc. (Camargo et al., 2009).

1.2 RESEARCH OBJECTIVES

There are two main objectives associated with this research:

The first objective of this work is to understand and evaluate the problems associated with the dispersion of carbon nanotubes in polymeric systems. Different dispersion techniques such as sonication, surfactants and covalent functionalization will be evaluated and the quality of the sample dispersion will be assessed by the constancy of the storage modulus with frequency in the low-frequency range.

The second objective is to obtain a basic understanding of the thermal, mechanical and morphological properties of single wall carbon nanotubes (SWCNT)/epoxy composites.

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CHAPTER TWO

DISPERSION OF SINGLE WALL CARBON NANOTUBES EPOXY SUSPENSION

2.1 INTRODUCTION

Carbon nanotubes (CNTs) as an important component in polymer nanocomposites have attracted considerable interest due to their unusual electrical, thermal and mechanical properties (Allaoui et al. 2002). Recent works have demonstrated a remarkable enhancement in the heat transfer efficiency of CNT-polymer nanocomposites (Thostenson et al. 2005) and success in mechanical reinforcement of polymers. In the early work, untreated CNTs or only purified CNTs were used and no significant mechanical improvement was observed, however at present, it is well recognized that to maximize the final performance of materials, uniform dispersion of CNTs in polymers and good interfacial adhesion are two critical issues in the fabrication of CNT-polymer nanocomposites (Uchida et al. 2005).

Pristine CNTs are generally incompatible with organic molecules including polymers and their extremely high aspect ratio (up to 1000) makes them easy to entangle with one another and create filler aggregates in suspensions due to strong Van der Waals attractions, which cause considerable difficulties in preparing CNT-nanocomposites. Advani et al. defined "a good dispersion" as uniformly distributed CNT aggregates in the suspending fluid (Fan et al. 2007). Thus, different procedures such as high shear mixing, sonication, surfactants and CNTs chemical functionalization have been used to aid in dispersion. The non-covalent functionalization of

CNTs has been demonstrated to be capable of improving the dispersion of CNTs in epoxy resin (Zhu et al. 2003) however, the covalent bonding between CNTs and polymers appear to be preferable in order to achieve the maximum interfacial shear stress (Suhr et al. 2005, Zinoviev et al. 1994).

In this chapter, sonication, surfactant-assisted dispersion and acid functionalization, have been evaluated. The quality of the dispersion was evaluated via different characterization techniques such as rheology and scanning electron microscopy.

2.2 MATERIALS

SWCNTs were purchased from Shenzen Nanotech Port. Co. Ltd., China. The diameter range for the SWCNTs was < 2 nm; the length range was 5-15 μm; the purity of CNTs was > 90 %.

A diglycidyle ether of bisphenol A epoxy (DGEBA, EPON 828 Miller-Stephenson Chemical Co. Inc.) was used as a matrix. The sample was dried in a vacuum oven before utilization.

Non-ionic surfactant, polyoxyethylene octyl phenyl ether (Triton X-100) was used as a surfactant agent. Tetrahydrofuran (THF), sulfuric acid (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (HCl) were purchased from Fisher Scientific. All the materials were used as received.

2.3 TECHNIQUES

2.3.1 Rheology

Rheology, defined as the study of deformation and flow characteristic of materials, is an effective method to understand the micro-structural changes and the filler/matrix interaction in a filler reinforced polymeric system. Rheology is a useful tool for studying viscoelastic materials, which show viscous and elastic properties (Han et al. 2007). These properties of viscoelastic materials can be explained with complex modulus which ($G^* = G' + iG''$, ($i = -1$)). G' is the elastic modulus or the storage modulus that provides information about the elastic nature of the materials and shows the deformational energy stored in the system. On the other hand, G'' is the viscous modulus or the loss modulus characterizes the viscous nature of the materials and shows the dissipated energy during the viscous deformation of the system (Gupta et al. 2000).

The rheological properties of the epoxy liquid suspensions were determined using a commercial strain controlled rheometer (AR-G2, TA Instruments). A cone and plate geometry (diameter 60 mm and 27 μm truncation) was used to register the viscoelastic response of the CNTs/epoxy suspensions. This geometry offers several advantages, such as smaller amount of sample, easier loading and cleaning condition and a homogenous deformation throughout the sample (Khan et al. 2000). Viscoelastic properties of all samples were measured at 25°C temperature. Dynamic strain sweeps at a constant frequency (1Hz) were used to find the linear viscoelastic region in which G' and G'' were independent of strain amplitude. For all samples, 1% strain was chosen in the linear viscoelastic region. A linear viscoelastic response characterized the entire range of frequency amplitudes used in this work (100 to 0.01 rad/s). Five minute rest time was used to eliminate the effect of loading history. For the orientation of CNTs in the epoxy suspension, 1/20 s shear rate was applied for 30 minutes.

2.3.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM, Cambridge 360) was used to observe dispersed samples deposited in carbon grids. Samples were sputter-coated with gold prior to SEM observation.

2.3.3 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA Q500, TA Instruments) was employed to quantify the weight percentage (wt %) of the organic component in functionalized-CNTs. Samples were heated to 800°C at 10°C /min under nitrogen.

Preparation of SWCNT Epoxy suspensions

The SWCNT powder was added directly into the solvent (THF) and mixed for one week. After one week of mixing, epoxy was added into the solution and mixed for 2 hours. The solvent was evaporated using a vacuum oven at 80°C. All experiments were made under room temperature.

Oxidation of SWCNTs

In this study, CNTs were oxidized based on a process developed by Liu et al. (61). According to the procedure (Figure 2.1), 1 g of SWCNT was dispersed in 250 mL of 3:1 H_2SO_4 (98 %) / HNO_3 (70 %). This solution was sonicated for 1 h followed by 3 h of stirring at room temperature. These conditions were selected to achieve moderate oxidation and maintain a higher aspect ratio. After exhaustive washes with deionized water, HCl was added to facilitate the formation of carboxylic acid groups –COOH (Figure 2.1). The solution was washed again with deionized water until a constant pH value around 5-6 was achieved. The acid-treated CNTs were obtained after centrifugation of the aqueous suspensions and dried overnight in a vacuum oven at 90°C.

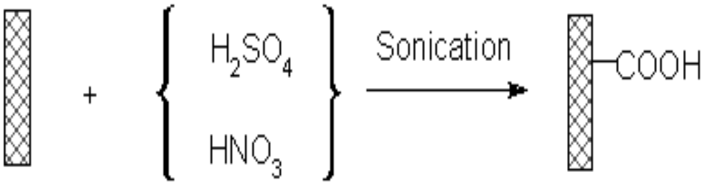

Figure 2.1: Oxidation process of SWCNT

TGA was employed to quantify the weight percent (wt %) of the organic group in the functionalized CNTs. This technique gives a basic idea about the mass fraction of organic modifier that can be attached to the CNTs. The TGA results for pure and functionalized SWCNTs are shown in Figure 2.2.

Pure CNTs mass loss (1.7 wt %) indicates the presence of amorphous carbon and impurities (Figure 2.2). The mass loss of organic compounds was observed at 600°C. The shape of the curves for the acidified SWCNT in Figure 2.2 shows that there was a fast weight loss process ending at about 300ºC, followed by a slowly and continuous weight loss process that is active in the whole temperature range. Most of the graft COOH groups in the SWCNT were lost at about 300ºC and this was followed by a degradation of CNT promoted by the previous acidification treatment. The mass fraction of the organic groups eliminated at 600ºC was calculated. The amount of organic acid groups (-COOH) attached to the structure of the fillers is 8.6 wt%.

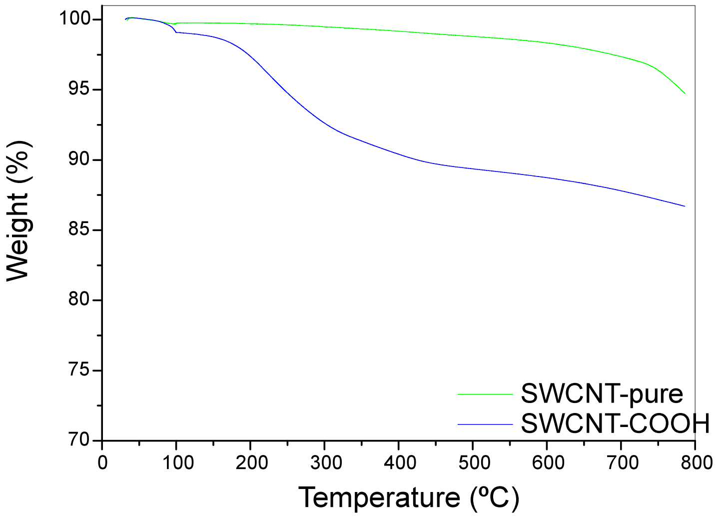

Figure 2.2: TGA result for pristine SWCNT and SWCNT-COOH

Scanning Electron Microscopy (SEM) was used to observe the morphology of SWCNTs before and after acidification. While the pristine SWCNT shows entangled structure and bundles, the oxidized SWCNTs (SWCNT-COOH) show less bundles and a less entangled structure (Figure 2.3).

