

**IMPROVEMENT IN THE MECHANICAL PROPERTIES OF
B-STAGED CARBON NANOTUBE/EPOXY BASED THIN FILM
SYSTEMS**

A Senior Scholars Thesis

by

KEVIN LEE WHITE

Submitted to the Office of Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

April 2009

Major: Mechanical Engineering

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Approved by:

Research Advisor:
Associate Dean for Undergraduate Research:

Hung Jue Sue
Robert C. Webb

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ABSTRACT

Improvement in the Mechanical Properties of B-staged Carbon Nanotube/Epoxy Based
Thin Film Systems. (April 2009)

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Polymeric systems have been the subject of tremendous interest to the aerospace industry due to their high strength per weight ratio but have not seen the use projected due to their poor compression after impact strength, fracture toughness, and electrical conductivity. This work has focused on the integration of single walled carbon nanotubes (SWCNTs) into polymeric systems to serve as interleaves to improve the mechanical properties of carbon fiber panels. Pristine, oxidized, and functionalized carbon nanotubes were produced and cast into B-staged (50% cured) thin film epoxy resin systems. Mechanical characterizations were carried out on bulk samples and showed that the introduction of well dispersed SWCNTs functionalized with sulfanilamide improved the Young's modulus of the neat epoxy by 16%, the tensile strength by 47%, the elongation at break by 157%, and the fracture toughness, as determined by K_{IC} , by 10%. Nylon was introduced into the system as a toughening agent at 10 wt% and showed an 8% increase in the Young's modulus, a 29% increase in

tensile strength, a 183% increase in elongation at break, and a 44% increase in fracture toughness. These composite films were successfully transferred into a carbon fiber interleave using Vacuum Assisted Resin Transfer Molding (VARTM).

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NOMENCLATURE

CAI	Compression After Impact
DGEBA	Diglycidyl Ether of Bisphenol A
DSC	Digital Scanning Calorimetry
DWCNT	Double-walled Carbon Nanotube
K_{IC}	Mode-I Critical Stress Intensity Factor
MWCNT	Multi-walled Carbon Nanotube
PAMAM-G0	Polyamidoamine Generation 0
SAA	Sulfanilamide
SEM	Scanning Electron Microscopy
SEN-3PB	Single-edge-notch 3-point Bending
SWCNT	Single-walled Carbon Nanotube
T_g	Glass Transition Temperature
VARTM	Vacuum Assisted Resin Transfer Molding
VdW	Van der Waals
XPS	X-ray Photoelectron Spectroscopy

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CHAPTER I

INTRODUCTION

This chapter will begin by describing some of the various technological developments that have been instrumental in generating the present interest in multifunctional composite systems for aerospace applications. It will introduce carbon nanotubes and detail the difficulties that have been encountered since their discovery. The discussion will shift toward the use of carbon nanotubes as a filler agent to create multifunctional nanocomposite systems, and will conclude with an outline detailing the material in this work.

Significance of epoxy/SWCNT based composite systems

The history of airplane development has shown a steady progression from lightweight, flexible materials, toward heavier, stiffer materials more capable of handling large payloads and high speeds. With the advent of polymer science, and the subsequent development of advanced polymer composite systems with tremendous strength to weight ratios, many speculated that there would be an exponential growth in the amount of composite materials used in aircraft. However, the growth has been significantly slower than expected due to the development of lightweight alloys, advanced joining

This thesis follows the style of Carbon.

techniques, low-cost castings, and high speed machining, extending the use of traditional materials in aircraft design [1]. To add to these developments, the uncertainty involving the fatigue life of polymer materials, and the typically poor fracture toughness and compression after impact (CAI) strength, have further mired the growth of polymer composite systems in structural applications.

In the last two decades there have been tremendous resources pushed toward the development of multifunctional nanocomposite materials using carbon nanotubes as a reinforcing agent within a polymer matrix. Multifunctional composite materials promise to simultaneously decrease weight, increase strength, and allow for improved performance over a range of mechanical, thermal, and electrical properties, but have and continue to face several obstacles.

Fundamental properties of carbon nanotubes

Carbon nanotubes are not a new discovery by any means. Recent work has shown that multi- and single-walled carbon nanotubes, along with carbon nanowires, were present in Damascus steel, used to make swords of legendary strength during the Crusades [2]. However, the actual observation and manipulation of carbon nanotubes has only been made possible with the development of high resolution electron microscopy, and even then their fundamental discovery was largely a matter of chance.

While there is a great deal of academic conjecture regarding who first discovered carbon nanotubes [3], there is little debate as to the progress that guided the research in the field. The first fundamental discovery that led to the observation of CNTs was during an experiment to understand the mechanisms of formation of long-chain carbon molecules in interstellar space [4]. A vaporization laser was focused on a single disk of graphite and produced a highly stable shell of carbon in a C_{60} arrangement, analogous to a soccer ball with 60 vertices and 32 faces. This molecule was termed a “Buckminsterfullerene,” as a reference to a geodesic dome based on a truncated icosahedral structure designed by architect Buckminster Fuller. This simple observation proved to generate tremendous interest because it fundamentally proved that there were more than two allotropes of carbon present in nature. Research began to focus on what other types of structures may result from manipulation of graphite sheets. This interest led to the observation of multi-walled carbon nanotubes by Iijima [5] and single-walled carbon nanotubes by Bethune [6] in the early 1990’s, igniting the imagination of the academic world as to the applications of these unique structures. In the two decades since, there has been a tremendous growth in research in this field, with early work focused on overcoming the difficulties in characterizing the material, and more recent work spent attempting to impart these characteristics to a matrix material.

A carbon nanotube is a hollow structure that is made up of one or more shells of concentric graphitic sheets. These graphitic sheets, also known as graphene, are planar sheets one atom thick and densely packed with carbon atoms in hexagonal arrangements.

Each carbon atom forms a hybridized sp^2 bond with its three neighbors that is immensely strong and stable [7]. The basic method of characterization of the CNTs is by the number of these concentric shells. Single-walled carbon nanotubes (SWCNTs) are made up of one shell of graphene rolled along a chiral vector. Multi-walled (MWCNT) carbon nanotubes are made of more than two shells and have significantly different properties than SWCNTs. Double-walled (DWCNTs) carbon nanotubes have also been observed [8]. SWCNTs typically have an inner diameter of about 1-3 nanometers and a length that may be 1 micron or longer, leading to observed aspect ratios of 1000 and greater [9]. MWCNTs typically have an inner diameter on the order of about 15 nanometers and aspect ratios closer to 100. The distance between the concentric shells in DWCNTs and MWCNTs is about 0.34 nm, corresponding to the interlayer spacing of graphitic sheets [7]. This work will largely focus on SWCNTs.

Mechanical properties of SWCNTs

The mechanical properties of SWCNTs are largely due to the hybridized bonds that exist between the carbon atoms making up the shells of the material. Theoretical calculations were made regarding the Young's modulus of the material by correlating the thermal oscillations of the tubes as a function of temperature and predicted a value of approximately 1 TPa [10], confirmed later experimentally [11]. This value suggests that the tubes have an extremely high degree of flexibility, implying that the strain and fracture characteristics of the matrix material should not be negatively impacted by their

addition. The maximum tensile strength was observed to be 30 GPa, demonstrating a strength to weight unparalleled by any other material [11].

