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NANOTUBE REINFORCED THERMOPLASTIC POLYMER MATRIX COMPOSITES

by

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ABSTRACT

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The inherent high strength, thermal conductivity, and electrical conductivity make nanotubes attractive reinforcements for polymer matrix composites. However, the structure that makes them desirable also causes highly anisotropic properties and limited reactivity with other materials. This thesis isolates these problems in two separate studies aimed at improving mechanical properties with single wall nanotube (SWNT) reinforced thermoplastic polymer composites. The two studies demonstrate the effect of solid freeform fabrication (SFF) and chemical functionalization on anisotropy and limited reactivity, respectively. Both studies showed mechanical property improvements. The alignment study demonstrates a maximum increase of 93% in tensile modulus with single wall nanotubes (SWNTs). The chemical functionalization study shows a larger increase in storage modulus for functionalized SWNTs as compared to purified SWNTs with respective increases of 9% and 44% in storage modulus. Improved interfacial properties are also observed as a decrease in mechanical damping.

Maximum property increases in composites are obtained when nanotubes are aligned, requiring additional processing consideration to the anisotropic structure. Melt spinning and extrusion processing effectively align nanotubes, but the end product of these techniques, composite fibers, requires further processing to be incorporated into
finished parts. Extrusion-based SFF is a novel technique for processing nanotube reinforced composites because it allows for the direct fabrication of finished parts containing aligned nanotubes. SFF processing produces parts containing preferentially oriented nanotubes with improved mechanical properties when compared to isotropic composites.

Functionalization of the nanotube surface disrupts the rope structure to obtain smaller ropes and promote further interfacial bonding. The chemically inert nature of nanotubes resulting from a structure containing few defects and the formation of larger, ordered ropes of SWNTs limits the amount of interfacial bonding and load transfer that occurs between nanotubes and a polymer matrix. Improved dispersion, interfacial properties, and mechanical properties are achieved through chemical functionalization. Subsequent partial removal of the functional groups created a direct bond between the nanotubes and the polymer matrix. The alignment and functionalization studies in this thesis further the knowledge of the use of nanotubes as reinforcements in polymer composites through understanding the sensitivity of the nanotubes' anisotropic properties and the nanotube/polymer interface.
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NOMENCLATURE

ABS  Poly(acrylonitrile-co-butadiene-co-styrene)
CAD  Computer Aided Drafting
DMF  Dimethyl Formamide
E'   Storage Modulus
E''  Loss Modulus
EFF  Extrusion Freeform Fabrication
F-SWNT Fluorinated Single Wall Nanotube
FDM  Fused Deposition Modeling
FTIR Fourier Transform Infrared
HB-ABS High Butadiene ABS
HDPE High Density Polyethylene
HiPco High Pressure Carbon Monoxide
IR   Infrared
LDPE Low Density Polyethylene
M-ABS MAGNUM® 213 ABS
MDPE Medium Density Polyethylene
P-ABS P400 ABS
P-SWNT Purified Single Wall Nanotube
P-VGCF Purified Vapor Grown Carbon Fiber
PAN  Polyacrylonitrile
ROM  Rule of Mixtures
<table>
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<tr>
<td>SAN</td>
<td>Styrene-Acrylonitrile Copolymer</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SFF</td>
<td>Solid Freeform Fabrication</td>
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<tr>
<td>SWNT</td>
<td>Single Wall Nanotube</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Glass Transition Temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
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<tr>
<td>TGA-IR</td>
<td>Thermogravimetric Analysis-Infrared Spectroscopy</td>
</tr>
<tr>
<td>TLCP</td>
<td>Thermotropic Liquid Crystal Polymer</td>
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<tr>
<td>VGCF</td>
<td>Vapor Grown Carbon Fiber</td>
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CHAPTER ONE

INTRODUCTION

Nanosize reinforcements in polymer matrix composites are unlike conventional macrosize composite reinforcements because they are touted as a method to improve mechanical properties and ductility simultaneously. In particular, a great deal of the enthusiasm is generated by the promise of single wall carbon nanotubes (SWNTs) as multifunctional reinforcements. Already, significant reductions in percolation compositions with respect to traditional fillers such as metal particles have been achieved with SWNTs to create viable replacement materials for electrostatic dissipation and electromagnetic interference shielding applications [1, 2]. However, improvements in mechanical properties are more difficult to achieve because nanotubes should be aligned and well bonded (mechanically or chemically) to the host polymer to fully exploit their exceptional properties. This thesis evaluates solid freeform fabrication (SFF) and chemical functionalization as routes to achieve these respective conditions separately in thermoplastic matrices. A comparison is also made between SWNTs and another carbon nanofiber, vapor grown carbon fibers (VGCFs), in the alignment study to examine the differences in processing behavior and composite properties. The functionalization study compares purified nanotubes to fluorinated nanotubes in order to elucidate the effect of covalent functionalization on composite properties and its stability through the processing protocol. Aspects of fiber alignment, dispersion, degradation, and interfacial bonding are evaluated in each study where applicable, and the success of these techniques is measured with static and dynamic mechanical testing. The result of this research is that SFF
techniques can produce composites containing oriented nanotubes with higher mechanical properties than the neat polymer and isotropically oriented composites and that functionalized SWNTs produce greater mechanical property increases than purified SWNTs in composites.

In this thesis, the SFF techniques deposit material via extrusion which is also used to orient SWNTs. The use of SFF directly creates a functional component directly unlike traditional fiber spinning which requires further processing steps to incorporate the fibers containing aligned nanotubes into the finished part. SFF also allows the use of conventional polymer processing techniques such as shear mixing to disperse nanotubes prior to SFF processing.

The type of chemical functionalization used in the second study is fluorination. Fluorine functionalization is a well established and well studied method that is chosen for two reasons. First, this method can produce suitable quantities of functionalized nanotubes for composite applications, and second, fluorination can produce controlled stoichiometries up to a composition of C\textsubscript{3}F. This second study is also part of a larger effort to produce light-weight, multifunctional radiation shielding materials in collaboration with researchers at Prairie View A&M University, Advanced Ceramics Research, and NASA Langley Research Center.

This thesis is organized into seven chapters, and in most chapters, both studies are discussed together. Following the introduction in Chapter 1, Chapter 2 contains the background information for the topics addressed in the alignment and functionalization studies. These topics include SWNTs, VGCFs, composites containing nanotubes and nanofibers, SFF, and chemical functionalization of nanotubes. Chapter 3 describes the
specific materials and processing techniques used to create the composites. Fiber treatment such as purification and functionalization, incipient wetting, conventional processing techniques such as high shear mixing, and solid freeform fabrication processes are detailed. Chapter 4 evaluates the quality of the composites with respect to nanotube and nanofiber alignment, dispersion, degradation, and interfacial properties. Each of these features impacts the mechanical properties, and broad conclusions are stated with respect to the effect of fiber treatment and type on the processing methods. Chapters 5 and 6 contain the static and dynamic mechanical testing results, respectively, and the thesis ends with the conclusions and suggestions for future work.

*Portions of this thesis are published in the following papers.


CHAPTER TWO

BACKGROUND

2.1 Introduction

Several separate topics are merged in this thesis which covers work aimed at achieving SWNT reinforced composites with increased mechanical properties. Each topic requires a separate background explanation. Chapter 2 is organized into sections concerning these subjects: carbon nanotubes, vapor grown carbon fibers, solid freeform fabrication, and nanotube functionalization. Section 2.2 summarizes the discovery, production, purification, properties, and polymer matrix composites of carbon nanotubes with emphasis on single wall carbon nanotubes. Section 2.3 complements the previous section with the corresponding information about vapor grown carbon fibers. Section 2.4 outlines SFF, concentrating on the extrusion-based methods used in this thesis and their application to processing composites. Section 2.5 is concerned with chemical functionalization of nanotubes to improve dispersion and interfacial bonding in composites. Subsequent chapters discuss the experimental details of this thesis such as materials, processing methods, aspects of the composite materials produced, and mechanical testing.