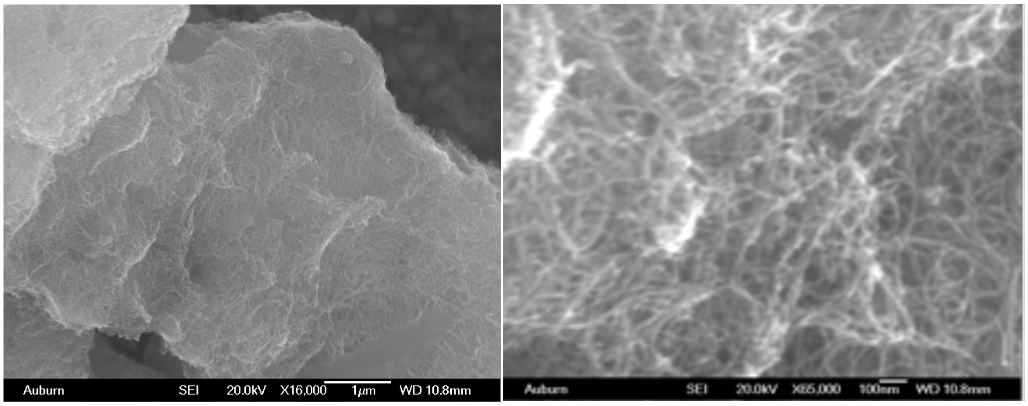

Figure 2.3: SEM images of a) Pristine SWCNT b) SWCNT-COOH

2.4 RESULTS and DISCUSSION

2.4.1 CNT/Matrix Dispersion

The final properties of polymer nanocomposites strongly depend on the dispersion of nanoparticles and the interaction between nanoparticles and the polymer matrix. Because of carbon nanotubes nanometric size and strong Van der Waals attraction between the tubes, efforts to enhance the mechanical properties of CNT-polymer nanocomposites have met with only modest success (Dyke et al. 2004). Therefore, CNTs stay together in the matrix which causes agglomeration. This agglomeration weakens structural integrity and the physical and mechanical properties of the composite.

To achieve a better dispersion, different methods were used in this work, such as mechanical dispersion methods (ultra-sonication and mixing) and surface modification methods which include oxidation of CNTs and non-ionic surfactant. During sonication, the agglomerated CNTs are mechanically separated. The use of surfactants lowers the surface tension of CNTs and this prevents the formation of aggregates (Geng et al. 2008). For both covalent functionalization and non-covalent modification, electrostatic repulsive forces are promoted. These repulsive forces help CNTs to overcome the Van der Waals attraction which is the mean reason for CNTs segregation and aggregation.

In order to obtain better understanding of structural characteristics of matrix/filler interaction such as the dispersion quality and filler alignment, rheological analysis is an effective tool. In this analysis, the rheological response of epoxy matrix without a curing agent can be characterized as a Newtonian liquid, thus, all of the viscoelastic and non-linear behaviors are caused by the addition of SWCNTs.

Effect of Dispersion Quality

The quality of dispersion determines how uniformly nanotubes are distributed in the suspension. A good dispersion of the tubes is particularly important for final properties. On the other hand, bad dispersion causes a phase separation due to the strong surface interactions between the tubes. Carbon nanotubes are present in the matrix in two forms: aggregated and separated nanotubes. Figure 2.4 shows a cartoon of the CNTs/epoxy suspension before and after an effective dispersion technique. Before an efficient dispersion technique is applied, the SWCNTs stay agglomerated forming bundles that act as spherical particles of considerable size and very low aspect ratio (micron size). The CNT network structure contains micro CNT aggregates connected by separated CNTs. After an effective dispersion technique, the fillers become better dispersed in the matrix. The entire tube interfacial area becomes effective transferring load between the filler and the matrix. Both of these CNT network structures exhibit distinct viscoelastic behavior, which can be observed as a Newtonian plateau of the storage modulus (G') developed at low frequencies during frequency sweep tests and considerable higher values of G' for the well dispersed sample.

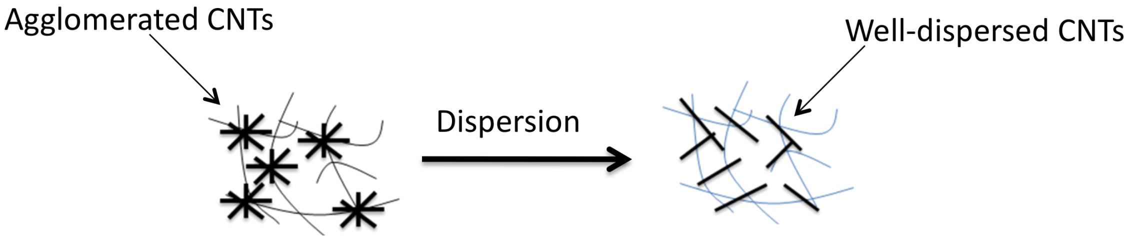

Figure 2.4: Effect of the dispersion quality on the SWCNT suspension

Effect of Functionalization

One way to accomplish uniform dispersion of nanotubes is to chemically modify the surface of the CNTs. Functionalized carbon nanotubes have the potential to form stable and uniform dispersions in organic solvents. Attached organic groups on the CNTs surface help the CNTs separate from each other and therefore improve the dispersion (Figure 2.5). Improved dispersion of CNTs and interfacial adhesion between CNTs and polymer matrices has been extensible reported in the literature (Zhu et al 2003, Koratkar et al. 2002).

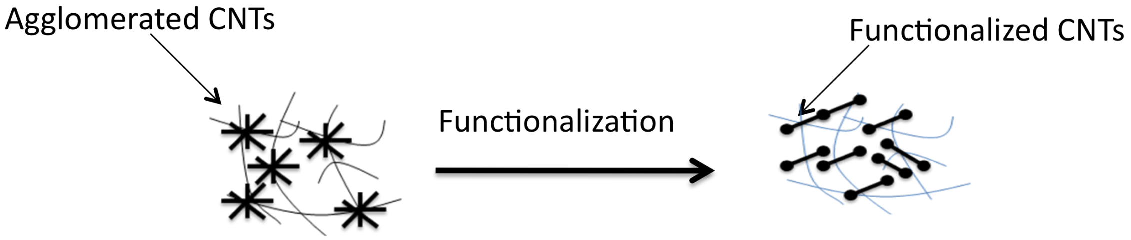

Figure 2.5: Effect of functionalization on the dispersion quality

Effect of Filler Concentration

The concentration of carbon nanotubes in a nanocomposite system is an important parameter which affects the processing and final properties of material. The quality and the degree of dispersion are also influenced by the concentration of the fillers. As concentration increases, the distance between SWCNTs will be smaller and there will be stronger entanglements and interaction between them. In general, two types of interactions are observed in nanocomposite systems which are filler-filler interactions and polymer-filler interaction (Kotsilkove et al. 2007).

At relatively low nanotube contents, clusters and individual flocks occur due to the ability of nanotubes to diffuse and stick together. Such structure can be defined as the first rheological threshold (flocculation) and the system behaves like viscous liquids with non-terminal zone behavior of viscoelasticity where G'<G''.

On the other hand, at high concentrations with a good dispersion, fillers show stronger inter-particle interactions due to shorter distances between individual fillers and flocks (Figure 2.6). These interactions increase the viscosity and present a high resistance to flow. After a critical concentration, these fillers form a 3D network characterized by a solid-like behavior where G' and G'' are independent against the frequency. This critical concentration where fillers form an interconnecting network is called the percolation, the second rheological threshold. After the percolation, viscosity, G' and G'' show a sharp increase (G'>G"). Percolation concentration is simply affected by the quality of the dispersion, the size of the fillers (aspect ratio) and the degree of alignment of the components. These ideas from the percolation theory are commonly applied to the properties of suspensions and composites of impenetrable particles. Equation 1 has been widely used in the literature to model the behavior of such systems (Du et al. 2004).

$$P \sim \left|\phi^{*} - \phi\right|^{\delta} \quad \text{Equation 1}$$

Where, ϕ is the volume fraction of the particles in the suspension, δ is the critical exponent, P is a property (i.e. electrical and thermal conductivity, shear modulus, dielectric constant, transport properties, such as the viscosity of fluid suspensions of rigid particles, etc) and ϕ^{*} is the threshold concentration.

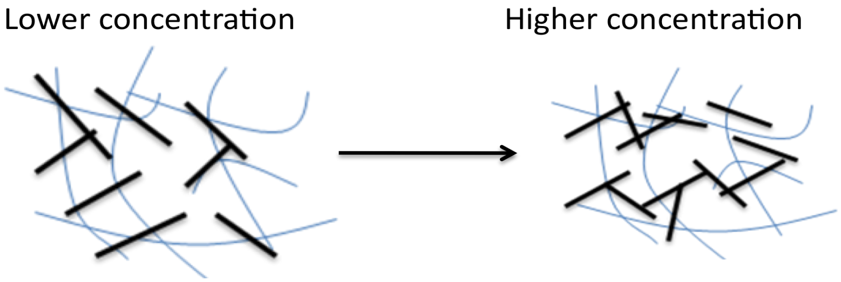

Figure 2.6: Effect of the SWCNT concentration on the dispersion quality

Effect of Aspect Ratio

The aspect ratio of CNTs is an important parameter which affects the rheological behavior of the suspension. High aspect ratio of CNTs is expected to increase the viscosity since the interaction between nanotubes increased. During the sonication process, nanotubes are fractionated, and the aspect ratio decreases (Figure 2.7). In order to evaluate the effect of CNTs aspect ratio, 2, 5, 10 and 30 min sonication times were used. SWCNTs were sonicated after dispersed in the solvent (THF).