Electrical properties of SWCNTs

Early work showed that, depending on how the tubes were rolled, the nanotubes could exhibit the electronic properties of either metals or semi-conductors [10]. The so-called “armchair” configuration, corresponding to a chiral angle of $\theta=30^\circ$, has been shown to behave electronically as a metal. The “chiral” configuration, corresponding to a chiral angle somewhere in the range between $0-30^\circ$, bears semi-conductive properties [8, 12].

Fig. 1 below illustrates this concept [7].

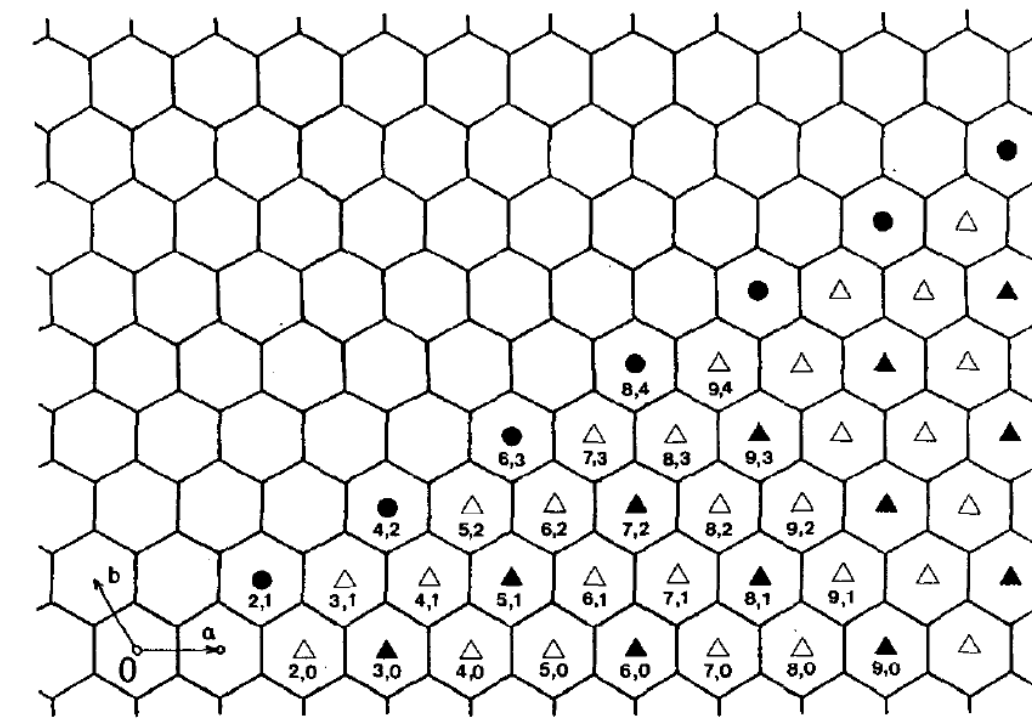


Fig. 1 – A carbon nanotube will behave as a metal (filled circles), narrow bandgap semiconductor (filled triangle), or moderate bandgap semiconductor (open triangle) if rolled in a way that the origin (0) is superimposed on a given hexagon (from [7]).

Thess et al. [13], observed that the electrical resistivity of a SWCNT with metallic chirality was on the order of 10^{-4} S/cm, with one peak observation of 0.34×10^{-4} S/cm, making it the most conductive carbon fiber known. Later work by Frank et al. [10], achieved a current density of 10^7 A/cm², indicating a very promising future for the material in the field of high powered electronics. In the same work, it was noted that the conductance of the tube is quantized and that it acts as a ballistic conductor. It was noted that the overall chirality of the tube has little impact on the mechanical properties of the material.

Due to the combination of these superior properties, carbon nanotubes have been exalted as being the solution for development of multifunctional composites [14]. However, a large problem exists when considering the interface between the carbon nanotubes and the matrix material. In order to fully impart the properties of the nanotubes to a material, it is necessary to achieve optimal dispersion, adhesion, and alignment [15-17].

Problems in integrating CNT systems

One of the basic features of a carbon nanotube is that it has an atomically smooth surface. Due to the hybridized bonds between the carbon atoms on the graphitic shells, there are no reactive groups to form bonds with a matrix material. Therefore, because there is no effective bond that will promote compatibility with a matrix material, there must be some group added to the surface of the CNT to promote a sidewall reaction. Another problem is that the high aspect ratio promotes an extremely high free surface

energy. In order to minimize the energy of the system, carbon nanotubes are attracted to each other and form bundles and ropes held together by van der Waals forces [18].

Attempts at achieving good dispersion have sought to debundle the clumps of CNTs and have them uniformly distributed throughout the matrix. While there are some applications where ropes are useful, such as in creating percolation networks for electrical conductivity [19-22], the greater the dispersion of the material in the matrix, the greater the mechanical properties should be. Poor dispersion allows the nanotubes to slip past one another when forces impact the composite material, significantly reducing their efficiency as reinforcing agents [16]. It is worth noting that the dispersability of a carbon nanotube is inversely proportional to the aspect ratio of the nanotube [23]. While the mechanical properties tend to degrade with increasing diameter and shortening length, the ability to transmit these properties to the matrix material has been observed to increase. It has been suggested that dual-walled carbon nanotubes (DWCNT) may strike a useful balance between dispersability and mechanical and electrical improvement [24, 25].

The second problem with the implementation of carbon nanotubes into a matrix material is poor interfacial adhesion. The atomically smooth and non-reactive surface characteristics of the carbon nanotubes restrict any degree of interfacial bonding between the nanotubes and the matrix material. This is shown in failure mechanisms where

carbon nanotubes were pulled out of the epoxy material without breaking, limiting their reinforcement effect [26-28].

The final consideration with regard to imparting the properties of a CNT filler material to a matrix material is alignment. Tremendous research efforts have sought to utilize the magnetic and electrical properties of carbon nanotubes in order to orient them to create conductive pathways. The most common methods have sought to align the CNTs *via* ambient electrical or magnetic currents while suspended in a viscous medium [29-36]. Of particular interest may be the application of electrical current during curing, such that as the viscosity of the material increases, the tubes will migrate toward the anode and grow backward toward the cathode, becoming locked in place as the degree of cure increases in the material [35]. Other techniques include mechanical deformation of thermoplastic networks [37] and epoxy infusion into nanotube networks that have been pre-aligned *via* catalytic deposition processes [11, 38-42], among many others [43].

There has been a large amount of effort put into the development of techniques to overcome these problems. The first problem, dispersion, depends largely on the medium of interest. Various mechanical means such as ultrasonication, high shear mixing, encapsulation, and surface functionalization have been considered [11, 44]. For thermoplastic networks, particular success has been reported for techniques involving shear mixing, stepwise dispersion, and elongational flow mixing. Gains of >300% have been reported [45]. More involved processing is required for thermosetting networks

due to the large shear forces that are required to achieve dispersion. Some reports have shown success using conventional means, such as lab scale twin-screw mixing [16], but these approaches appear limited in their scope. Other groups have employed the calendaring approach, utilizing adjacent cylinders of different sizes to impart high shear stresses to achieve good dispersion [46, 47], which shows good potential for scalability.

The problem of adhesion remains unaddressed by the above techniques. In order to achieve an interfacial bond between the CNT and the matrix, there must be a chemical interface that promotes the transfer of stress to the reinforcing material. To produce composite materials for structural applications, the surface of the nanotubes must therefore be functionalized to create reactive groups. The two primary methods of functionalization are non-covalent and covalent functionalization [43, 48].