2.2 Carbon Nanotubes

Carbon nanotubes are carbon fibers with diameters on the order of a nanometer and with a structure resembling a graphene sheet rolled to form a cylinder capped with half spheres similar to a \( C_{60} \) molecule. Within this structure, many variations exist, based
on the orientation of hexagons with respect to the nanotube axis. This orientation, shown in Figure 2.1, is called chirality and is used to classify nanotubes into three groups: armchair, zigzag and chiral. The chiral angle has been shown theoretically [3, 4] and experimentally [5, 6] to impact the electronic properties of individual nanotubes and the van der Waals interaction between nanotubes [7].

![Figure 2.1: Three types of nanotubes based on chiral angle: armchair (a), zigzag (b), and chiral (c) [8].](image)

The chiral angle also serves as a manner for indexing nanotubes through the chiral vector, \( C_h = n a_1 + m a_2 \), where \( a_1 \) and \( a_2 \) are the hexagonal lattice unit vectors and \( n \) and \( m \) are integers [9]. These integers are used to identify nanotube configurations with the notation \((n,m)\). The nanotubes pictured in Figure 2.1a, b, and c are \((5,5)\); \((9,0)\); and \((10,5)\), respectively. If the difference between \( n \) and \( m \) is zero or a multiple of three, then
the nanotube’s electronic structure is metallic. Otherwise, it is semiconducting. From this relationship, armchair nanotubes (n=m) are solely metallic in nature, but zigzag (m=0) and chiral nanotubes may be either metallic or semi-conducting. This relationship is shown schematically in Figure 2.2.

![Graphene Sheet with Chiral Vector Indices](image)

**Figure 2.2:** Chiral vector indices plotted on a graphene sheet. Metallic and semiconducting chiralities are denoted. The numbers listed below the indices indicate the number of unique caps that can be attached to that specific nanotube [8].

The discovery of nanotubes was made by Iijima in 1991 [10]. He observed multi-walled carbon nanotubes (MWNTs) which are nested arrays of SWNTs. Following the discovery of multi-walled nanotubes, SWNTs were observed simultaneously by Iijima and Ichihashi [11] and Bethune *et al.* [12]. Due to van der Waals forces, the SWNTs are attracted to each other and occur in the form of ropes as shown in Figure 2.3. These ropes on average have diameters between 10 and 20 nm and lengths of many micrometers [13]. This is the form of SWNTs used in this research.
2.2.1 Production

Three main routes for producing macroscopic quantities of SWNTs are currently used: arc-discharge [11, 12, 14], pulsed laser vaporization [13, 15], and high pressure carbon monoxide (HiPco) [16]. Of these three methods, nanotubes produced by the pulsed laser vaporization and HiPco methods are used in the alignment and functionalization studies, respectively. The arc-discharge method is mentioned here for completeness. The arc-discharge method relies on a current and voltage applied across electrodes to vaporize carbon from graphite rods in the chamber. Nanotubes are deposited on the cathode from the plasma as shown by the apparatus schematic in Figure 2.4. General parameters used to produce nanotubes by arc-discharge are electrode diameters of 5-20 mm, an electrode separation of 1 mm, an applied voltage of 20-25 V, a current of 50-120 A, a purge gas of helium, and a gas pressure of 500 Torr. Transition metal species, such as iron, nickel, or cobalt, are normally used to catalyze the production
of SWNTs [9]. The SWNT yield of this process is approximately 80%, and the average diameter of SWNTs is 1.4 nm [14].

Figure 2.4: Schematic of an arc-discharge apparatus. Electrodes consisting of graphite and metal catalyst are used as the precursor materials for nanotubes. Applied current and voltage are used to vaporize the electrodes and nanotubes condense from the plasma [17].

The SWNT yield of the pulsed laser vaporization technique is similar to that of the arc-discharge process, with reported yields between 70 and 90% [13]. Instead of an applied current, this method uses a laser to vaporize the carbon from a graphite target impregnated with nickel and cobalt catalysts. The nanotubes deposit on a collector at the opposite end of the reactor. A representative reactor is shown in Figure 2.5. Optimization of this method leads to a narrow diameter distribution (~1.4 nm) of nanotubes being produced [15].
Figure 2.5: Pulsed laser vaporization apparatus. A laser source is used to vaporize the graphite target to produce nanotubes [18].

Unlike the arc-discharge and pulsed laser vaporization techniques, the third technique does not use a solid source of carbon but rather uses carbon monoxide gas as the precursor material. The process is termed HiPco which stands for high pressure carbon monoxide, and a schematic is shown in Figure 2.6. An iron pentacarbonyl catalyst is added to flowing carbon monoxide. The catalyst decomposes when exposed to the high temperature and pressure used in the process, and nanotubes grow onto the newly formed iron clusters. The SWNT yield is reported as high as 97% [16]. The average size of nanotubes produced by this process is approximately 1.1 nm [19], and as will be shown in subsequent chapters, a larger distribution of diameters is seen with this process.
Figure 2.6: Schematic of HiPco reactor. Nanotubes are produced from a precursor gas containing an iron species catalyst [16].

2.2.2 Purification

In spite of differences in the production methods, the purification procedures are similar. Both methods rely on oxidation to remove the majority of the amorphous carbon and metal catalyst, and some changes to the nanotube surface occur because of purification. Specifically, carboxyl and hydroxyl groups are attached to the nanotubes at defect sites [15]. The methods differ in complexity with the pulsed laser vaporization nanotubes being purified by the simpler procedure. These nanotubes are subjected to oxidation by nitric acid for 45 hours [15]. Approximately 70% of the weight is lost during this step. Then, the majority of the acid is removed by decanting the supernatant liquid after centrifuging the nanotube/acid suspension. The sediment is suspended in water and subjected to further centrifuging cycles to remove the trapped acid. The HiPco nanotubes go through a more rigorous process [19]. The purification procedure begins with a heat treatment cycle in a wet Ar\textsubscript{2}/O\textsubscript{2} atmosphere. The parameters of this step vary
with the initial metal content, but a typical temperature and time is 225°C and 18 hours. This step opens the carbon surrounding the metal particles and oxidizes the metal particles. In the next step, the exposed, oxidized metal particles are removed by suspending them in hydrochloric acid either for short times (~15 minutes) using sonication for long times (~12 hours) using magnetic stirring. The nanotubes are then filtered and rinsed with water. A similar procedure is developed for nanotubes produced by the pulsed laser vaporization method [20], but that purification procedure is not used on the nanotubes purchased for the alignment study here. For more detailed information concerning nanotube purification, the reader is directed to references [15, 19, 20].

2.2.3 Properties

The unique structure of SWNTs creates superior multifunctional properties that make them candidate materials for a variety of applications. Experimental work concerning measured properties of SWNT ropes estimates their strength in the range of 13 to 52 GPa and their tensile modulus on the order of 1 TPa exceeding the values for steel by factors of at least 10 and 5, respectively [21-23]. When separated from a rope, these properties are expected to increase because it is easier for individual nanotubes to slide within a rope than for carbon-carbon bonds to break [24]. Electrical resistivity and thermal conductivity measurements along the length of the rope indicate values of approximately $10^{-4}$ $\Omega$ cm and 200 W/m K, respectively, for SWNTs [13, 25]. These values are one order of magnitude lower than graphite [26]. Overall, the properties of SWNTs are superior to those for VGCFs and Polyacrylonitrile-Based (PAN) carbon fiber as shown in Table 2.1. However, the measured properties are lower than those predicted
theoretically for SWNTs. Aspects of roping and different chiralities contribute to these discrepancies.