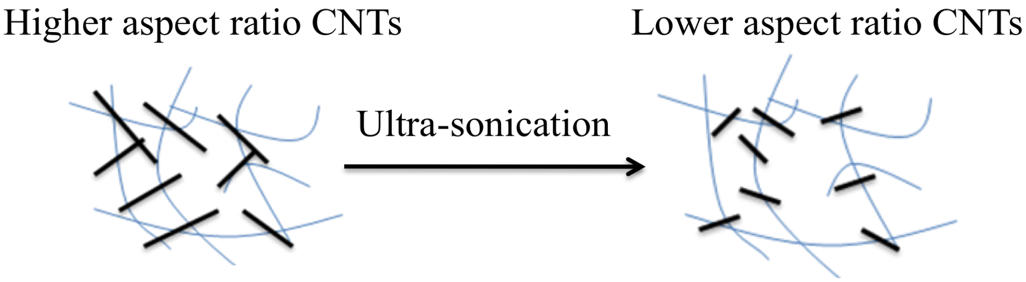

Figure 2.7: Effect of the aspect ratio on the dispersion quality

Effect of Orientation

The last approach of this chapter is the effect of the orientation of carbon nanotubes on the suspension behavior. In order to observe the orientation effect, CNTs/epoxy suspensions were pre-sheared. This pre-shear process orients the nanotubes in the shear direction (Figure 2.8). It is expected that oriented fillers have a lower viscosity than randomly dispersed suspension. This alignment usually aids to increase electrical conductivity or mechanical properties in the shear direction.

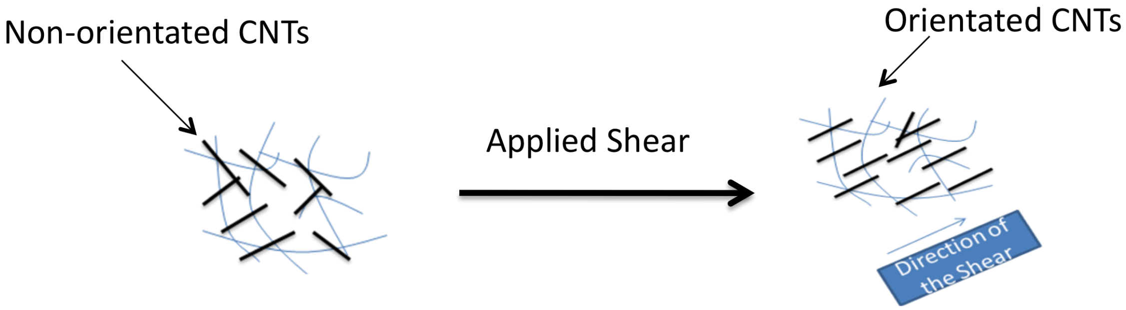

Figure 2.8: Effect of the pre-shear on the dispersion quality

2.4.2 Experimental Results

2.4.2.1 Effect of Dispersion Quality

Figure 2.9 shows the change of G' vs. frequency for the 1 wt% of pristine, surfactant assisted, and surfactant-sonication assisted SWCNTs/epoxy suspensions. This figure shows how a better dispersion of SWCNTs produces considerable changes in the storage modulus particularly at lower frequencies (terminal regime). The sonicated-surfactant assisted SWCNT suspension exhibited the higher dynamic and loss modulus. Table 2.1 shows the storage modulus (G') values at low frequency ($\omega = 0.01\ s^{-1}$). The lowest G' value was observed for pristine SWCNT, and the highest one was observed for the sonicated-surfactant assisted SWCNT.

Surfactants attached onto the SWCNTs surface providing repulsion forces which separated the SWCNT in the suspension. It also needs to be mentioned that using surfactants helps in avoiding the harmful effect of strong acids and long sonication time. It is also observed that sonication-surfactant assisted SWCNT behaved like a solid compared to the other dispersions, showing higher plateau at lower frequencies.

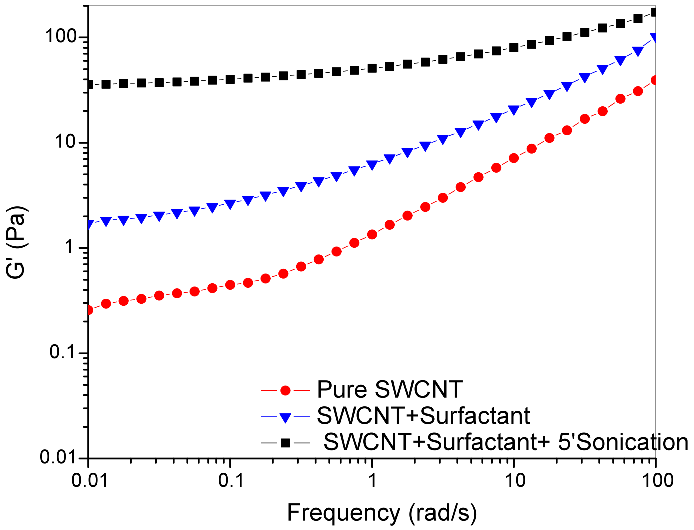

Figure 2.9: Change of G’ (Pa) with frequency for different SWCNT-epoxy suspensions

Table 2.1: G’ values at low angular frequency ($\omega = 0.01\ s^{-1}$)

The Type of the filler	**G’ (Pa)**
Pure SWCNT	0.3864
Surfactant-Assisted SWCNT	1.755
Sonication+Surfactant-Assisted SWCNT	38.86

2.4.2.2 Effect of Functionalization

Figure 2.10 shows the effect of the functionalization on the storage modulus (G’). Acidification increased the G’ since the organic acid groups attached onto the SWCNT surface provide a repulsion force between the CNTs which separate the SWCNT in the suspension. Table 2.2 shows the G’ values at low frequency and it indicates that the acidified SWCNT/epoxy suspension has higher G’ value than pure SWCNT, however this plateau is lower than surfactant-sonicated SWCNT/epoxy suspension.

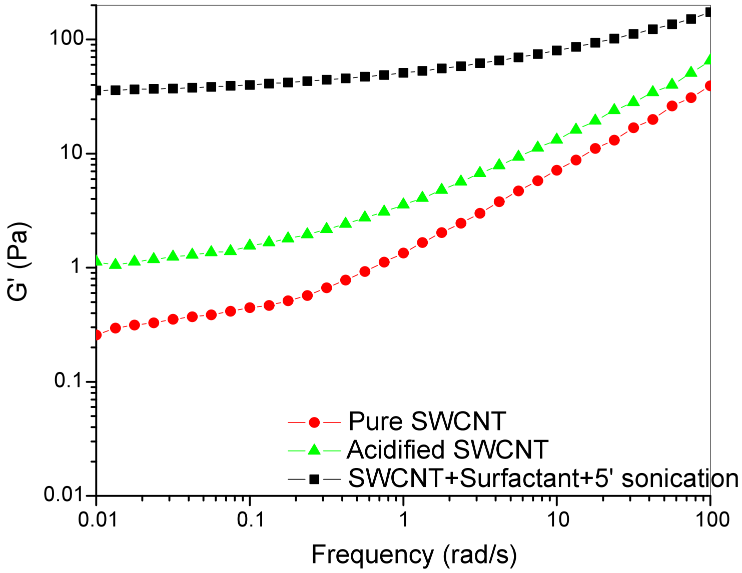

Figure 2.10: Change of G’ (Pa) with frequency for pure, acidified and surfactant plus sonicated SWCNT-epoxy suspensions (1wt %).

Table 2.2: G' values at low angular frequency ($\omega = 0.01\ s^{-1}$)

The Type of the filler (1 wt%)	**G' (Pa)**
Pure SWCNT	0.3864
Acidified SWCNT	1.357
Sonication+Surfactant-Assisted SWCNT	38.86

2.4.2.3 Effect of Concentration

Figure 2.11 shows the change of G' with the frequency at different concentration of SWCNT/epoxy samples prepared by the aid of surfactant. As the concentration is increased, the storage modulus increases due to the reducing mobility and the increased resistance to flow. From figure 2.11 is clear that after 0.5 wt% of SWCNTs a rubbery plateau is developed which indicates the formation of interconnecting network (change form a liquid to solid like behavior at low frequencies). The neat resin presents relaxed terminal behavior at low frequencies where G' is proportional to the square of frequency (ω^2). The addition of small amount of carbon nanotubes (more than 0.5wt %) makes a qualitative change in the liquid suspension and causes disappearing of the terminal behavior observed in the neat epoxy sample. At higher concentrations, the dependence of G' on frequency decreases until a plateau is clearly formed at low frequencies. The sudden change in G' indicates that the system has reached the rheological percolation. At high frequencies the effect of fillers on the rheological behavior is weaker and the structures break down into individual particles.

Figure 2.12 shows the storage modulus values at 0.01s^{-1} frequency for different concentrations. As it is mentioned before, the G' increased sharply after the system reached the percolation concentration (~ 0.5 wt %).