Non-covalent functionalization is based largely on VdW attractive forces and primarily consists of either encapsulation or wrapping [49-51]. Molecules are added to the surface of the carbon nanotubes, often in the form of amphiphilic surfactants, that promote electrostatic repulsions between the carbon nanotubes, preventing agglomeration after initial dispersion. These effects are limited in application due to the lack of chemical bonding between the molecules and the surface of the CNT, thus limiting the amount of stress that can be effectively transferred and significantly diminishing the effect of mechanical property improvement within the composite system.

Covalent surface functionalization appears to be the best alternative with regard to load bearing structural applications because it simultaneously encourages dispersion while creating reactive surface groups that promote strong interfacial bonding. There are many approaches presented in literature, but all bear the common aspect that there must be an intermediate reaction to alter the surface of the carbon nanotube [52]. The basic approach is to introduce the carbon nanotubes into an extreme environment, typically acidic, such that some carbon atoms are broken from their ordered structure and form carboxylic acid groups upon oxidation [53, 54]. These exposed –OOH groups can be subsequently functionalized with a group that will react with the epoxy media. Other approaches, such as fluorination, are also popular [18, 27, 55, 56].

Of particular interest to this work are those functionalizing agents that will bond strongly within a diglycidyl ether of bisphenol A (DGEBA) epoxy system. Amine functionalization has been reported extensively within literature [57-59], and appears to be a highly viable route toward achieving strong interfacial bonding because it will serve as a potential cross-linking agent within the system [18, 49]. A drawback to this approach is that the extreme conditions imposed by the reaction introduce defects into the carbon nanotubes and limit their potential strength [50, 60]. This effect has been speculated to be small in reference to the expected performance increase from the SWCNTs, as theoretical modeling has shown that even with a high degree of sidewall functionalization, mechanical strength of SWCNTs should only be diminished by about 15% [14].

The processing techniques involved with the application of CNTs to the epoxy matrix become critical when considering the substantial increase in cost and relative decrease in processability that will result from a high loading percentage. An approach that shows great promise is that, instead of building a material composed entirely of nanocomposite material, the CNTs will be placed only at locations of particular interest. With regard to this work and the aerospace industry, the problem of how to strengthen carbon fiber panels has been approached. Instead of creating an entire panel doped with a CNT filler, the strength of an existing panel can be tremendously improved by the use of epoxy/CNT nanocomposite films as interleaves within a laminated panel.

The approach of this work has been to create 0.5 wt% epoxy/SWCNT composite thin films to be used as interleaves within a composite laminated panel. Other approaches have been suggested to prepare laminated composites, such as spraying a CNT mixture on a substrate [61, 62], but these involve the incorporation of the nanotubes throughout the entire material. In the proposed approach, the SWCNTs are oxidized *via* covalent oxidization and subsequently functionalized using sulfanilamide (SAA). SAA was chosen following work by Sun and Warren [63, 64] where a polyamidoamine generation 0 (PAMAM-G0) dendrimer was used as a functionalizing agent. Work is also presented to improve the fracture toughness of composite panels by introducing nylon-12 particles to absorb fracture energy within the system. Nylon-12 particles have been used extensively in research to promote toughenability within polymer materials, specifically by introducing modes of matrix shear yielding or crack pinning [65, 66]. This system

was cast as an interleave to enhance the inter-laminar strength and toughness of laminated composite systems [67-69]. These improvements should result in an improvement in the compression after impact (CAI) strength of the material as well [70].

A particularly interesting approach toward maximizing the potential for mechanical reinforcement while retaining the processability of the material is to create partially cured (B-stage) thin films that can be processed using Vacuum Assisted Resin Transfer Molding (VARTM). Using covalent oxidation and functionalization, a high degree of dispersion and interfacial bonding will be achieved and subsequently locked into place following a partial cure. Upon later heating, these properties should be passed to the composite panel.

This approach brings with it the potential for other applications outside of the aerospace industry, such as in micro-devices and electronic packaging [71-73]. It is unique because it allows a large quantity of nanotubes to be incorporated into a system for mechanical and, potentially, electrical property improvement without the sacrifice of processability. Future work will consider approaches intended to promote electrical conductivity within these systems, as well as the potential of aligning the CNTs to achieve further improvements in the mechanical, thermal, and electrical properties of the nanocomposite system [15].

Thesis layout

This thesis will focus primarily on the preparation and characterization of epoxy/SWCNT thin films. Chapter II will introduce work accomplished so far on this project regarding the processing of F-SWCNTs using PAMAM-G0 dendrimer, and detail the observed relationships between dispersion and mechanical properties. It will also consider the use of sulfanilamide (SAA) as a functionalizing agent and the resulting mechanical properties. Chapter III will discuss the introduction of nylon-12 particles into the system as a toughening agent. Chapter IV will discuss the processing and characterization of B-staged epoxy/SWCNT thin films, with specific focus on the characterization of the degree of cure and the flow properties of the system. Chapter V will conclude this work and highlight specific interests that may give rise to continued research.

CHAPTER II

PRODUCTION AND CHARACTERIZATION OF FUNCTIONALIZED SINGLE WALLED CARBON NANOTUBES

This thesis is a continuation of the tremendous effort by Dr. Luyi Sun and was done largely as part of an assistantship under Graham Warren. This chapter will highlight previously published work by these two individuals, specifically dealing with the determination of the degree of oxidation achieved with O-SWCNTs and the characterization of the mechanical properties of epoxy/F-SWCNT(PAMAM-G0) composite systems. This will be used as a framework to introduce work done in this thesis using sulfanilamide (SAA) as an improved functionalizing agent.

Experimental

Materials

XD-grade pristine single-walled carbon nanotubes (P-SWCNTs) were purchased from Unidym (formerly Carbon Nanotechnologies, Inc.) with a reported density of ca. 1.35 g/cm³, an aspect ratio of >1,000, and a composition of 2/3 SWCNT, 1/3 'few wall' CNT, and <5 wt% iron impurities. Concentrated sulfuric acid (95.4%) and nitric acid (70%) were obtained from Fisher Scientific for the oxidation reactions. Polyvinylidene difluoride (PVDF) filter membranes were purchased from Millipore to recover the O-SWCNTs and had a reported pore size of 45 μm.

Initial work from Sun et al., used a polyamidoamine generation 0 (PAMAM-G0) dendrimer functionalizing agent, purchased from Sigma-Aldrich. Later work, from Warren and this report, used sulfanilamide (99%) purchased from Sigma-Aldrich. EPIKOTE™ 862 resin (formerly Epon 862), a diglycidyl ether of bisphenol A (DGEBA) epoxy, was used as a matrix material in previous and current work, with EPIKURE™ W (formerly Epicure W), a di-amine hardener, used as a curing agent. Both epoxy resin and curing agent were purchased from Hexion Specialty Chemicals, Inc.

Preparation of F-SWCNT

Oxidized single-walled carbon nanotubes (O-SWCNTs) were prepared using a strong acid treatment. A sample of 1.0 g of untreated P-SWCNT were oxidized using a mixture of 180 mL sulfuric acid and 60 mL concentrated nitric acid (3:1 ratio) in a round-bottom flask, followed by 2.5 hours sonication in an ultrasonication bath. Following initial sonication, 760 mL of de-ionized water was added to the sample and subsequently sonicated for another 3 hours. The O-SWCNTs were collected through a PVDF filter and washed several times with de-ionized water. The cleaned O-SWCNTs were collected and re-dispersed in 500 mL acetone, followed by an additional three hours sonication. The degree of oxidation was confirmed using X-ray photoelectron spectroscopy (XPS).