Table 2.1: Comparison of properties for SWNT ropes, VGCFs, and PAN carbon fiber. Theoretical values are in bold font. The PAN fiber properties are from Chawla [27]. HS denotes high strength fibers, and HM denotes high modulus fibers.

<table>
<thead>
<tr>
<th>Carbon Fiber</th>
<th>Fiber Diameter (nm)</th>
<th>Fiber Length (μm)</th>
<th>Tensile Strength (GPa)</th>
<th>Tensile Modulus (GPa)</th>
<th>Electrical Resistivity (Ω cm)</th>
<th>Thermal Conductivity (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>7000-10,000</td>
<td>Continuous</td>
<td>2.2(HM) 2.7(HS)</td>
<td>390(HM) 250(HS)</td>
<td>$18 \times 10^{-4}$</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

2.2.4 Nanotube/Polymer Composites

Nanotube reinforced polymer composites using MWNTs and SWNTs have shown promise with increased mechanical properties. Qian et al. [31] observes effective load transfer with TEM indicating good interfacial adhesion and reports 42% and 25% increases in tensile modulus and breaking strength, respectively, with 1 wt.% MWNT in polystyrene. Composite materials consisting of MWNTs and poly(methyl methacrylate) produced by Jin et al. [32, 33] possess improved storage modulus and the improvements are enhanced through the use of a compatibilizer to improve the interface. The storage modulus of a 30 wt.% MWNT/PMMA composite is 600% greater than the unfilled PMMA at 120°C. By adding poly(vinyldene fluoride) as a compatibilizer, the storage modulus at low temperatures also increases. Cooper et al. [34] utilizes three different kinds of carbon nanofibers: VGCFs, MWNTs, and SWNTs in a comprehensive study with PMMA. Good interfacial adhesion is not observed for any of the composites, and
the nanotube composites are more sensitive to the quality of the interface. The VGCF/PMMA composite possess improved tensile modulus and impact resistance, but the MWNT and SWNT composites demonstrate improvements only in impact properties.

Fiber spinning is used by other researchers to align nanotubes in a polymer matrix and produce greater mechanical property increases by utilizing the anisotropic nature of SWNTs. Haggenmuller et al. [35, 36] aligns SWNT in PMMA, polyethylene, and polystyrene matrices by fiber spinning and observes increases in yield strength as the draw ratio of the composite fibers increased. For a SWNT concentration of 5 wt.%, the yield strength doubled as the draw ratio increased from 40 to 300. Modulus increased with nanotube concentration, and modulus improvements greater than 450% are observed at nanotube loadings of 20 wt.%. However, the degree of alignment decreases with increasing nanotube concentration and increases with increasing draw ratio. Kumar et al. [37] also use fiber spinning to produce aligned SWNT/poly(p-phenylene benzobisoxazole) (PBO) composite fibers with improved mechanical properties. In addition to increased tensile strength, the presence of SWNTs increase the strain to failure fulfilling the promise of nanocomposites to increase tensile strength, tensile modulus, and strain to failure simultaneously. These initial results are promising, but they do not fulfill the potential of nanotubes to produce order of magnitude increases. Issues relating to interfacial bonding and roping are responsible for the discrepancy.

2.3 Vapor Grown Carbon Fibers

VGCFs are also carbon fibers with diameters on the nanometer scale. Unlike SWNTs, VGCFs do not form larger, ordered structures such as ropes. An individual
VGCF has a diameter between 70 and 200 nm and a length between 50 and 100 μm [38]. Due to the method by which they are made (chemical vapor deposition), the diameter may be increased to the micron scale. The structure is different from that of the SWNTs. It consists of graphene planes oriented around the fiber axis, resembling a tree-ring structure as shown in Figure 2.7. The outer surface is amorphous carbon in the as-produced form, but heat treatment can graphitize the surface.

![Figure 2.7: Typical cross section of a VGCF showing the concentric planes of graphite. Adapted from Tibbetts et al. [30].](image)

2.3.1 Production

These fibers were developed in the 1970's and 1980's and commercialized in the early 1990's [9], but the technology on which it is based originates from the production of electric lamp filaments in 1889 [30]. The method is similar to the HiPco method for producing SWNTs, but a hydrocarbon gas is used instead of carbon monoxide as the precursor material. The fibers are produced from the catalytic pyrolysis of the hydrocarbon gas where the specific catalyst is iron pentacarbonyl. A small amount of hydrogen sulfide is also added to melt the iron catalyst thereby increasing the VGCF yield [39]. A schematic of the reactor for producing VGCFs is shown in Figure 2.8.
2.3.2 Properties

The electrical, thermal and mechanical properties of VGCFs are attractive but less favorable than those of SWNTs by approximately one order of magnitude as shown in Table 2.1. The electrical resistivity and thermal conductivity are $10^{-3}$ Ω cm and 20 W/m K, respectively [30]. High temperature heat treatment can raise these values to $5 \times 10^{-5}$ Ω cm and 3000 W/m K [40], but the VGCFs used in this research are not heat treated. The tensile modulus and strength are 240 GPa and 2.9 GPa, respectively [30]. Their size and properties make VGCFs a reasonable model nanofiber for optimizing processing techniques before using SWNTs, and VGCFs also serve as a comparison nanofiber for SWNTs [41-45].
2.3.3 VGCF/Polymer Composites

VGCF properties make them desirable for use in polymer matrix composites. Experimental results from previously published research efforts indicate that VGCFs are suitable reinforcing agents for polymers. Lozano et al. demonstrates a 100% increase in dynamic mechanical properties with only 2 wt.% VGCF in a polypropylene matrix [46]. Other work by Tibbetts and McHugh with a higher loading of VGCFs in polypropylene produces 200% and 400% increases in tensile strength and modulus, respectively through post processing treatment of the VGCFs [47]. Patton et al. [48] combines VGCFs with an epoxy and poly(phenylene sulfide) to improve the flexural properties of the matrix materials. They obtain 68% and 91% increases in flexural strength in epoxy and poly(phenylene sulfide) respectively with a nominal fiber loading of 20% by volume. These increases are similar to those seen with SWNTs in spite of decreased properties with respect to SWNTs.

2.4 Solid Freeform Fabrication

Solid freeform fabrication (SFF) describes a class of additive manufacturing processes that build parts in a series of successive layers. Though many variations exist between the processes, the general manufacturing methodology is as follows. A three dimensional computer aided drafting (CAD) model is generated of the desired part. The CAD model is exported in the form of a .STL file and loaded into the software that runs the SFF process. The software slices the .STL file into layers with a thickness of less than a millimeter. The geometrical information about each slice is relayed to the SFF machine, and each layer is built, one on top of the other, until the part is complete. This
technology allows for the manufacture of parts with complex shapes, models on demand, and molds [49]. SFF is advantageous for the processing of nanocomposites because it allows for direct production of a part from a CAD model, which is also termed rapid prototyping. However, the mechanical properties of SFF parts are dependent on fusion between layers and deposited filaments. Insufficient fusion may lead to greatly reduced mechanical properties in the SFF part.