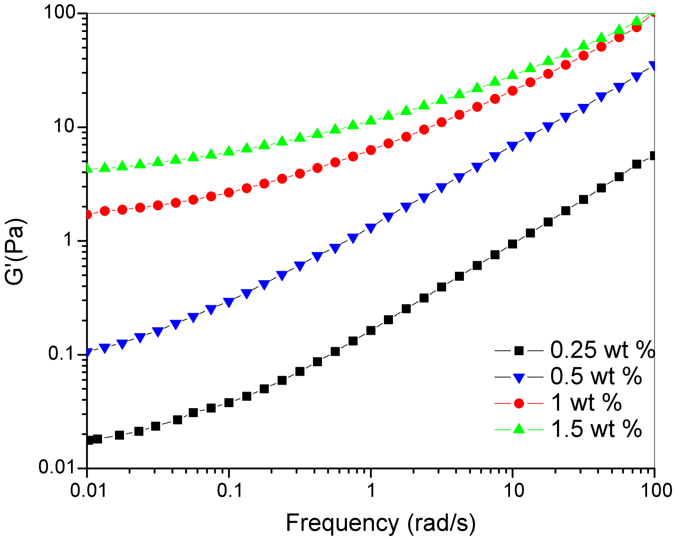

Figure 2.11: Change of G' (Pa) with frequency for different SWCNT concentrations

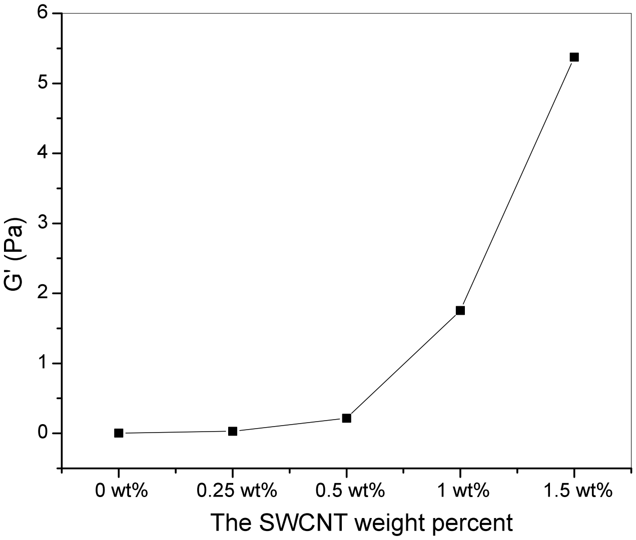

Figure 2.12: G' values at low frequency ($\omega = 0.01\ s^{-1}$) for different concentrations

Beside the change of G', complex modulus (G*) versus phase angle (δ) is also shown in Figure 2.13. This type of plot is called Van Gurp-Palmen plot (Meincke et al.2004). According to this, the pure epoxy, which shows Newtonian liquid behavior, is expected to be completely out of phase (δ = 90º). For the different concentration of SWCNT suspension, it is expected to observe viscoelastic behavior in which the phase angle is nearly 90º at high frequencies but decreases at lower frequencies with the concentration of filler. The Van Gurp-Palmen plot does not clearly differentiate between liquid viscoelastic and solid viscoelastic behavior; however, it gives idea about the range of the concentration where the change occurs (Marcovich et al. 2006). From this picture it is observed that the system change from a liquid (δ ~ 90º) to a solid (δ ~ 0º) behavior at approximately 0.5 wt% of SWCNTs.

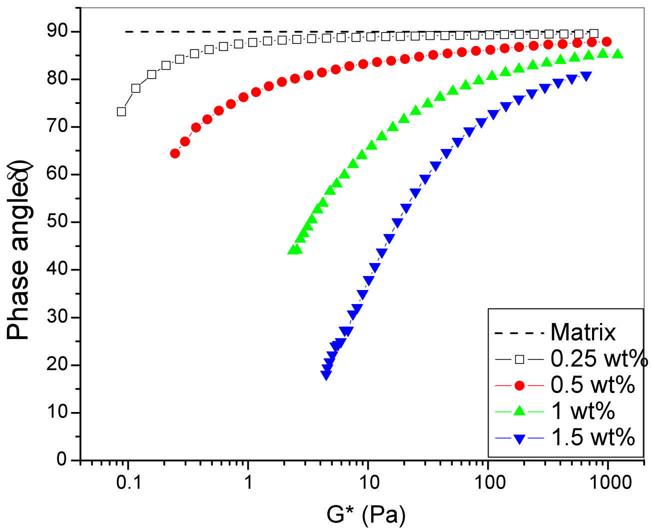

Figure 2.13: Van Gurp-Palmen plot for different concentration of SWCNTs

The figure 2.14 shows the complex viscosity at different concentration of SWCNT. As the concentration increases, the mobility is reduced and the suspension's resistance to flow is increased as well. For higher concentrations beyond the threshold, it is observed that complex viscosity increased sharply at low frequencies. It is also found that at low concentrations below threshold, the suspension behaved more like a simple dispersion system where the nanofiller interaction can be almost neglected.

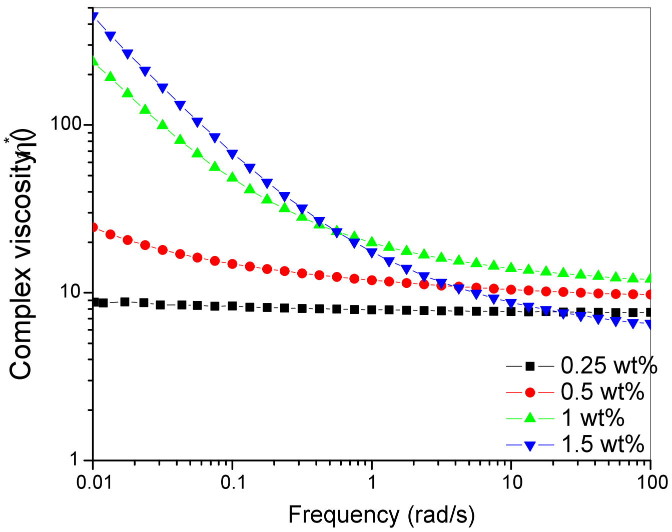

Figure 2.14: Change of complex viscosity for different SWCNTs concentration

2.4.2.4 Effect of Aspect Ratio and Concentration

By changing the sonication time, the effect of carbon nanotubes aspect ratio is evaluated. The sonication process aid to the dispersion of the tubes and also shortens the carbon nanotubes. In this study, surfactant assisted SWCNT/epoxy suspensions with different amounts of CNTs concentrations (0.25, 0.5, 1, 1.5 wt %) were sonicated for different periods of time (2, 5, 10, 30 min.).

According to the Figure 2.15, the storage modulus (G') was increased as the sonication time is increased. For the sample with 1wt% of SWCNT, at 5 min., the storage modulus reaches the highest value. Our hypothesis is that the sonication helps to separate the CNT aggregates into single tubes. It is also expected that the suspension without sonication present considerable amount of aggregates. However after 5 min. sonication, G' started to decrease. The reason is that the entanglement of CNTs was separated using longer sonication time which caused weaker interconnection between the carbon nanotubes and a possible decrease at the aspect ratio. The same results were observed for the complex viscosity (η*) at the same frequency range. It means that both G' and η* are sensitive to CNT aspect ratio (Figure 2.16).

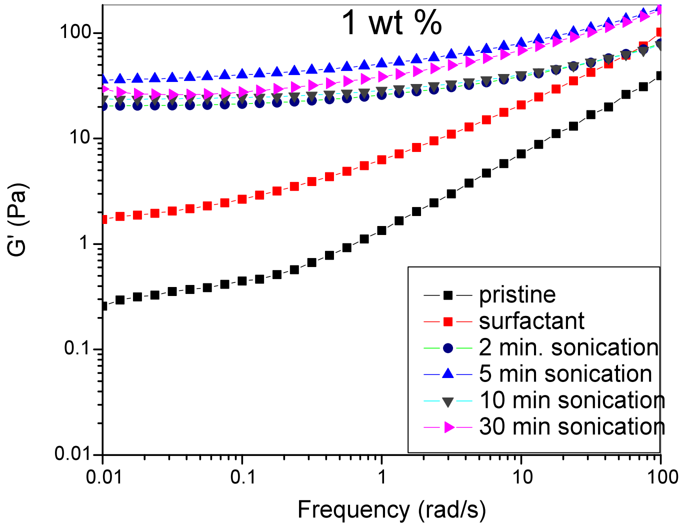

Figure 2.15: Effect of the sonication time on the storage modulus (G') of 1 wt% SWCNT surfactant-epoxy suspension

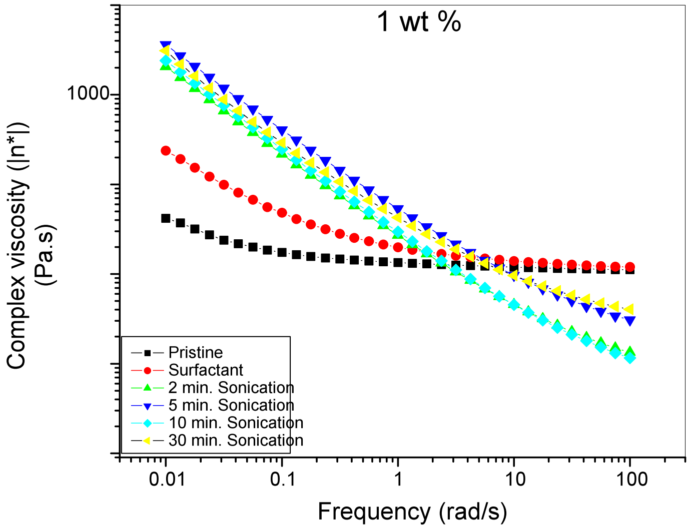

Figure 2.16 Effect of the sonication time on the complex viscosity of 1 wt% SWCNT surfactant-epoxy suspension

The same procedure was followed for 0.25, 0.5 and 1.5 wt % surfactant assisted SWCNT suspensions with different sonication times. The results are shown in Figures 2.17, 2.18 and 2.19, respectively. It is observed that as the concentration increased, the ultimate sonication time, where the SWCNTs still have a good interconnection, increased. It is clear that at high concentrations, the SWCNTs are closer to each other and more bundles occurred. Therefore, in order to separate the SWCNTs and build a good network take more sonication time for higher concentrations.