Initial work by Sun determined that a 64:1 stoichiometric ratio of PAMAM-G0 was needed to promote interaction among the reactive sites on the SWCNT surfaces. A 1:1

wt% of sulfanilamide (SAA) was used in later work. The functionalizing agent was added to the O-SWCNT and ultrasonicated for 1 hour to ensure good mixing and interaction.

Plates were cast from neat epoxy, epoxy/P-SWCNT, epoxy/O-SWCNT, epoxy/F-SWCNT(PAMAM-G0), and epoxy/F-SWCNT(SAA) nanocomposite systems. The epoxy monomer was added to the F-SWCNT/acetone solution at a predetermined ratio to achieve a desired loading by wt% in the final nanocomposite. The epoxy/F-SWCNT/acetone mixture was sonicated for 15 minutes to promote dispersion. Curing agent was added at 26.4 parts by weight curing agent per 100 parts by weight epoxy monomer. Acetone and entrapped air were removed from the system using a rotary evaporator in a water bath at 70°C. Mechanical samples were prepared using a pre-heated glass mold coated with a release agent. The samples were pre-cured at 121°C for 2 hours, followed by a post-cure at 177°C for 2 hours.

XPS spectroscopy

In order to determine the degree of oxidation, a surface chemical analysis technique known as X-ray photoelectron spectroscopy (XPS) was used. The XPS spectra of the O-SWCNTs was obtained to determine the elemental composition, empirical formula, and electrochemical state of elements on the surface of the tubes. A Kratos Axis Ultra multitechnique spectrometer with non-monochromatic Mg K_α photos was used for all measurements with a binding energy for C(1s) set at 284.5 eV as a reference for all other

peaks [74]. The composition of the O-SWCNT surface was found from the high resolution peak areas for the XPS main core line of each element. Sensitivity factors were used as provided by the instrument manufacturer, along with Shirley-type background correction.

Results and discussion

Covalent oxidation and functionalization of SWCNT

The initial goals of this work were to increase the dispersion of the SWCNT and to promote interfacial bonding between the SWCNT and the epoxy monomer. In order to accomplish this, the surface of the tubes needed to be altered. It has been reported that the treatment of SWCNTs with strong acids will distort the perfect structure of the tubes and leave exposed carbon end groups available for reaction, subsequently forming carboxylic acids in the presence of an oxidizing agent [67, 68]. This formation of carboxylic groups provides a reactive site that may link the O-SWCNT and the epoxy monomer. Even more promising is that this site allows for additional groups to be grafted onto the tube surface to promote a stronger bond that has the potential to act as a cross-linker within the system, possibly even acting to absorb fracture energy and promote toughening mechanisms within the nanocomposite. It should also reduce the free energy in the system and prevent both agglomeration and flocculation, promoting a more uniform dispersion.

The overall degree of oxidation on the tube surface can be estimated from the XPS characterization of the O-SWCNT. As determined by Sun et al., the XPS spectra of the O-SWCNT treated with the above procedures is shown in Fig. 2 below. The presence of the carboxylic acid groups can be observed due to the shoulder at the higher bonding energy. This allows a quantitative relationship to be determined regarding the number of carbon atoms on the tube surface with carboxylic acid groups [74].

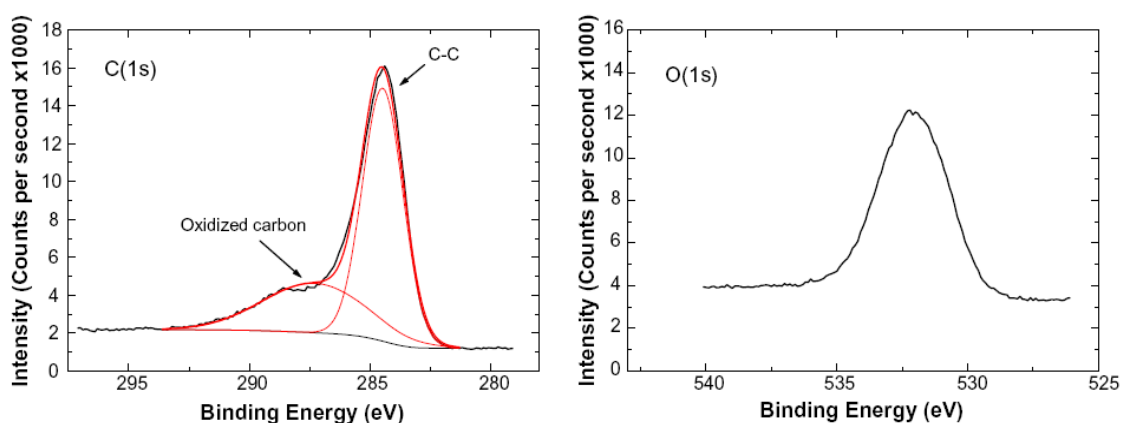


Fig. 2 – XPS Spectra of oxidized SWCNTs (from [64]).

From Fig. 2, it can be observed that the ratio between carbon and oxygen on the O-SWCNT surface is approximately 4:1. Each carboxylic acid group contributes 2 oxygen atoms, suggesting that the ratio of carboxylic acid groups to carbon atoms is 8:1.

Therefore, a stoichiometric ratio can be determined for the functionalizing agent by considering that each carboxylic acid group on the surface can form a bond with a single functionalizing group. In the case of the PAMAM-G0 dendrimer, there are 4 primary amine groups and 4 secondary amine groups that may act as functionalizing sites. An overall stoichiometric ratio of 64:1 was therefore determined to be optimal. However, in

order to account for possible steric hindrance effects, as well as to promote co-curing between the matrix material and the amine groups on the functionalizing agents, slightly more was used [64].

Following initial work using PAMAM-G0, sulfanilamide (SAA) was selected as a surface functionalizer. SAA is a particularly interesting functionalizer because it is a small molecule, and therefore unlikely to lead to the high increases in viscosity as was observed with the PAMAM-G0, and has a controllable bifunctionality [75]. This effect is due to its chemical structure, in that it is made up of a highly reactive aniline end group with a melting point of 120°C, and a less reactive sulfonamide group with a melting point of about 165°C. This allows the cross-linking density to be manipulated by varying the temperature. More importantly, it allows for a low viscosity during B-stage processing due to the low melting point of the aniline group. Finally, the use of sulfanilamide as a functionalizer should strongly impact the modulus and T_g of the epoxy materials due to its backbone rigidity [76, 77]. This should give rise to an improvement in the toughness, as the well known correlation between molecular length and its ability to act as a toughening agent does not hold in the case of a molecule with strong backbone rigidity [75, 78]. Figure 3 shows a schematic of the process involved in the functionalization of the SWCNT by sulfanilamide.

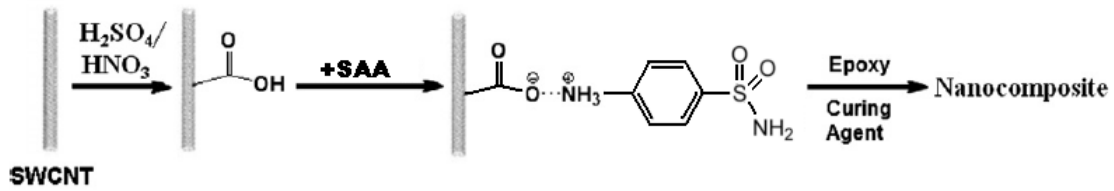


Fig. 3 – Schematic (not to scale) of functionalization of SWCNT by sulfanilamide.