Most of the commercial processes in use today have their starts in the 1980’s, but the ideas behind layer manufacturing date back much further. Blanther suggests a similar layered method to fabricate molds for topographical maps in 1890. Using information from surveys, Blanther traces the outline of each topographical contour line onto a wax plate and cuts along the line to produce a positive and negative impression. The impressions are stacked and smoothed to create the positive and negative molds. A printed paper map is placed between the positive and negative forms and is pressed creating a relief map [49].

Another ancestor of SFF is photosculpture. This process dates to 1860 and used photos to create a sculpture. The apparatus consists of an array of cameras placed at 15° intervals in a circle around the subject. The cameras simultaneously photograph the subject. Each photo is used to create a cylindrical fraction of the sculpture, and the sections are put together to create the complete sculpture [49].

SFF techniques are generally classified according to the state of their starting materials: gas, liquid, or solid. This thesis focuses on two processes: Fused Deposition Modeling (FDM) and Extrusion Freeform Fabrication (EFF). FDM and EFF use solid
starting materials and an extrusion based deposition of material to induce prescribed alignment of the nanotubes and nanofibers.

Scott Crump developed FDM in 1988, and Stratasys, Inc. (Eden Prairie, MN) markets this technology [50, 51]. FDM uses continuous filament feedstock with a nominal diameter of 1.8 mm as its base material. The feedstock is fed into a heated extrusion head by a set of rollers. As the feedstock enters the heated head, it is liquefied and extruded through a nozzle of varying orifice size. The deposition pattern consists of a perimeter trace and a raster fill of the shape. The heated head moves in the X-Y plane to create the layer, and the support base moves down in the Z direction when a layer is complete. The material is subsequently deposited on a support base as shown in Figure 2.9. Its compact size and feedstock material also enable FDM with remote manufacturing capabilities, and the form of the starting material makes FDM a potential candidate for space-based manufacturing unlike other SFF techniques with liquid or powder starting materials [52].

Figure 2.9: Schematic of the FDM apparatus. Continuous filament feedstock is extruded through a nozzle and deposited to produce a part. Adapted from Shofner et al. [53].
A number of feedstock materials are available for FDM, including investment casting wax, thermoplastic polyester-based elastomer, poly(acrylonitrile-co-butadiene-co-styrene) (ABS) copolymer, polycarbonate, and polyphenylsulfone [54]. Most of these materials do not possess the strength to produce fully functional parts using FDM. The development of new materials for FDM is a way to overcome this limitation and extend its application range. In addition to intrinsically stronger materials such as ceramics and metal, reinforced polymers are being successfully developed with discontinuous fibers [55, 56]. These materials have shown initial gains in tensile strength and interlayer strength, often the weak link in an FDM part. In particular, nanofiber polymer composites are perceived as materials that should significantly enhance SFF methods because of their unique multifunctional properties (i.e., structural/electrical, structural/thermal, and structural/impact).

The majority of research concerning filled feedstock for FDM relates to the production of functional ceramic parts. Ceramic particles are combined with a polymeric binder to create the feedstock. The parts produced from this material are subjected to binder burn out cycles. Then, they are infiltrated with another material, sintered to densify the ceramic part, or considered finished. The concepts used to create functional ceramic parts with FDM could be used to remove the polymer matrix surrounding nanofibers such as VGCFs and SWNTs to create a part consisting of only nanofibers or a nanofiber template to be infiltrated with another material [46]. Novel piezoelectric ceramic/polymer composite materials, functional ceramic materials and porous ceramic biomaterials are produced in this manner [57-60]. A part of the research to produce these ceramic filled feedstock materials focuses on achieving dispersion and controlling
viscosity to attain uniform dispersion of the ceramic particles in the polymer binder [57-62]. These investigations are useful and relevant to the current research because issues of viscosity and dispersion are essential to their success.

As with ceramic filled feedstock materials, homogeneous dispersion of reinforcements and melt viscosity are crucial to fiber reinforced polymers for direct use with FDM. Two polymer matrix composite materials previously studied in this regard are glass fiber in ABS and thermotropic liquid crystal polymer (TLCP) fibril reinforced polypropylene [55, 56]. With the glass fiber reinforced materials, the researchers found that the addition of fibers to the ABS reduced the flexibility of the material to an extent that it could not be used with the FDM process. The addition of a plasticizer and compatibilizer to the glass fiber/ABS composite facilitated its use with FDM and produced gains in longitudinal mechanical properties and in interlayer strength. The TLCP fibril reinforced material also produced substantial increases in modulus with respect to polypropylene and ABS in a preliminary study. In addition to improved mechanical properties, both materials showed some preferential orientation of the fibers following processing by FDM. The alignment of fibers through FDM is a desirable outcome with nanofiber filled polymers. To obtain enhanced mechanical, electrical, and thermal properties in these composite materials, the fibers should have a high degree of alignment as dictated by their high aspect ratios.

The second SFF technique used in this research, EFF, is based on FDM technology. The Arizona Materials Laboratory at the University of Arizona and Advanced Ceramics Research developed EFF in the early 1990's. The original equipment consists of a syringe pump and a support stage. Modifications have included a
pump interfaced with a three-axis gantry system and a stationary support stage, a
stationary syringe pump with a moveable stage, and the inverse of the FDM equipment.
The starting material for this apparatus is generally a thixotropic liquid to prevent oozing
from the syringe pump and deformation of the part after deposition [63-65].

Advanced Ceramics Research modified the technology by retrofitting a FDM
Modeler from Stratasys, Inc, with a heated high-pressure extrusion head to enable the
processing of thermoplastic materials. The deposition procedure is similar to FDM, but
the starting material is usually a cylindrical billet (feedrod) not a continuous filament.
The extrusion head moves in the X-Y plane and the support stage indexes in the Z-
direction as shown in Figure 2.10. The high-pressure extrusion head allows softer
materials and more viscous materials that could not be processed by FDM to be used with
EFF [64, 66].

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Figure 2.10: Schematic of the EFF extrusion head and stage. The extrusion head moved
in the x-y plane and deposited material on the stage in the specified pattern to create a
layer of the part. The stage moved in the z direction to allow another layer to be built
upon the finished layer [67].
Previous work by Calvert *et al.* has demonstrated the capabilities of fiber filled feedstock using a process termed reactive EFF [63, 64, 68]. The starting material is a thixotropic slurry containing the monomer, crosslinking agent, fibers, and fumed silica. The material is loaded into a syringe pump and extruded in a similar manner as described above. The material can be polymerized as the build cycle continues if the base is heated, or the part can be cured after the part is complete. Epoxidized soybean oil and acrylate resins with micron-size glass, mineral and carbon fiber reinforcements have been processed [65, 68]. Like the composite research performed with FDM, these materials demonstrate improved mechanical properties and fiber alignment. Processing fiber filled-materials with EFF also allows the properties of the composite to be tailored by controlling the orientation of the fibers by changing the direction of extruded paths in the part. This effect is observed previously in reactive EFF with mineral fiber in epoxidized soybean oil [65]. The tensile properties increase approximately 70% as the orientation changed from perpendicular to parallel to the testing direction as shown in Figure 2.11. Therefore, previous work in the fields of carbon nanotube and nanofiber composites and SFF indicate that processing these composites with extrusion based SFF techniques has the potential to create a condition of controlled fiber alignment. By manipulating the orientation of the nanotubes and nanofibers, mechanical, electrical, and thermal properties of carbon nanotubes and nanofiber composites could be customized to create useful parts with multifunctional properties. This work represents the first step in creating multifunctional composites by evaluating the compatibility of nanofibers and SFF.
Figure 2.11: Effect of fiber alignment on the mechanical properties of Franklin fiber composites. All materials have 15.6 wt.% Franklin fiber. As the material aligns with the testing direction, mechanical strength and modulus increase. Adapted from Shofner et al. [53]. All data used is obtained from Liu et al. [65].