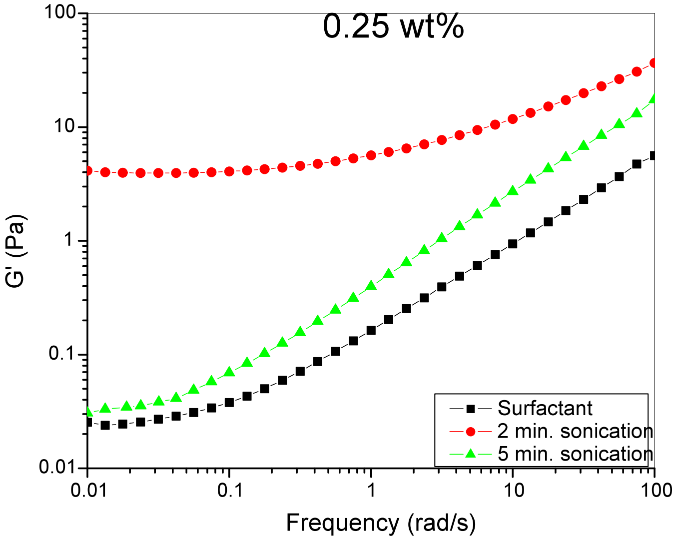

Figure 2.17: Effect of the sonication time at 0.25 wt% surfactant-assisted SWCNT epoxy suspension

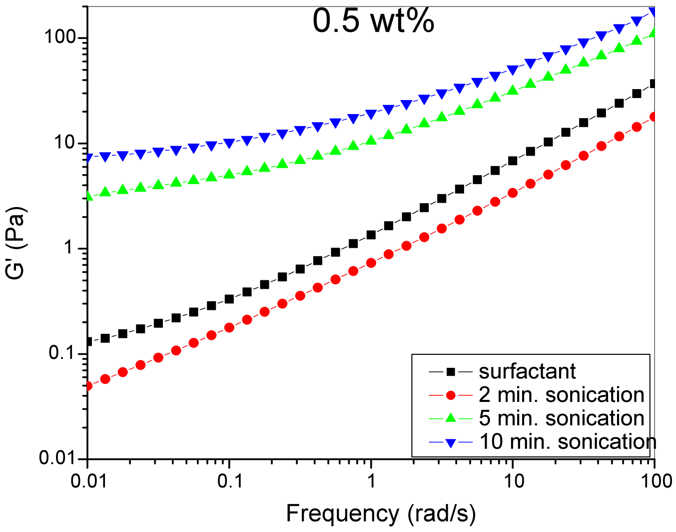

Figure 2.18: Effect of the sonication time at 0.5 wt% Surfactant-assisted SWCNT epoxy suspension

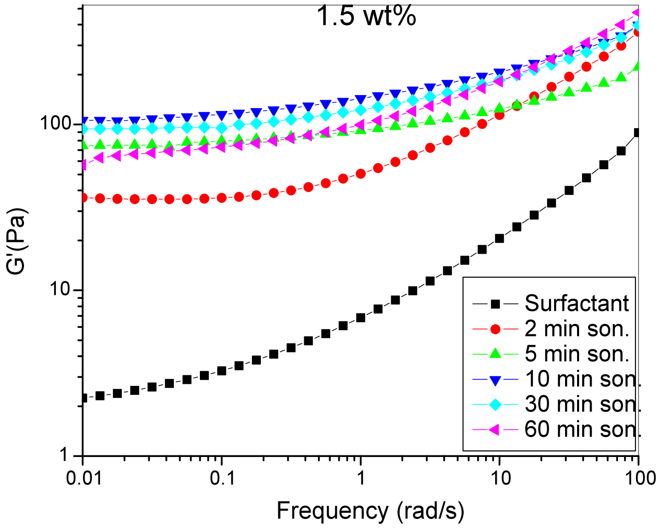

Figure 2.19: Effect of the sonication time at 1.5 wt% Surfactant-assisted SWCNT epoxy suspension

In addition, Figure 2.20 shows the change in the storage modulus at low concentration with different sonication times for each weight fraction of SWCNTs.

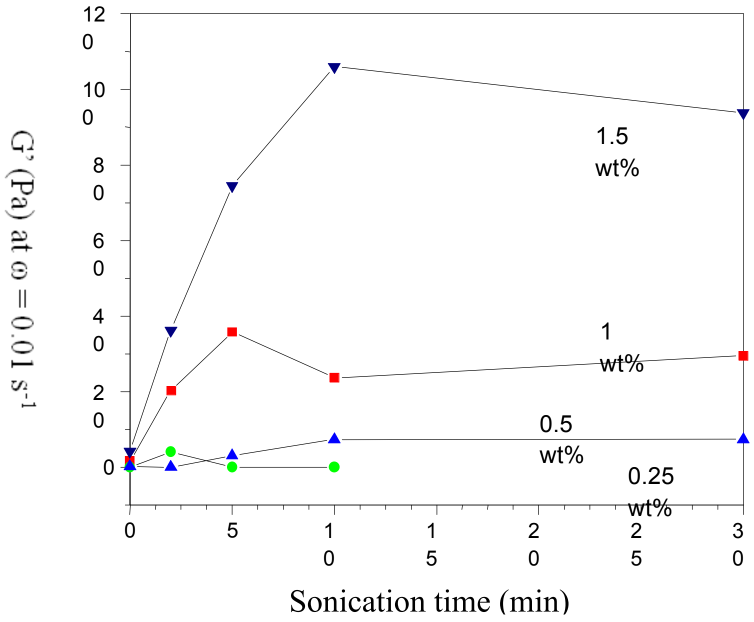

Figure 2.20: Storage modulus at low frequency versus sonication time for different concentration of surfactant assisted SWCNT-epoxy suspension

Analytical Model

An analytical model was used to estimate the aspect ratio of the SWCNTs in the epoxy suspension. Aspect ratio and volume fraction of non-spherical particles are considered by many simple models for describing the viscosity of particle in a suspension. Einstein was the first in develop one of the simplest model to describe this behavior (Einstein 1956). Einstein models take into account the hydrodynamic effects of the particles on the flow field. The mathematic equation that respects this model is showed in equation 2.

$$\eta/\eta_m = 1 + 0.67\phi f + 1.62 \phi^2 f^2 \quad \text{Equation 2}$$

where η is the viscosity of the suspension, η_m is the viscosity of the matrix, ϕ is the volume fraction of the particles, and *f* is the aspect ratio of the filler (length/diameter). (Volume fraction of the SWCNT was calculated by using the nanotube density 1.1 g/ml)

Based on the Figure 2.21, the experimental data and analytical model show good agreement using aspect ratio between 75 and 100. These values are consistent with observations of the SWCNTs after they were broken up by the 10 min sonication. These values are consistent with data reported in the literature (M.D Frogley et al. 2003)

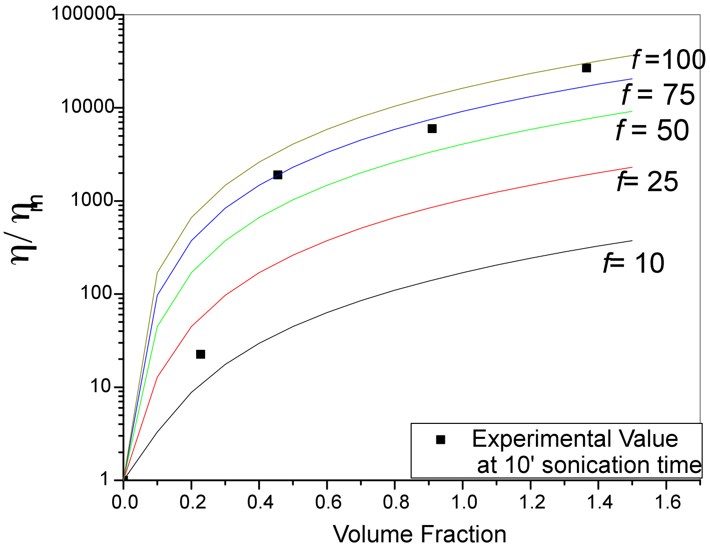

Figure 2.21: Initial dynamic viscosity of the suspension as a function of SWNCT volume fraction. (The solid curves are the analytical results with different aspect ratios (*f*).)