Mechanical characterization

Several samples were prepared for each system and cast into plates. These plates were machined and characterized by tensile testing to determine the Young's modulus, tensile strength, and elongation at break. Fracture testing was also conducted to determine the mode-I critical stress intensity factor (K_{IC}). Initial work done by Sun and Warren determined the impact of the addition of PAMAM-G0 functionalizing agent into the system *via* procedures described above. These results are summarized in Table 1 below.

Table 1: Summary of mechanical properties of epoxy/SWCNT (0.5 wt%) nanocomposites (from [63])

Property	Neat Epoxy	Epoxy/ P-SWCNT	Epoxy/ O-SWCNT	Epoxy/ F-SWCNT
Young's Modulus (GPa)	2.77 ± 0.01	2.84 ± 0.05	3.17 ± 0.01	3.21 ± 0.15
Tensile Strength (MPa)	60.1 ± 5.6	74.2 ± 0.5	76.5 ± 3.9	82.7 ± 3.2
Elongation (%)	1.98 ± 0.22	2.57 ± 0.18	2.97 ± 0.40	4.88 ± 0.91
K_{IC} (MPa·m ^{1/2})	0.78 ± 0.01	0.76 ± 0.03	0.83 ± 0.05	0.93 ± 0.04

These results showed a high correlation between the dispersion of SWCNT in the matrix and the overall mechanical strength of the system. It was suggested that the reinforcement characteristics due to the P-SWCNT were limited due to large agglomerates and bundles present, as evidenced by optical microscopy, scanning

electron microscopy, and Raman spectroscopy (images available in [63]). Following oxidation, there was a significant improvement in the Young's modulus of the material, coupled with a slight increase in the tensile strength and a significant improvement in the elongation at break.

The best results were generated after grafting functional groups onto the surface of the O-SWCNT, as indicated by the 16% improvement in the Young's modulus and 38% improvement in the tensile strength. The increase in dispersion and interfacial adhesion allowed for a tremendous increase in the structural reinforcement of the material, as compared to the neat epoxy. The elongation at break was also observed to increase by 146%, likely due to the introduction of the long chain dendrimer as a functionalizing agent, allowing ductile failure and an overall transmission of stress throughout the material, rather than being focused at specific points due to poor dispersion and limited adhesion.

Use of sulfanilamide as a functionalizing agent

While the PAMAM-G0 returned good mechanical results, its overall utility was limited. Due to its large branch structure, achieving good dispersion within the epoxy equated to a significant increase in the viscosity of the system, limiting the processability. It was also prohibitively expensive. Sulfanilamide (SAA) was chosen as a potential replacement due to reasons mentioned previously. Initial optical microscopy results

suggested that SAA showed a heightened dispersion when compared to PAMAM-G0.

The optical microscopy results are shown in Fig. 4 below.

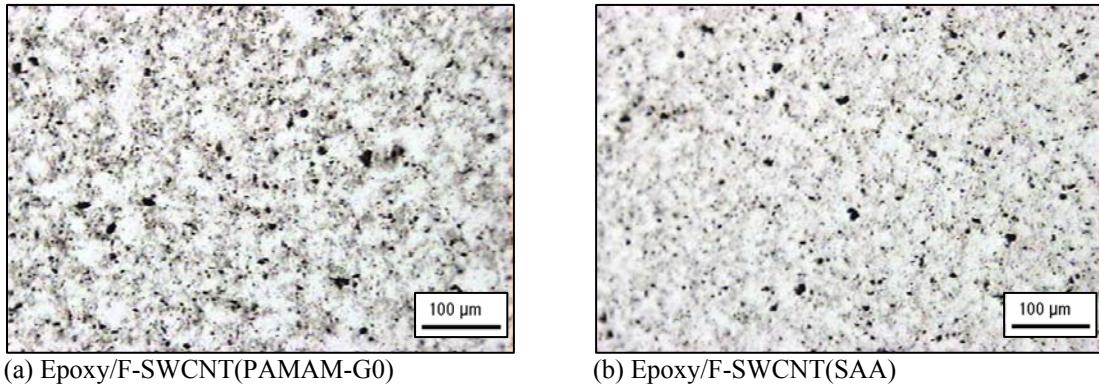


Fig. 4 – Optical microscopy of F-SWCNT with PAMAM-G0 dendrimer and SAA as functionalization agents (from [79]).

From Fig. 4, it appears that the overall dispersion is improved with the use of sulfanilamide as a functionalization agent. From previous work, this is anticipated to correlate with an improvement in the mechanical characteristics of the system. To verify this, tensile tests were conducted on the Epoxy/F-SWCNT(SAA) samples. The values are summarized in Table 2 below.

Table 2: Summary of mechanical properties of epoxy/F-SWCNT(PAMAM-G0) and epoxy/F-SWCNT(SAA) (0.5 wt%) nanocomposites (data available from [79])

Property	Epoxy/F-SWCNT (PAMAM-G0)	Epoxy/F-SWCNT (SAA)
Young's Modulus (GPa)	3.21 ± 0.15	3.21 ± 0.16
Tensile Strength (MPa)	82.7 ± 3.2	88.3 ± 0.61
Elongation (%)	4.88 ± 0.91	5.08 ± 0.30
K_{IC} (MPa·m ^{1/2})	0.93 ± 0.04	0.86 ± 0.08

The results show that the sulfanilamide offers an improvement in the tensile strength and elongation at break (7% and 4%, respectively) of the nanocomposites, with an 8% reduction in the K_{IC} value. This reduction in the fracture toughness of the material is likely due to the reduction in the chain length of the functionalizer. With the smaller size of the sulfanilamide molecule, there is less ability for the fracture energy of the system to be absorbed in the chains. The increase in the tensile strength and elongation at break was deemed significant enough to select SAA as the primary functionalizer for the remainder of this work.

CHAPTER III

PROCESSING AND CHARACTERIZATION OF EPOXY/SWCNT/NYLON NANOCOMPOSITES

Experimental

Materials

Nylon particles (Nylon-12) were donated by Toray Industries. The nylon particles had a reported particle size of ca. 10 μm and melting point of 165 $^{\circ}\text{C}$.

Preparation of epoxy/F-SWCNT/nylon nanocomposite plates

XD-grade pristine single-walled carbon nanotubes (P-SWCNTs) were treated with strong acids to obtain oxidized single-walled carbon nanotubes (O-SWCNT) as described in the previous section. Sulfanilamide (SAA) was added at a 1:1 weight ratio and stirred to promote reaction between the exposed carboxyl groups on the tube surfaces and the amine end groups of the SAA. The mixture was diluted with acetone to reduce viscosity and ultrasonicated for 1 hour to encourage interaction. Nylon particles, pre-dispersed in an acetone mixture, were added to the mixture to ensure a final loading of 10 wt% nylon-12. A predetermined ratio of epoxy monomer was added to the system and ultrasonicated for 15 minutes. Curing agent W was added at a ratio of 26.4 parts by weight per 100 parts by weight of epoxy monomer. The acetone was removed from the system, along with any entrapped air, using a rotary evaporator with a water bath at

70°C. The samples were poured into pre-heated glass molds coated with release agent and pre-cured for 2 hours at 121°C, followed by a post-cure at 177°C, before being removed from the mold.

Results and discussion

The objective of this chapter was to improve the fracture toughness of the nanocomposite systems with minimal degradation to the mechanical properties observed in the previous chapter. To do this, nylon-12 was introduced to the system as a toughening agent. The mechanical properties were characterized using tensile testing approaches described in the previous chapter. The summary of results from the epoxy/SWCNT/nylon systems are shown in Table 3 below.