2.5: Chemical Functionalization of Nanotubes

The unique structure of nanotubes responsible for their remarkable properties also creates a challenge to exploiting these properties in composites. Nanotubes possess few defects resulting in a low reactivity, and van der Waals attractive forces between individual nanotubes cause the nanotubes to assemble into a hexagonal arrangement forming long ropes of nanotubes. Ineffective interfacial bonding and sliding of individual nanotubes within the ropes inhibits load transfer from the matrix to the fiber, limiting the amount of mechanical reinforcement achievable in polymer matrix composites [24]. The diameter of the rope is directly related to its load carrying capacity [22], and individual nanotubes are expected to provide the most reinforcement. Functionalization of the nanotube surface is a method to introduce reactive species, to disrupt the rope structure, and to obtain smaller diameter ropes and possibly individual
nanotubes. Functional moieties are attached to open ends and sidewalls, primarily to improve the solubility of nanotubes [69-77]. Among these methods, fluorination [74] is one of the few methods that is easily scalable and does not require a solvent for the reaction to take place making it an ideal method for creating the quantity of functionalized nanotubes required for composite applications.

In fluorination, fluorine atoms bond covalently to the nanotube sidewalls. STM studies show that the fluorine atoms tend to attach in circular bands around the diameter of the nanotube [78]. Longitudinal bands are also possible but less stable. These two types of fluorination are termed 1,4 and 1,2 fluorination, respectively, and are shown in Figure 2.12. The designations indicate which carbons in the hexagonal structure are bonded to fluorine.

![1,4 Fluorination][1,2 Fluorination]

Figure 2.12: Possible fluorine configurations on a nanotube sidewall [78].

Introducing fluorine functional groups onto the nanotube sidewall also creates a repulsive force between nanotubes, leading to a driving force for better dispersion in composites [79]. In addition to the results of this thesis, improved dispersion and
increased mechanical properties of fluorinated nanotubes with respect to purified nanotubes are observed in the works of Zhu et al. [80] and Geng et al. [81] in epoxy and poly(ethylene oxide) matrices, respectively. Both works follow a similar procedure for fluorinating nanotubes, but the work by Zhu et al. uses purified single wall nanotubes cut with acid as the precursor material for the fluorinated single wall nanotubes [73]. Beyond improved composite properties, this work provides insight into the thermal stability of the fluorine functional group and into the thermal decomposition of composites containing F-SWNTs. Also, it goes beyond the two studies by using traditional polymer processing techniques to study the real-world applicability of composites containing functionalized nanotubes and the effect of these processing techniques on the carbon-fluorine bond.
CHAPTER THREE

MATERIALS AND PROCESSING METHODS

3.1 Introduction

Chapter 3 details the materials and processing methods used to create the nanofiber and nanotube reinforced polymer matrix composites that are studied in this thesis. Section 3.2 details the composite starting materials: nanofibers, nanotubes, ABS, and polyethylene. The VGCF purification procedure is described because it was performed as a part of this research. The SWNT purification procedure is referenced because all purification is performed by the supplier. The SWNT fluorination procedure is described briefly to identify reaction temperatures and times, but the fluorination procedure development is not a focus of this research. Similarly, the polymers are purchased from commercial sources, so aspects of their polymerization and structure are included for completeness. Section 3.3 contains the processing steps common to both studies: incipient wetting, composite mixing, and compression molding. The first two processes encourage fiber dispersion, and the last step is used to form a flat sheet of the composite material. The next two sections describe aspects of the processing unique to each study: SFF processing and chemical functionalization characterization. The chapter ends with a conclusion.

3.2 Materials

The two separate studies covered in this thesis concern two composite materials. In the alignment study, as-received SWNTs, and P-SWNTs and P-VGCFs are
independently dispersed in ABS matrices. All of the SWNTs in the alignment study are produced by the pulsed laser vaporization method [15] and purchased from Tubes@Rice (Houston, Texas). ABS is commonly used in extrusion-based SFF techniques and is the preferred matrix of NASA Johnson Space Center, who partially sponsored this work. In the functionalization study, P-SWNTs produced by the HiPco method [16] and purchased from Carbon Nanotechnologies, Inc. (Houston, Texas) are used. A portion of these nanotubes are subsequently fluorinated. The matrix is polyethylene, and it is chosen based on the projected end use of the composites, light weight radiation shielding for space applications [82].

3.2.1 Fiber Preparation

The as-received VGCFs from Applied Sciences, Inc. (Cedarville, Ohio) are purified to remove soot and impurities and produce surface functionalization including hydroxyl groups, carboxyl groups, hydrocarbons, and quinone structures [83]. The fiber treatment consists of refluxing in methylene chloride, refluxing in water, and drying steps as outlined by Lozano et al. [84]. The procedure also helps in separating them from each other which aids in achieving homogeneous dispersion into the polymer matrix. All VGCFs used in this thesis are prepared by this method and are designated by P-VGCFs.

In contrast, four different forms of SWNTs are used: as-received laser, purified laser, purified HiPco, and fluorinated HiPco. All purification is performed by the supplier according to previously published techniques [16, 19]. The fluorination reaction is performed in Dr. Margrave's laboratory at Rice University according to previously published techniques [85]. P-SWNTs are the precursor material for the F-SWNTs. The
P-SWNTs are made into bucky papers before fluorination to maximize the batch size because they are received as a fluffy powder. To prepare the bucky papers, the SWNTs are put into solution with dimethyl formamide (DMF) by sonication. Then the SWNT solution is filtered using Teflon membranes with 1 micron pore size and then rinsed with methanol. To ensure complete removal of the solvent, the bucky papers are subjected to an additional drying step in a vacuum oven for at least eight hours. Fluorination is achieved in a temperature-controlled Monel reactor with a nominal batch size of 500 mg. The chamber is purged with helium gas, and then SWNTs are exposed to a mixture of gases including fluorine at a temperature of 175°C for six hours. The gas mixture generally includes helium, hydrogen, and fluorine with a gas flow ratio of 30:1:2, respectively [80, 86]. The fluorine gas usually is purchased mixed with helium for economical reasons, and the hydrogen catalyzes the reaction and strengthens the C-F bond [87]. The final stoichiometry is C₂F. Previous work has established this stoichiometry as the maximum degree of fluorination achievable without permanently destroying the nanotube structure [74]. Weight gain and X-ray photoelectron spectroscopy are used to verify the composition. Specific information about the characterization of the F-SWNTs is contained in Section 3.5.

3.2.2 ABS

ABS, one of the two thermoplastic polymer matrices used, is a moderately priced, easily fabricated, nontoxic, dimensionally stable, and water resistant thermoplastic copolymer [88]. Typical uses of ABS include housings for telephones, radios, televisions, and computers [89]. The combination of acrylonitrile, butadiene, and
styrene creates a polymer with the best attributes of each constituent. Acrylonitrile possesses good chemical resistance and mechanical properties. Butadiene has high toughness, and styrene eases processing. The three monomer constituents are joined in the form of a graft polyblend in the majority of ABS polymers available. They consist of discontinuous polybutadiene domains surrounded by styrene-acrylonitrile (SAN) continuously. The SAN is connected to the polybutadiene domains through styrene and acrylonitrile monomers. Figure 3.1 shows a TEM image of neat ABS stained with OsO₄. The dark and light regions are the polybutadiene domains and the SAN copolymer, respectively.