2.4.2.5 Effect of Orientation

The use of high shear flow aligns the nanotubes in the shear direction and this aligned suspension shows a lower viscosity than randomly orientated suspension because the resistance to flow decreases with the orientation of the filler. In addition, high shear flows may break down the 3D network formed by the filler and decrease the viscosity. In order to study the effect of the orientation, all samples were tested before and after being shear at a shear rate of $20\ s^{-1}$ for 30 min.

Figures 2.23, 2.24 and 2.25 show the behavior of the 1 wt% of SWCNTs/epoxy suspensions before and after shear flow. It is observed that G' decreased after the shear flow for acidified SWNCT, surfactant-assisted SWCNT and 5min sonicated surfactant-assisted SWCNT.

The reason is that the shear flow provided an alignment for CNTs and this makes the interconnection weaker. The difference for sonicated sample was considerable because the sonication separates the nanotubes and the shear process increased the orientation more than the other samples. On the other hand, for pure SWCNT, G' increased after the shear flow compared to the no shear (Figure 2.22). Since the amount of the SWCNT bundles is higher for pure SWCNT system, the shear flow process possible helped to disentangle the flocculated bundles of nanotubes that exist for the pristine samples.

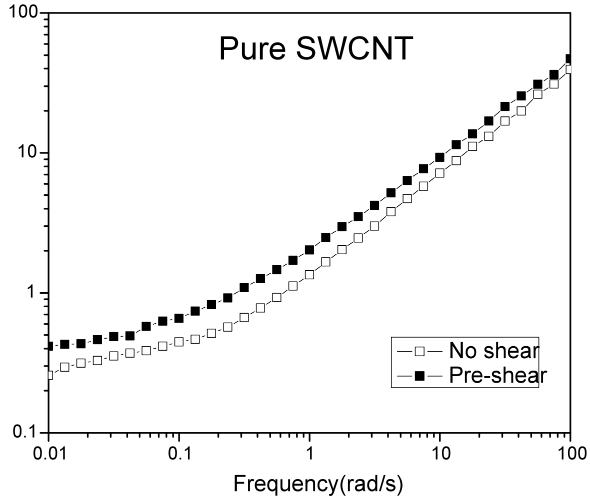

Figure 2.22: Effect of orientation on G’ for pure SWCNT suspensions

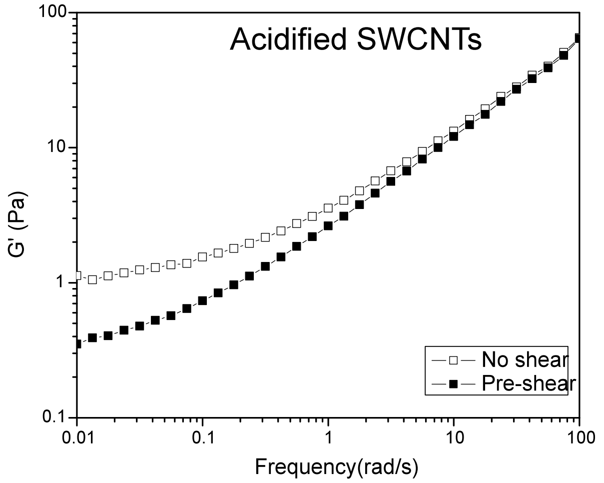

Figure 2.23: Effect of orientation on G’ for acidified SWCNT suspensions

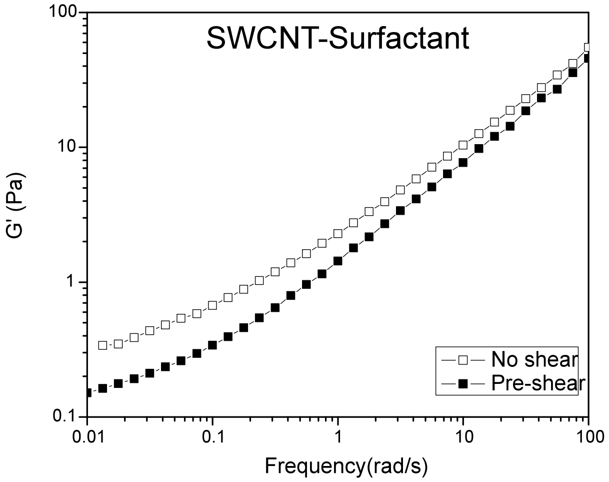

Figure 2.24: Effect of orientation on G’ for SWCNT-Surfactant suspensions

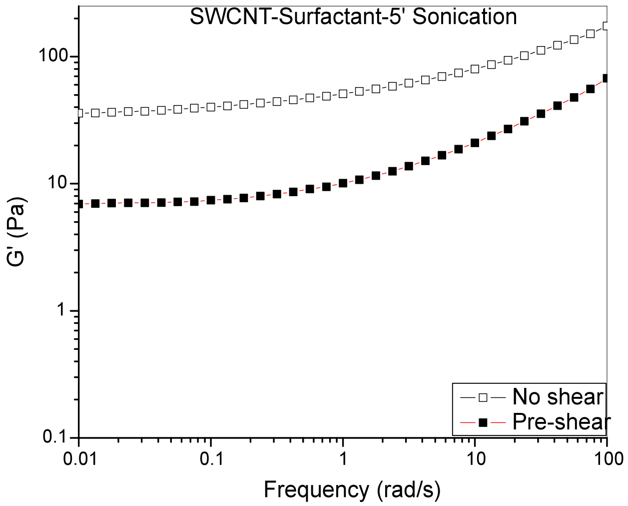

Figure 2.25: Effect of orientation on G’ for 5 min sonicated SWCNT-Surfactant suspensions

2.5 CONCLUSION

In this chapter, the dispersion quality of the different SWCNT/epoxy suspensions was discussed. The effect of the SWCNT modification on dispersion quality was examined. The amount of the organic groups attached onto the SWCNT after the acid functionalization was observed with TGA experiment and it is found that 8.6 wt% acid groups were attached onto the SWCNT.

In addition, the effect of different sonication time, SWCNT concentration, and nanotube orientation were studied using rheological experiments. The highest storage modulus (G') value was observed for sonicated-surfactant assisted SWCNT suspension. It was observed that as the nanotube concentration increased, the suspension showed a noticeable transition between a liquid to solid like behavior. The percolated threshold concentration was estimated to be approximately at 0.5 wt% of SWCNTs, where G', G" and viscosity increased dramatically.

It is also observed that the G' value increased as the sonication time increased. For 1 wt% SWCNT suspension, the highest G' was found at 5 min sonication time. It was noted that for 1 wt% SWCNT after 5 min sonication time, the SWCNTs built a good 3-D network. However at longer sonication time storage modulus (G') started to decrease. The reason is that the entanglement of CNTs were separated by the longer sonication time and causing weaker interconnection between the carbon nanotubes. Therefore, in order to separate the SWCNTs and build a good network longer sonication times are required for higher concentrations.

The effect of the orientation was also discussed. The orientation of SWCNTs in the suspension decreased the resistance to flow and thus decreased the storage modulus were found.

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CHAPTER 3

MECHANICAL AND THERMAL PROPERTIES OF SWCNT/EPOXY COMPOSITES

3.1 INTRODUCTION

Carbon nanotubes have been attractive for reinforcement in composite materials due to their high aspect ratio, fiber-like structure, low density, and extraordinary mechanical and barrier properties (Cantournet et al. 2007, Jonathan et al. 2006). Particularly, carbon nanotubes and carbon nanofibers have shown to have a unique combination of high modulus (640 GPa to 1 TPa) and strength (150-180 GPa) (Krishnan et al. 1998). These fillers offer the possibility of enhancing thermal, electrical, damping and mechanical properties with relatively lower amounts (1-5wt %) and with minimal degradation of the original systems (Schadler et al. 1998). Zhu et al. have shown that using of 1 wt% of SWCNT the Young's modulus of epoxies was increased up to 30% and the tensile strength up to 18% (Zhu et al 2003). They are excellent candidates to substitute or complement the conventional fillers in the fabrication of multifunctional polymer composites.

At present, it is well recognized that to maximize the final performance of these materials, uniform dispersion of CNTs in polymeric system and good interfacial adhesion are two critical issues during the fabrication of CNT-polymer nanocomposites. (Song et al. 2005)

Dispersion is the key issue in nanocomposite fabrication. The high surface area of nanotubes is an advantage for load transfer; however it also induces strong attractive forces between the tubes that cause agglomeration which causes bad dispersion (Penumadu et al. 2003). Various dispersion methods (sonication, intensive shear mixing, aid of surfactants, and covalent functionalization) were reported to provide better dispersion and separate the agglomerated bundles into individual tubes.

Another challenge for SWCNT/polymer composites is the interfacial adhesion between the CNTs and the matrix. In order to provide an efficient structural reinforcement with CNTs, an effective stress transfer from matrix to the tubes is required. The interfacial bonding between CNTs and matrix can be improved by chemical functionalization of CNTs. The covalent bond between the polymer and the nanotubes improves the interfacial stress transfer and also provides better dispersion as mentioned before.

The aim of this chapter is to compare the influence of different dispersion techniques and different concentrations of SWCNTs on the mechanical and thermo-mechanical properties of epoxy-based nanocomposites. Sonication plus surfactant modification and acid functionalization were used in order to achieve better dispersion and improve the stress transfer mechanism between the epoxy matrix and SWCNTs. Simple theoretical model where use in order to study the effect of the carbon nanotubes concentration and aspect ratio on the final modulus of the composite.