Table 3: Summary of mechanical properties of epoxy/F-SWCNT(SSA)(0.5 wt%)/nylon (10wt%) nanocomposites (from [79])

Property	Epoxy/nylon	Epoxy/P-SWCNT /nylon	Epoxy/O-SWCNT/ nylon	Epoxy/F-SWCNT/ nylon
Young's Modulus (GPa)	2.61 ± 0.16	2.73 ± 0.16	2.79 ± 0.10	2.98 ± 0.09
Tensile Strength (MPa)	78.3 ± 1.4	80.4 ± 1.4	84.0 ± 1.7	77.3 ± 0.4
Elongation (%)	7.11 ± 0.76	2.52 ± 0.50	5.49 ± 0.82	5.60 ± 0.84
K _{IC} (MPa·m ^{1/2})	0.95 ± 0.09	0.99 ± 0.07	1.02 ± 0.10	1.12 ± 0.09

These results indicate that the addition of 10 wt% nylon diminishes the strength characteristics of the bulk material, with the Young's modulus and tensile strength being lowered 7% and 12%, respectively, but substantially increases the ductility and toughness of the nanocomposite, with a 10% gain in the elongation at break and a 30% increase in the K_{IC} observed. The decreases in the strength of the material are expected,

as nylon should act as a defect due to its low modulus (<1.5 GPa), but this reduction can be viewed as moderate when considered against the gains in the toughness of the material. When compared to the original neat epoxy system, the nanocomposite containing epoxy/F-SWCNT/nylon still shows an 8% improvement in Young's modulus and 29% improvement in tensile strength. The true strength in the incorporation of nylon into the material is in the improvements in the elongation at break and K_{IC} . The observed improvements in these parameters are 183% and 44%, respectively.

Fracture analysis

In order to consider the impact of these modifications to the system on the fracture mechanics, scanning electron microscopy was performed on the fracture surfaces of the material, as shown in Fig. 5 below.

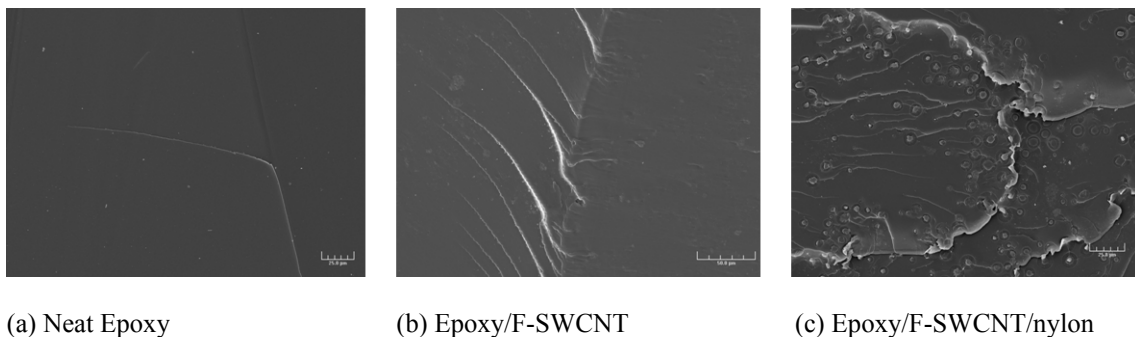


Fig. 5 – SEM images of fracture surface of neat epoxy, epoxy/F-SWCNT, and epoxy/F-SWCNT/nylon (10 wt%) (from [79])

From the fracture surface of the neat epoxy, it can be observed that there are no toughening mechanisms present in the system and that brittle fracture occurs, with the

crack propagating along the fracture surface with no deviation in growth. With the introduction of F-SWCNT, there appears to be some deflection of the fracture energy, likely due to energy absorbed in the interfacial bond between the SWCNT and the epoxy matrix. There is no propagation of micro-cracks or other effects to suggest that the SWCNT is active in the absorption of the fracture energy.

In the epoxy/F-SWCNT/nylon system, there are clear toughening mechanisms present as the crack tip is split into hundreds of micro-cracks that appear to be pinned by the nylon particles. In many cases, as shown in Fig. 5c, the fracture energy appears to be completely absorbed by the nylon particles, leading to the increase in the fracture toughness values observed in Table 3.

This section has detailed the preparation and characterization of bulk panels of epoxy/SWCNT/nylon samples. It has shown that the fracture toughness of epoxy/SWCNT panels can be greatly increased with the introduction of nylon-12 particles, and that the overall degree of mechanical reinforcement agrees with the general correlation that mechanical properties are enhanced with heightened dispersion. The fracture characteristics were investigated, and it was shown that there is some drop in the tensile properties of systems incorporating nylon particles, but that the improvement in the fracture characteristics is significant enough that this drop is acceptable for certain applications. Continued effort will be made to further optimize

the dispersion and adhesion of the system to continue to improve the mechanical properties.

CHAPTER IV

PROCESSING AND CHARACTERIZATION OF B-STAGED EPOXY/SWCNT/NYLON THIN FILMS

The primary focus of this research has been to develop methodologies to produce strong, tough nanocomposite materials that can be cast as thin films for further processing *via* VARTM. The VARTM processing will be conducted by a separate group and is not a part of this work. The concern of this group has been to develop methodologies for preparing thin films and to characterize them based on their flow properties.

Specifically, the degree of cure and flow temperatures are of the greatest importance. The methodologies used in this chapter were initially developed by Warren et al., as reported in [63], with subsequent improvements being made as part of this work, as reported in [79].

Experimental

Materials

The thin film coater used in this work was purchased from Elcometer Inc. (Rochester Hills, Michigan) and modified by the addition of a temperature control system in our lab. Release paper was donated from Hexcel Corporation (Salt Lake City, Utah).

Thin film preparation

SWCNT of various states were prepared using methods described in the previous chapters. P-SWCNT, O-SWCNT, and F-SWCNT were made, with sulfanilamide (SAA) as the functionalizing agent. Samples were prepared by adding the epoxy monomer to a representative SWCNT sample at a predetermined ratio and sonicated for 15 minutes to achieve a final SWCNT loading of 0.5 wt%. SAA was added at a 1:1 wt% with the O-SWCNT. Nylon was added as a toughening agent for a separate set of a samples using methods described in the previous chapter. Curing was added at 26.4 parts by weight per 100 parts by weight of EPIKOTE™ 862 prior to removal of acetone and entrapped air by rotary evaporator in a water bath at 70°C. Samples were B-stage cured at 121°C for 70 minutes in an oven. Samples were quickly transferred to the thin film coater, preheated to 90°C, and cast into thin films at a thickness of approximately 50 µm on release paper. Neat epoxy thin films were also prepared with the same procedures.

Differential scanning calorimetry

In order to determine the degree of cure, a Mettler Toledo (Model DSC821^o) differential scanning calorimeter was used to obtain DSC thermograms. Differential scanning calorimetry (DSC) is a technique of thermal characterization that measures the difference in the amount of heat required to increase the temperature of a sample and the temperature of a reference (typically air) as a function of temperature. A B-stage curing process was mimicked by keeping a sample isothermal at 121°C for 3 hours. A full

curing process was mimicked by maintaining an isotherm at 177°C for two hours. The experiments were carried out under a nitrogen gas purge (80 mL/min).