![Image](image.png)

**Figure 3.1:** Transmission electron microscopy image of ABS microstructure. Polybutadiene domains (dark) are dispersed with a SAN continuous copolymer (light).

Two different blends of ABS are used in the alignment study. The ABS material processed by FDM is MAGNUM® 213 ABS (M-ABS) from Dow (Midland, Michigan). The M-ABS is in pellet form. The ABS is chosen because it has similar physical properties to the P400 ABS (P-ABS) sold by Stratasys (Eden Prairie, Minnesota) for
FDM processing as shown in Table 3.1. M-ABS and P-ABS are proprietary ABS blends. However, most commercial ABS polymers have compositions within the following ranges: 20-30% acrylonitrile, 20-25% butadiene, and 50-60% styrene by weight [88]. The ABS polymer used for the EFF study is purchased from Aldrich (Milwaukee, Wisconsin) in powder form and is designated HB-ABS (High Butadiene ABS). The composition is approximately 40% acrylonitrile, 45% butadiene, and 15% styrene by weight. The higher butadiene content increases the toughness and viscosity but lowers the mechanical properties.

Table 3.1: M-ABS, P-ABS and HB-ABS properties [90, 91].

<table>
<thead>
<tr>
<th>Property</th>
<th>M-ABS</th>
<th>P-ABS</th>
<th>HB-ABS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.04</td>
<td>1.05</td>
<td>1.04</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>34.5</td>
<td>34.5</td>
<td>22.0*</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>2.48</td>
<td>2.48</td>
<td>0.27*</td>
</tr>
<tr>
<td>Softening Point (°C)</td>
<td>104</td>
<td>104</td>
<td>104*</td>
</tr>
</tbody>
</table>

*Properties measured experimentally by the author.

3.2.3 Polyethylene

Polyethylene, the second polymer matrix used, is a ubiquitous thermoplastic polymer used in applications ranging from packaging to children’s toys. Low cost, chemical resistance, and tunable mechanical properties make it the most common thermoplastic polymer available on the market [92]. The tuning of mechanical properties is accomplished through varying the polymer’s crystallinity and molecular weight; therefore, polyethylene is classified by its density. Low density polyethylene (LDPE) has the lowest crystallinity and the lowest mechanical properties due to chain branching. LDPE is typically used in non-structural applications such as coatings. Conversely, high
density polyethylene (HDPE) has higher degrees of crystallinity and higher mechanical properties with little chain branching [92]. HDPE can be used in applications such as shopping bags where a load is sustained for a short time. Polyethylene is generally not used in structural application due to its propensity to creep, though cross-linked polyethylene will show improved creep properties [93]. Medium density polyethylene (MDPE) has a degree of crystallinity and properties intermediate to those of LDPE and HDPE [92]. Typical properties of polyethylene as a function of density are shown in Figure 3.2

![Graph showing properties of polyethylene as a function of density.](image)

Figure 3.2: Physical properties of polyethylene polymers as a function of density. LDPE has densities between 0.91 and 0.95 g/cc; HDPE has densities between 0.94 and 0.965 g/cc (not shown in this figure). MDPE has densities intermediate to these values [92].

The polyethylene used in the functionalization study is a MDPE purchased from Aldrich (Milwaukee, Wisconsin). The polymer has a density of 0.94 g/cm³, a melting point range of 109-111°C, and a molecular weight of approximately 6000. The polymer was selected based on low molecular weight and availability in powder form. The low
molecular weight causes individual polymer chains to be on the same dimensional scale as an individual nanotube, and powdered polymers are desirable for the incipient wetting processing step described in the next section.

3.3 Composite Processing

Carbon nanofiber and nanotube reinforced polymer composites are prepared using multi-step processing protocols. This section outlines the processing steps common to both studies. The processes unique to each study, SFF and chemical functionalization characterization, are described in the following sections of this chapter. Three steps are used for all materials containing P-SWNTs and F-SWNTs: incipient wetting, composite mixing, and compression molding. All other composites and neat polymer samples are prepared with the composite mixing and compression molding steps only. The steps are presented in the order they are performed. The materials processing continues to SFF processing for the alignment study and ends with these steps for the functionalization study. Table 3.2 lists the composites prepared for the alignment and functionalization studies.

<table>
<thead>
<tr>
<th>Table 3.2: Material compositions processed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanotubes</td>
</tr>
<tr>
<td>Alignment: FDM</td>
</tr>
<tr>
<td>As-received laser</td>
</tr>
<tr>
<td>Purified VGCF</td>
</tr>
<tr>
<td>Alignment: EFF</td>
</tr>
<tr>
<td>Purified laser</td>
</tr>
<tr>
<td>Purified VGCF</td>
</tr>
<tr>
<td>Functionalization</td>
</tr>
<tr>
<td>Purified HiPco</td>
</tr>
<tr>
<td>Fluorinated HiPco</td>
</tr>
<tr>
<td>Fluorinated HiPco</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
3.3.1 Incipient Wetting

The first step in the processing protocol, incipient wetting, aids in dispersing SWNTs by creating an initial dispersion of SWNTs on the polymer surface prior to mixing [34, 36, 94], and the P-SWNT/HB-ABS, P-SWNT/MDPE, and F-SWNT/MDPE composites experience this step. In this method, nanotubes are dispersed in a solvent to break up larger agglomerated structures. The solution is combined with a polymer, and the solvent is evaporated using an oil bath. After the solvent is removed, an additional furnace heating step is performed to ensure that all of the solvent is removed. Polymer powders are particularly well suited to this processing step because they have more surface area than pellets have. The solvent chosen is specific to the polymer being used. It is desirable for the boiling point of the solvent to be lower than the polymer’s melting temperature to allow coating of the polymer particles. Table 3.3 details the incipient wetting parameters used in each of these systems. Different solvents are used in the MDPE composites because the P-SWNTs display a higher solubility in tertiary butanol than in isopropanol, so an additional 1.5 wt.% P-SWNT/MDPE composite is processed for comparison using isopropanol to determine the effect of solvent.

Table 3.3: Composites processed by incipient wetting.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Nanotubes</th>
<th>Solvent</th>
<th>Oil bath temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB-ABS</td>
<td>5 wt.% P-SWNT laser</td>
<td>Toluene</td>
<td>110°C</td>
</tr>
<tr>
<td>MDPE</td>
<td>1.5 and 5 wt.% P-SWNT HiPco</td>
<td>Tertiary Butanol</td>
<td>80°C</td>
</tr>
<tr>
<td>MDPE</td>
<td>1.5 wt.% P-SWNT HiPco</td>
<td>Isopropanol</td>
<td>80°C</td>
</tr>
<tr>
<td>MDPE</td>
<td>1.5 and 5 wt.% F-SWNT HiPco</td>
<td>Isopropanol</td>
<td>80°C</td>
</tr>
</tbody>
</table>
Prior to exposure to the solvent, both starting powders are white in color and free-flowing, and after incipient wetting, the changes in the powders' appearance are indicative of the solvent/polymer interaction. When the HB-ABS polymer powder is exposed to the toluene suspension, the polymer swells, so that as the solvent is removed, the remaining SWNTs are captured on the surface of the polymer. The MDPE powder does not show similar behavior because its inherent chemical resistance inhibits the ability of the MDPE to swell when exposed to solvent. The reaction is the same to tertiary butanol and isopropanol. Whereas the coated ABS particles tend to agglomerate and become black in color, the MDPE powder remains free-flowing and becomes gray in color. The difference in interaction is shown in Figure 3.3. The swelling of the polymer causes an intimate initial interaction between the HB-ABS and the nanotubes, and the limited swelling of the MDPE powder results in SWNTs coating the surface but not being captured by the polymer.