3.2 MATERIALS

The SWCNTs were purchased from Shenzen Nanotech Port. Co. Ltd., China. The diameter range for the CVD grown SWCNTs was < 2 nm; the length range was 5-15 μm; the purity of CNTs was > 90 %.

A diglycidyle ether of bisphenol A epoxy (DGEBA, EPON 828 Miller-Stephenson Chemical Co. Inc.) was used as a matrix and a polyether triamine (Jeffamine T-403, Huntsman) with a molecular weight of 440 was used as hardener. The cured product had a glass transition temperature located above room temperature.

Non-ionic surfactant, polyoxyethylene octyl phenyl ether (Triton X-100) was used as a surfactant agent. Tetrahydrofuran (THF), sulfuric acid (H_2SO_4), nitric acid (HNO_3) and hydrochloric acid (HCl) were purchased from Fisher Scientific. All the materials were used as received.

Composite Preparation

Epoxy nanocomposites were prepared with 0.25, 0.5 and 1 wt% of surfactant assisted SWCNT; additionally samples with 1 wt% of SWCNT-COOH and 1 wt% pure SWCNT were also prepared. The corresponding amount of modified SWCNTs was dispersed in THF by mixing one week. After one week, epoxy resin was added into the mixture and mixed two hours. Finally, THF was evaporated at $50^{o}C$ in a vacuum oven overnight. The corresponding hardener, Jeffamine T-403 was added to the mixture at an epoxy/hardener weight ratio of 100/42. Further mixing (5 minutes) and degasification (15 minutes) were performed. The blend was cast into Teflon mold. The curing cycle was 3 hours at $80^{o}C$, followed by another 3 hours at $125^{o}C$.

3.3 TECHNIQUES

3.3.1 Flexural Experiment

The mechanical properties of different type of SWCNT epoxy nanocomposites were evaluated. Samples were tested with 3-point bending using a dynamic mechanical analysis machine,(RSA3, TA Instruments) tool and the flexural modulus was calculated by using equation of $E = ((L^3 \times m) / (4 \times b \times d^3))$ (ASTM D790M) where E is the modulus of elasticity in bending (MPa), L is the support span length which is 10mm in this study, b is the width of the beam tested (mm) and m is the slope of the tangent to the initial straight-line portion of the load-deflection curve (N/mm of deflection).

3.3.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (RSA3 TA instruments) was carried out to assess the storage modulus (E'), loss modulus (E'') and tan delta (δ) of CNTs-epoxy composites. Epoxy/T-403 samples were performed with 3-point bending fixture. For the T-403 samples, the dynamic temperature ramp test was performed at 0.1% strain at a frequency of 1Hz from 25°C to160°C with a heating rate of 5°C/min.

3.4 RESULT and DISCUSSION

3.4.1 Mechanical Properties

Table 3.1 summarizes the effect of the SWCNT dispersion on the flexural modulus of the epoxy nanocomposites. The neat epoxy matrix that was used in this study exhibited a flexural modulus of 2.2 GPa. It is observed that the addition of pristine SWCNT increased (15 % increase) the modulus of the composite under the given processing conditions. Moreover, the addition of acid functionalized SWCNTs increased modulus 20 %. It is clear that the acid groups located on the surface of SWCNT aid in dispersion and the filler. In addition they could react with the epoxy matrix as reported by other authors (Chen et al. 2006) and form covalent bond with epoxy, thus, inducing the interfacial adhesion. In addition, surfactant assisted SWCNT/epoxy systems (without sonication) has flexural modulus higher than pristine SWCNT system. The surfactant provides better dispersion of SWCNTs in the epoxy matrix which activates effective mechanisms of load transfer. It is also noted that surfactant plus sonication assisted SWCNT samples have the highest flexural modulus (48% increase compared to the matrix). Sonication process aids to separate the bundles of SWNCT providing better dispersion. As it is reported in the previous chapter, the surfactant plus sonication assisted SWCNT samples showed the highest storage modulus (G') that indicates a better degree of dispersion compared to the other systems.

Table 3.1: Properties of neat epoxy resin and nanocomposites for different systems of 1 wt% of SWCNTs

Filler	**Flexural Modulus (GPa)**	**% improvement**
Matrix	2.2 ± 0.289	-
Pristine SWCNT	2.53 ± 0.105	15
Acidified SWCNT	2.62 ± 0.074	19
SWCNT-Surfactant	3.05 ± 0.102	39
SWCNT Surfactant-sonication	3.26 ± 0.135	48

Table 3.2 shows the effect of carbon nanotubes concentration on the mechanical properties of SWCNT epoxy system. The sample modulus increased with increasing filler content. The addition of 1 wt% SWCNT produced a 50% increase in the flexural modulus with respect to the neat system

.

Table 3.2: Properties of neat epoxy resin and nanocomposites for different SWCNT concentration

The amount of SWCNT Plus surfactant (wt %)	**Flexural Modulus (GPa)**	**% Improvement**
0	2.2 ± 0.289	-
0.25	2.71 ± 0.013	23
0.5	2.83 ±0.013	29
1	3.26 ± 0.135	48

Mechanical Model:

One of the simplest mechanical models commonly used for filled polymer is the modified Halpin-Tsai theory (Agarwal et al.1980, Chen et al 2009). The Halpin–Tsai equations are a set of empirical relationships that enable the property of a composite material to be expressed in terms of the properties of the matrix and filler together with their proportions and geometry (Kim et al. 2009). For low loadings of rod-like fillers which are much stiffer than the matrix, it reduces to;

$E_{long} = E_m ((1+2f\xi V_f)/(1-\xi V_f))$ Equation 3.1

$E_{trans} = E_m ((1+2f\zeta V_f)/(1-\zeta V_f))$ Equation 3.2

$\xi = ((E_f /E_m)-1)/(E_f/E_m+2f)$ Equation 3.3

$\zeta = ((E_f /E_m)-1)/(E_f/E_m+2)$ Equation 3.4

$E_c = 3/8\ E_{long} + 5/8E_{trans}$ Equation 3.5

where E_{long} and E_{trans} are the longitudinal stiffness and transverse stiffness of the composite, respectively. V_f and f are the volume fraction and aspect ratio of the nanotubes, respectively and E_c is the stiffness of the composite which fibers are randomly oriented in three dimensions. The model was developed for short fiber composites and considers that there is no interaction between the fibers (Frogley et al. 2002).Furthermore, Radosta suggested that this equations are versatile enough to be used also for flexural modulus (Radosta, 1975,Nielsen 1970).

All results were also compared to Reuss and Voight model (Bhagwan et al. 2006, Tibbettsa et al. 1999) where;

$E_{long} = E_f V_f + E_m V_m$ (Reuss model) Equation 3.6

$1/E_{trans} = V_f/E_f + V_m/E_m$ (Voight model) Equation 3.7

Figure 3.1 shows the experimental and analytical results for SWCNT-epoxy system with different SWCNT aspect ratios. Each experimental point represents the average of five test values. The predicted composite modulus based on Halpin-Tsai micromechanics were compared with the experimental values of the SWCNT-epoxy composites. For these calculations, a modulus of 1 TPa and aspect ratio of 100, 75 and 50 were assumed and the flexural modulus for epoxy matrix was taken as 2.2 GPa. Reuss and Voight models (equation 3.6 and equation 3.7 respectively) gave us the upper and lower boundaries of the mechanical properties of nanocomposites.

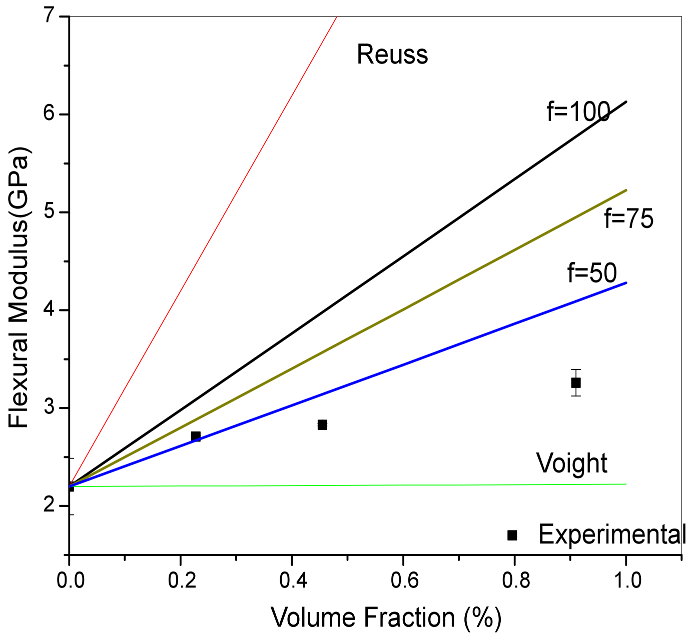

Figure 3.1: The comparison of experimental and analytical results for flexural modulus of SWCNT-epoxy system

3.4.2 Thermo-mechanical Properties

The viscoelastic behavior of SWCNT-epoxy nanocomposites was explained with DMA technique. In DMA technique the linearized stress-strain relation can be expressed as σ = (E' + jE")ε where the E' is the in-phase component which determines the storage or elastic modulus and E'' is the out-phase component which shows the loss modulus. In this study, the effect of temperature on dynamic-mechanical properties is summarized on Table 3.3 and can be visualized in Figure 3.2 for different SWCNT epoxy systems. In Figure 3.2, it was observed that at the glassy state (below the glass transition of the composite), surfactant plus sonication assisted SWCNTs system has the highest storage modulus (E'). At room temperature, the storage modulus of the matrix increased 249 % after adding surfactant plus sonication assisted SWCNTs. Moreover, adding pure SWCNTs and acidified SWCNTs increased the storage modulus of the matrix. It is also noted that the elastic properties of the epoxy system was improved at elevated temperatures. This behavior can be explained in terms of an interaction between the CNTs and the epoxy due to the high surface area. The interfacial interaction between the CNTs and epoxy reduces the mobility of the epoxy matrix around the nanotubes and leads to the observed increase in thermal stability.