Results and discussion

The most important characteristics of thin films that require further processing on VARTM are the degree of cure, which dictates if the dispersion and alignment achieved in the samples is sufficiently locked in place, and the melt range of the sample, which determines the ease in which future processing can be carried out. The objective should be to achieve a degree of cure as high as possible while maintaining a reasonable melt range, likely in the range of about 50°C.

In this work, thin films were prepared from epoxy/SWCNT of various states. B-stage curing, with a degree of cure of about 50%, was determined to be optimal because it offers a compromise between limited particle mobility and reduced void formation on the surface of the film, while maintaining low enough viscosity to allow for processing. The thin film coater was kept at 90°C to allow for the film to be prepared prior to excessive hardening.

Determination of degree of cure

In order to determine the degree of cure, differential scanning calorimetry was used. Two samples were prepared for each state of SWCNT and neat epoxy, with the first undergoing a B-stage curing cycle and the second undergoing a full cure, as described

previously. The degree of cure was estimated from the ratio of exotherm during the B-stage curing cycle (ΔH_B) and the exotherm during the full curing cycle (ΔH_C). The thermograms for these samples are shown in Fig. 6 below.

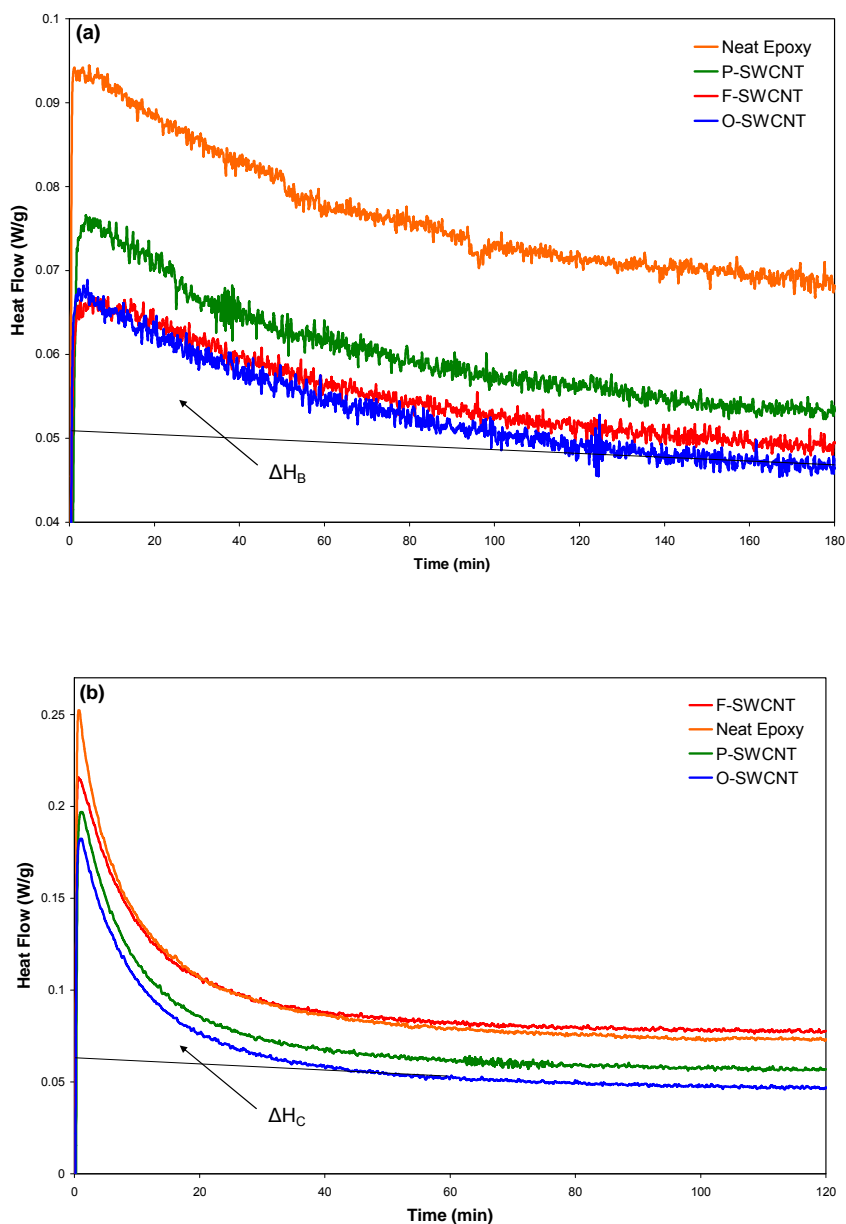


Fig. 6 – DSC thermograms of epoxy/SWCNT (0.5 wt%) thin films: a) samples cured at 121°C for 3 hours, and b) samples cured at 177°C for 2 hours (data from [63])

The ratio of the exotherm between the B-stage and full curing cycles gives an idea of the overall network structure that has formed within the nanocomposites. From the data in Fig. 6, it was determined that each nanocomposite system requires about 70 minutes to achieve a 50% degree of cure. From data presented in [63, 64, 79], it was shown that the T_g of each system considered is similar, indicating that though there is some stoichiometric variation following the addition of SWCNT and functionalizing agents into the system, the overall change of the thermal characteristics of the system is not significant enough to bring about large changes in the thermal properties of the nanocomposite. From these considerations, a time of about 70 minutes was projected to be the optimal time for each system. These values also allow future calculations to be made on completed panels to project the quality of the thin film, as determined by its degree of cure.

In order to determine the melt range of the systems, DSC samples were taken of B-stage cured and fully cured thin films with temperature ramps from 30°C-180°C. The overall melting point in the system could therefore be easily observed, along with the glass transition properties of the fully cured samples. This data is shown in Fig 7. below.