Figure 3.3: Overcoated HB-ABS (left) and MDPE (right) powders. The nanotubes are integrated into the powder surface of the HB-ABS, but because of the limited solvent/polymer interaction, the nanotubes inertly coat the MDPE surface. Adapted from Shofner et al. [67].
3.3.2 Composite Mixing

After creating an initial dispersion of nanotubes, they must be dispersed in the polymer matrices at the nanoscale. Dispersing particles with dimensions less than 1 μm (small particles) presents an additional challenge when compared with particles with larger dimensions because interparticle forces such as electrostatic, van der Waals, and dipole-dipole forces can cause the small particles to agglomerate [95]. High shear mixing has been shown to effectively overcome these particle-particle interactions and promote better dispersion of VGCFs in polypropylene by Lozano et al. [45]. This processing technique exploits the shear thinning behavior of nanotube reinforced polymer composites and overcomes the processing difficulties associated with melt viscosity increases caused by the addition of nanotubes in bench top mixing.

High shear mixing is accomplished in a Haake Polylab Rheomix 600 internal batch mixer with roller type rotor blades and a 30 cm³ mixing bowl. A schematic of this type of mixer is shown in Figure 3.4. The mixer bowl is formed by three plates with internal heaters and thermocouples to maintain the set temperature, and internal channels in the middle plate allow active cooling with an air supply. The front plate is solid and contains a thermocouple to monitor the melt temperature independent of the set temperature. The middle plate has a cavity shaped like two connecting circles and a vertical channel for material loading. The rotor blades are placed into bronze bushing fitted into the back plate. The rotor blades do not intermesh and turn in opposite directions at different speeds. Both rotors turn toward the center of the mixing bowl and usually the speed ratio is 3:2 [83]. During mixing, a ram is lowered through the vertical
channel in the middle plate to form part of the mixing bowl boundary. The ram is held in place by a weight above it.

![Diagram of internal batch mixer schematic](image)

1. Back Plate
2. Bushings
3. Rotor Shafts
4. Rotors
5. Air-Cooling Channels
6. Center Plate
7. Melt Thermocouple
8. Front Plate
9. Heaters
10. Air Exhaust
11. Air Valve and Metering Plate
12. Ram

Figure 3.4: Internal batch mixer schematic. Adapted from Cheremisinoff [96].

Mixing can be classified into two broad categories: dispersive and distributive; both types of mixing are present in an internal mixer [97]. Dispersive mixing breaks down agglomerates of small particles by overcoming the interparticle forces, and distributive mixing involves the random rearrangement of the minor phase (particle) in the major phase (polymer) without any change in size of the minor phase. Distributive mixing takes place in the center of the mixing bowl and dispersive mixing near the rotor.
tips when close to the mixing bowl wall. Both types of mixing are required to create an ideal state of mixing for nanofiber composite because dispersive mixing breaks up the agglomerates and distributive mixing spreads out the fibers. In the case of VGCFs, individual fibers are dispersed and distributed, and for SWNTs, ropes are dispersed and distributed but not observed to be broken down into individual nanotubes.

All materials and neat polymers are processed by high shear mixing in nominal 20 g batches. The mixing temperature, time, and speed are tailored to the material system. The temperature and time are chosen with consideration to both thermal and thermomechanical polymer degradation, respectively. The mixing speed must be high enough to produce a shear stress larger enough for dispersive mixing to occur but not so high as to introduce microbubbles into the melt [98]. The mixing behavior is characterized by mixing torque as a function of mixing time. A plot of this data, called a rheogram, is shown in Figure 3.5. The torque increases sharply as the material is loaded into the mixing bowl. As the materials melt or soften, the torque lowers to a steady state value. Achieving steady state indicates that the highest degree of mixing capable by the equipment has occurred [98]. The mixing parameters used in this work are the result of process optimization performed by the author as well as other members of the Barrera Research group, specifically Dr. Karen Lozano and Fernando J. Rodriguez-Macias. The mixing parameters used for the M-ABS materials are a mixing time of approximately 10 minutes, an initial mixing speed of 60 rpm, and a mixing speed of 90 rpm during the last two minutes. The neat and VGCF reinforced M-ABS polymer are mixed at 165°C, and the SWNT/M-ABS composite is mixed at 185°C. The mixing torque is not increased by the presence of VGCFs and SWNTs in the M-ABS materials as shown in Figure 3.5. The
torque is noticeably lower for the SWNT composite because of the higher mixing temperature. The peak torque positions are offset from one another because of differences in material loading time.

![Graph showing mixing torque over time]

**Figure 3.5:** Rheogram of M-ABS materials showing no detrimental effect from the addition of nanofibers.

The HB-ABS materials are mixed with the following parameters: mixing time of approximately 10 minutes, mixing speed of 60 rpm, and mixing temperature of 140°C. The higher butadiene content of this polymer increases the elasticity and allows the melt to be mixed at a lower temperature. As shown in Figure 3.6, the torque required to operate at these conditions is similar to the torque seen in the rheograms of the M-ABS materials. The torque is also not increased with the addition of nanofibers.
Figure 3.6: Rheogram of HB-ABS materials showing equal steady state mixing torque for the neat polymer and 5 wt.% nanofiber composites. Adapted from Shofner et al. [67].

The polyethylene composite shows a different mixing behavior than the ABS polymers because of its low melt viscosity resulting from the low molecular weight and narrow melting point range. The viscosity, evidenced by mixing torque, is observed to increase with increasing nanotube loading in the polyethylene matrix, but the same loading of F-SWNTs causes a larger increase to the melt viscosity than P-SWNTs as shown in Figure 3.7. The greater mixing torque of the F-SWNT materials is not intuitive because previous studies show that melt viscosity increases with nanotube loading [35, 99]. The composition of the F-SWNT composites include the weight of the fluorine functional groups, so the composite materials loaded with F-SWNTs have less carbon nanotube component than the composites prepared with the same loading of P-SWNTs. The 1.5 wt.% and 5 wt.% F-SWNT composites contain approximately 0.8 wt.% and 2.8 wt.% SWNTs, respectively. The higher SWNT content in the P-SWNT composites is
expected to produce the larger torque. However, the fluorination disrupts the larger bundles of nanotubes, so the isolated, smaller ropes act similarly to a larger loading of nanotubes.

![Graph showing torque vs loading for F-SWNT and P-SWNT composites](image)

**Figure 3.7:** Mixing behavior of the neat MDPE and composites. The mixing torque was greater in F-SWNT/MDPE composites despite lower carbon nanotube content, indicating that the fluorination has created a larger number of smaller diameter nanotube ropes.