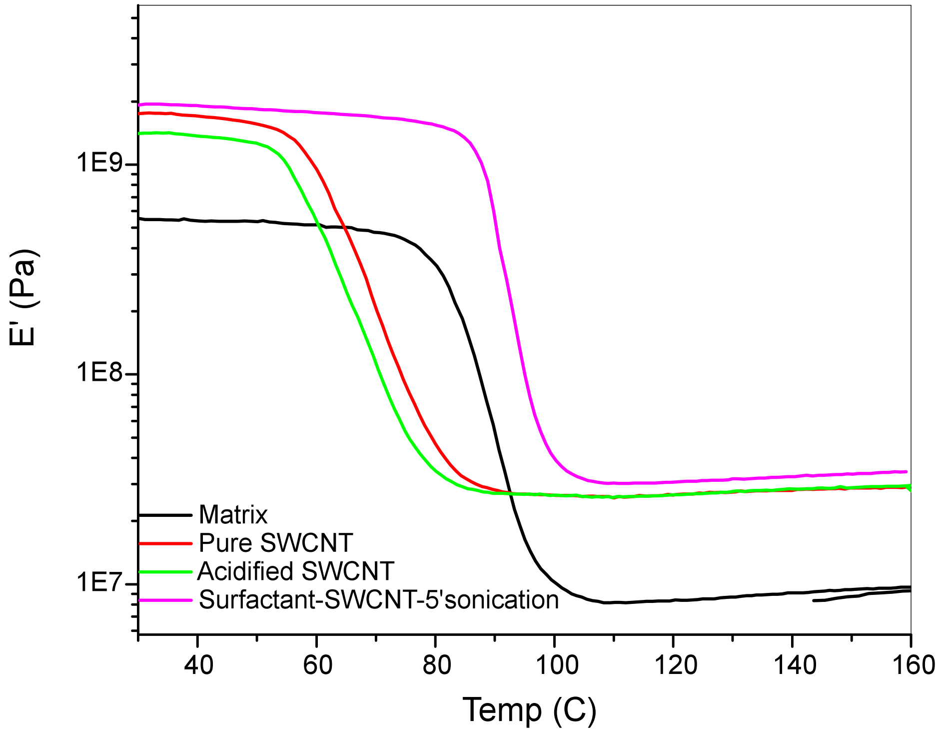

Figure 3.2 Storage modulus (E') vs. temperature for different SWCNT-epoxy system

Figure 3.3 shows that the T_g of the SWCNTs/epoxy resins nanocomposite increases 4°C and the width of tan δ peaks becomes broader, with the presence of SWCNT. The increased T_g and broadened loss peak observed in polymer nanocomposites could been attributed to the constraint effect of nanoparticles on the segmental motion of polymers. Similar results were observed by Goh et al. (Goh et al. 2003). According to the coupling model theory suggested by Ngai et al. as the more segments are restricted due to the presence of nanofiller, the activation threshold for the motion of some segments becomes higher. (Ngai et al. 1996). As a consequence, the glass transition trends to become wider with increasing restriction effect.

For pristine and acidified SWCNT systems, a decrease in T_g was observed. It could be due to possible partitioning mechanism of the monomers at the interphase of the epoxy-filler.

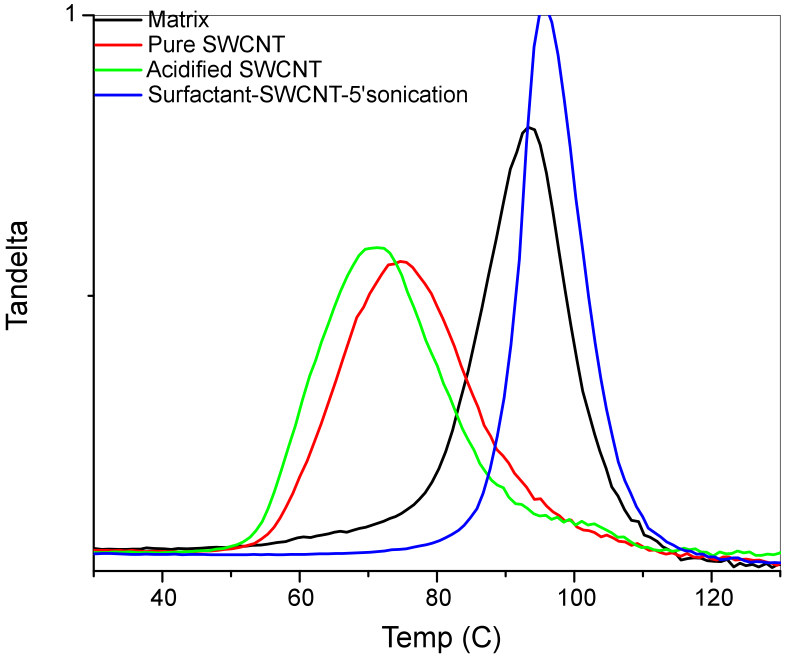

Figure 3.3 Tandelta vs. temperature for different SWCNT-epoxy system

Table 3.3 Properties of neat epoxy resin and nanocomposites

Type of composite (1 wt%)	**E' (GPa) at 30° C**	**E' (GPa) at 150° C**	**T_g (C°)**
Matrix	0.55	0.009	94
Pure SWCNT/Epoxy	1.75	0.028	75
Acidified SWCNT/Epoxy	1.4	0.028	71
Surfactant+ Sonication/Epoxy	1.92	0.035	97

3.5 CONCLUSION

In this chapter, the mechanical and thermo-mechanical properties of SWCNT epoxy nanocomposites were investigated. When carbon nanotubes are properly dispersed in the matrix, carbon nanotube reinforcement influenced properties of the matrix. It was observed that sonication plus surfactant assisted SWCNT epoxy system has the highest flexural modulus. It was also reported in chapter 2 that this system has better dispersion quality compared to the other systems. Furthermore, the effect of the concentration on the flexural modulus was analyzed and it was noted that as the concentration increases, the flexural modulus of the composite system increases. The experimental results were also compared with the analytical results. It was noted that the experimental results were between the upper and lower boundaries results which were derived from Reuss and Voight model.

In addition, the mechanical and thermo-mechanical properties of SWCNT-epoxy system were studied. It was concluded that well dispersed SWNCTs into the epoxy system increased the storage modulus and the glass transition of the matrix.

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CHAPTER 4

CONCLUSION

Using a combination of techniques (microscopy, thermal gravimetric analysis, rheology and dynamic mechanical analysis), an attempt was made to characterize single wall carbon nanotube/epoxy systems. The aim of this research was to understand the effect of the dispersion quality on the final properties (mechanical and thermo-mechanical) of single wall carbon nanotube/epoxy composites.

Several dispersion techniques were chosen such as oxidation of CNTs, surfactant assisted systems and ultra sonication. The quality of the dispersion was evaluated through rheological studies. The highest storage modulus (G') value, which indicates better dispersion, was observed for sonicated-surfactant assisted SWCNT suspension.

The effect of carbon nanotubes concentration on the final dispersion was also studied. It was observed that as the carbon nanotube concentration increased, the suspension showed a noticeable transition between a liquid-like to solid-like behavior (percolation concentration). The percolated threshold concentration was estimated to be approximately at 0.5 wt% of SWCNTs, where the storage (G') and loss (G") modulus and the viscosity increased several orders of magnitude compared to the unreinforced system.

It was also observed that the sonication time produced considerable effect on the final dispersion of the fillers. The G' value increased as the sonication time increased indicating a better disentanglement of the SWCNTs bundles. However at longer sonication time storage modulus (G') decrease causing weaker interconnection between the carbon nanotubes and possible degradation of the final structures. The effect of the orientation on the storage modulus was also discussed. The orientation of SWCNTs in the suspension decreased the resistance to flow and thus decreased the storage modulus of the suspensions.

Finally, the mechanical and thermo-mechanical properties of SWCNT epoxy nanocomposites were investigated. It was observed that the highest flexural modulus was obtained for sonication plus surfactant assisted SWCNT epoxy system which has better dispersion quality compared to the other systems. Furthermore, the effect of the concentration on the flexural modulus was analyzed and it was noted that as the concentration increases, the flexural modulus of the composite system increases. The experimental results were also compared with analytical results. It was noted that the experimental results were between the upper and lower boundaries results which were derived from Reuss and Voight model. The thermo-mechanical properties of SWCNT-epoxy system were also studied. It was concluded that the addition of sonicated SWNCTs into the epoxy system increased the storage modulus and glass transition of the matrix. These effects were produced by the restrictions introduced by the stiff tubes in the local motion of the matrix.