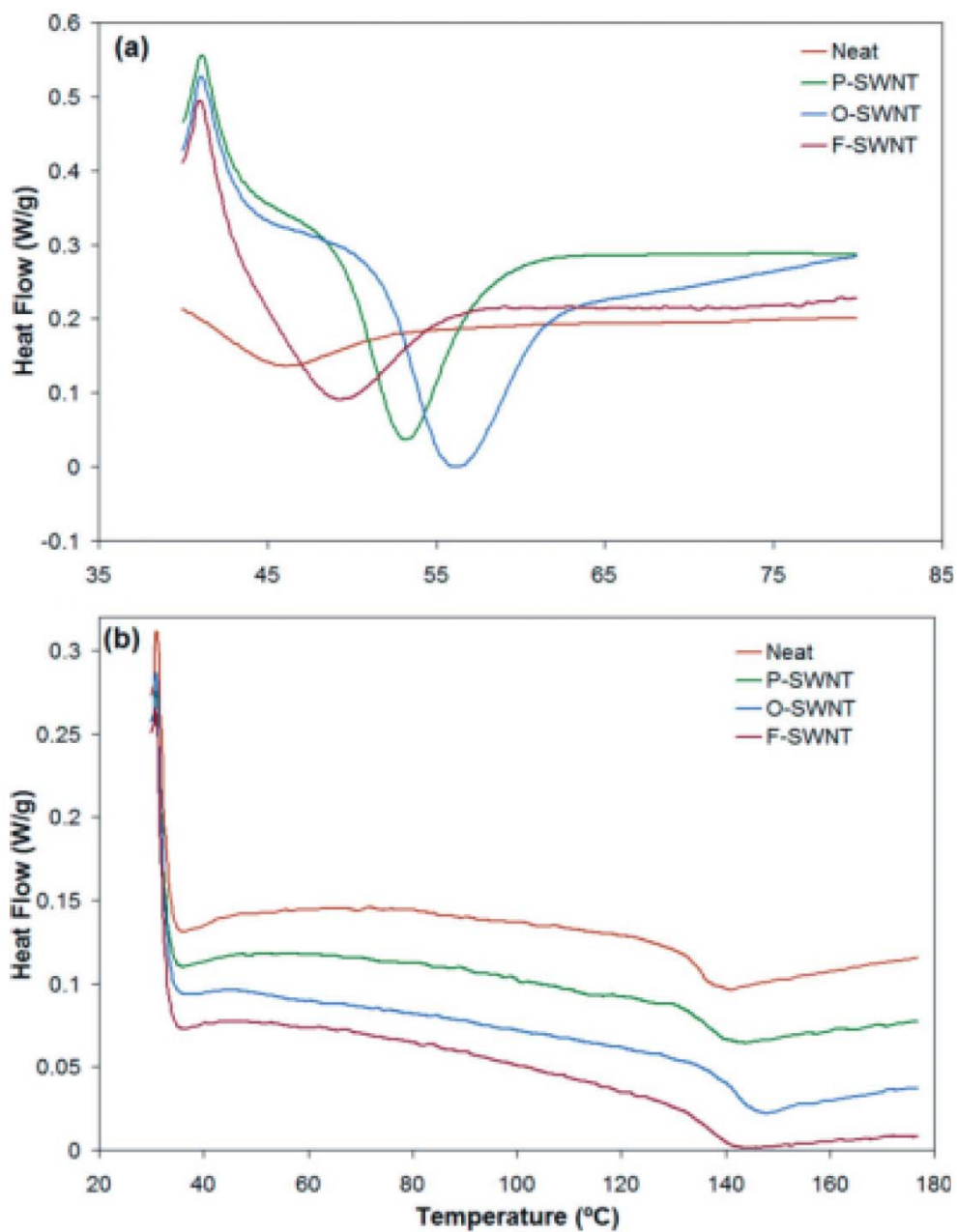


Fig. 7 – DSC thermograms of (a) 50% cured thin film and (b) 100% cured thin film (from [63])

From this data, it is clear that the melt range of the 50% cured thin film samples is within the range needed for VARTM applications. Also, it can be observed that the glass transition temperatures of the fully cured thin films are about the same, with slight increases in the T_g being observed for the heightened processing of the nanocomposites. This increase in the T_g is likely due to the increase in the interfacial bonding between the SWCNT and the epoxy monomer, and may suggest that there is some alteration in the stoichiometric ratio between the epoxy monomer and the curing agent due to the presence of the functionalizing agent in the system.

In summary, it has been shown the incorporation of 0.5 wt% SWCNT in epoxy has little effect on the overall curing process of the material. These results allow high quality, defect free thin films to be prepared with the present methods. These films are stable at room temperature and may be used to serve as interleaves between layers of composite materials in VARTM applications.

CHAPTER V

SUMMARY AND CONCLUSIONS

Carbon nanotubes have brought about a tremendous interest in the field of material science and generated remarkable amounts of research regarding multifunctional materials that may define the next century of materials science and engineering. This work has been focused on using carbon nanotubes to improve the mechanical strength of thin films in order to enhance the mechanical properties of laminated composite materials.

Prior research on this topic was conducted by Sun and Warren and confirmed the oxidation of SWCNT by strong acid reaction and showed a correlation between the dispersion achieved with the functionalization of SWCNT and the overall mechanical properties of the nanocomposites. This work considered the use of sulfanilamide as a functionalizing agent and quantified the mechanical properties that resulted from it, indicating that the smaller molecular size contributed to a reduction in the amount of fracture energy that can be absorbed, but the improved dispersion allowed for an increase in the Young's modulus, tensile strength, and elongation at break. With sulfanilamide as a functionalizing agent, tensile testing showed that the Young's modulus and tensile strength of the epoxy system could be improved by 16% and 38%, respectively, with the addition of F-SWCNT. The elongation at break was improved by 146%, indicating a greatly improved toughness and shifting from brittle to ductile

failure. The fracture toughness was improved by 19%, as indicated by the mode-I critical stress intensity factor (K_{IC}).

Work was also carried out to introduce nylon particles into the nanocomposite system to promote toughening mechanisms. These samples showed somewhat diminished mechanical properties when compared to the results from the epoxy/SWCNT systems, due to the low mechanical reinforcement of the nylon particles loaded at 10 wt%, but showed an improvement in the Young's modulus (an 8% gain) and tensile strength (a 29% gain) when compared to the neat epoxy system. The elongation at break was improved by 183% over the neat epoxy system, and the K_{IC} results showed an improvement of 44% from the original system. Fracture mechanisms were investigated using SEM and showed that the nylon particles absorbed the fracture energy of the system and dispersed the energy from a single crack into a large number of micro-cracks. These results indicate that the addition of nylon particles is an effective method of toughening the system, though lower weights and different processing techniques may be needed in order to further optimize the balance of loss in mechanical properties and improvement in the fracture characteristics of the nanocomposite systems.

As an assistant to Warren, thin-films were created to utilize the properties defined by the bulk samples. These samples showed good uniformity in thickness. Results showed that these thin films were high quality, stable at room temperature, and able to be processed with the addition of low levels of heat. These characteristics were made using

differential scanning calorimetry (DSC), which showed that the melt range of the nanocomposites varied between 50-57°C and that the T_g of the systems was relatively stable between 136-144°C. The variation in the T_g was attributed to the trapping of curing agents around SWCNT bundles and excess curing agent in the system due to increased cross-linking and reactions with the oxidative and functionalizing groups on the SWCNT surface, altering the curing ratio within the system.

These findings show that epoxy/SWCNT/nylon nanocomposites thin films are ideal candidates to be used as interleaves for VARTM composite panel applications for concentrated improvement in mechanical and fracture toughness characteristics of composite laminates.

Future work

The tremendous potential of SWCNTs lie in their inherent multi-functionality across a regime of properties. Nanocomposites have the potential to offer tailored conductivity based on chirality, and may be able to exhibit isotropic electrical and thermal conductivity if well dispersed. Future work should focus on continued improved in the dispersion and interfacial bonding of the system, but should consider less harsh techniques to limit the degradation of the electrical properties of the tubes. An alternative method may be to use multi-walled carbon nanotubes in an attempt to maintain the integrity of the inner shells to promote ballistic conduction of electrons and

phonons. This approach may allow for mechanical, electrical, and thermal property improvements to be achieved with low loadings.

Further work should also focus on the use of electrical and magnetic currents to promote alignment of SWCNT systems within the epoxy materials. A consequence of this may be that there is tremendous anisotropic strength enhancements that lend a directionality to the composite panels. If this improvement in strength is large enough, layered thin films in known direction be used to create material of immense strength in all directions, much in the way that carbon fibers developed. These panels could potentially have extremely high electrical conductivities, as well as high thermal conductivities, and could serve as replacements for heavy, brittle components in aircraft design.

Applications for this work extend, obviously, well beyond the aerospace industry that it has so far been targeted at, and may extend to high-power electronics, electromagnetic interference uses, and most any application where high strength and low weight are desired. As the ability of manufacturing firms to produce SWCNT at lower costs increases, applications will continue to abound, promising tremendous growth for this industry and ongoing research to continue to improve the methodologies.

Limited to the scope of this work, efforts will continue to be made toward development electrically conductive thin films, thinner films using different techniques, and more advanced methods of characterizing the thickness of the films.

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