### 3.3.3 Compression molding

Following mixing, the materials are pressed into sheets using heated compression molding. A Carver press with heated plates and integral water cooling is used. Aluminum molds are used to create 100 mm by 100 mm sheets with a nominal 1 mm depth. Mylar® sheets are used as the mold release. The materials are pressed at temperatures similar to their mixing temperature for approximately five minutes at forces between 6 and 10 metric tons. Cooling is achieved under pressure using the water cooling system.
3.4 Solid Freeform Fabrication

Nanotube and nanofiber alignment is achieved through two extrusion-based SFF techniques: FDM and EFF. FDM requires starting material in the form of continuous filament feedstock, so the granulated sheet materials are extruded using a HAAKE Polylab Rheomex 252 extruder. It is a single screw extruder with an L/D ratio of 25 and three heating and cooling zones. The materials are extruded at a temperature profile starting at 185°C and ending at 200°C and with a screw speed of approximately 8.5 rpm. The composite feedstock is spooled by hand onto a FDM reel. Some variation in feedstock diameter results from manual material collection. Each filament has a nominal diameter of 1.8 mm to facilitate FDM processing. In the case of the VGCF/M-ABS and SWNT/M-ABS materials, the composite granules are preceded and followed by neat ABS pellets to enable recovery of all the material and to reduce the amount of composite material needed to fill the extruder barrel. Consequently, limited porosity is observed in the VGCF/ABS filament material resulting from the different size distributions of the ABS pellets and the VGCF/ABS pellet granules used during the extrusion process and not from the initial shear mixing. Eliminating the neat ABS pellets before and after the VGCF/ABS granules during extrusion should remove the porosity from future work. Also, the composition of the feedstock varies over the length of the filament with the maximum composition (10 wt.%) at the middle of the extrusion run. A spool of neat ABS is also extruded from the plain pellets to use as a comparison material. Figure 3.8 shows the spools of neat M-ABS, 10 wt.% VGCF/M-ABS and 5 wt.% SWNT/M-ABS with approximately 20 meters of feedstock on each spool.
The composite filament feedstocks are less flexible than the neat ABS is, but they could be collected on FDM spools manually and processed by FDM unlike previous work with glass-fiber filled ABS feedstock [56]. The prepared spools are used in a Stratasys FDM 1600 Modeler. Neat M-ABS, VGCF/M-ABS, and SWNT/M-ABS materials are used to fabricate straight bar and three types of dogbone tensile samples for the mechanical property measurements with different layer orientations as described in Table 3.4.

In this research, an orientation of $0^\circ$ indicates the extruded path is parallel to the long axis of the sample and testing direction. Conversely, an orientation of $90^\circ$ indicates that the extruded path is perpendicular to the long axis of the part and to the tensile testing direction. The straight bar samples have 11 layers, and the samples have layer orientations of $0^\circ/90^\circ$, $90^\circ/0^\circ$, and $45^\circ/45^\circ$. The first angle indicates the alignment of the top layer (last built), so in the case of the $0^\circ/90^\circ$ samples, six layers are parallel to the
long axis of the part. The second set of samples processed has a dogbone shape and nine layers. The layer orientation is $90^\circ/0^\circ$. The third set of samples manufactured has a dogbone shape and six layers. The shape is similar to an ASTM D638 Type V specimen but with a slightly wider gage section. The layers of these specimens are oriented in a $10^\circ/90^\circ$ arrangement.

Table 3.4: FDM tensile sample descriptions. Adapted from Shofner et al. [100].

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Sample Shape</th>
<th>Nominal Dimensions (mm)</th>
<th>Materials</th>
<th>Layer Orientation</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Straight bar</td>
<td>9.4 (Width) 3 (Thickness) 51 (Overall Length)</td>
<td>M-ABS</td>
<td>$0^\circ/90^\circ$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VGCF/M-ABS</td>
<td>$0^\circ/90^\circ$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$90^\circ/0^\circ$</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$45^\circ/45^\circ$</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Dogbone</td>
<td>4.8 (Width) 2.4 (Thickness) 12.7 (Gage Length)</td>
<td>M-ABS</td>
<td>$90^\circ/0^\circ$</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VGCF/M-ABS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>SWNT/M-ABS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Dogbone</td>
<td>4.8 (Width) 1.6 (Thickness) 12.7 (Gage Length)</td>
<td>M-ABS</td>
<td>$10^\circ/90^\circ$</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VGCF/M-ABS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ASTM D638 Type V Dogbone</td>
<td>3.2 (Width) 1.3 (Thickness) 7.6 (Gage Length)</td>
<td>P-ABS</td>
<td>$0^\circ/0^\circ$</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M-ABS</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VGCF/M-ABS</td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>

The fourth set of samples is made to the Type V dogbone geometry outlined by ASTM D638, and all five layers of these specimens are oriented parallel to the long axis of the part. This set of samples also contains tensile samples made from the P-ABS for
comparison. Whereas the first two sets of dogbone samples are made using the default build parameters, the Type V specimens are made using optimized build parameters by Rodriguez et al. [101] to maximize the strength of the parts. Work by Rodriguez et al. [101-103] has led to an increased understanding of the relationship between build parameters and properties for the P-ABS. The build parameters for the filled samples are adjusted to accommodate the reduced swelling of the filled feedstock.

In contrast to the continuous filament feedstock of FDM, the EFF starting material is in the form of cylindrical billets called feedrods. The granulated material is consolidated into feedrods for EFF by packing the pellets into a 15.87 mm diameter mold with a hydraulic ram and heating to 150°C. After 10 minutes, the mold is cooled, and the feedrod is removed using the ram. The finished feedrod has a diameter of 15.75 mm and a length of approximately 115 mm. The feedrods are loaded into the EFF head and extruded using a 0.6 mm nozzle. The increased viscosity of the composite materials with respect to the neat ABS mandates that a higher temperature and force be used to fabricate the composite parts. Unlike the mixing step, EFF uses a shear rate that is not large enough to produce dramatic shear thinning behavior. The values are shown in Table 3.5. As the amount of material decreases, the force required to extrude the material decreases, so the force values used for the composite materials are expressed as a range with the higher force initially and the lower force at the end of the extrusion cycle. The material is deposited in the shape of an ASTM D638 Type V tensile sample. Each part has 5 layers, and the extruded paths are all parallel with the long axis of the part creating an anisotropic fiber orientation. Composite fibers are made using 0.3 mm and 0.6 mm nozzles to study the alignment capabilities of EFF, but mechanical properties are
measured for composite fibers produced using the 0.6 mm nozzle only. The composite material is not subjected to further drawing after leaving the extrusion nozzle, and similar amounts of thermal contraction are observed for all of the materials. Changing the rate at which the extruder head moves could be used in future work to induce drawing as the material is deposited.

Table 3.5: Extrusion parameters used during EFF processing. Adapted from Shofner et al. [67].

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat HB-ABS</td>
<td>180</td>
<td>1330-890</td>
</tr>
<tr>
<td>5 wt.% VGCF/HB-ABS</td>
<td>200</td>
<td>3110-2220</td>
</tr>
<tr>
<td>5 wt.% SWNT/HB-ABS</td>
<td>200</td>
<td>3560-2890</td>
</tr>
</tbody>
</table>

3.5. Chemical Functionalization Characterization

The F-SWNTs used in the functionalization study have a dramatically different electronic structure due to the fluorine bonded to the sidewalls, so additional characterization steps are needed to establish the starting condition of the nanotubes. Prior to processing in Section 3.3, the chemical bonding structure of the nanotubes used in the functionalization study is shown with XPS and Raman spectroscopy. XPS measurements are done using a Physical Electronics 5700 instrument and non-monochromatic Al Kα incident radiation. Survey scans are used to identify peaks of interest, and then high-resolution scans of these peaks are conducted on each sample. Raman spectroscopy measurements are done using a Renishaw MicroRaman spectrometer with 780.6 nm laser and a resolution of 2 cm⁻¹. The objective used is 50X with a 0.55 μm aperture.
XPS analysis shows that carbon, oxygen, and iron are present in the P-SWNTs and that carbon, fluorine, and oxygen are present in the F-SWNTs. The residual iron catalyst is not observed, but it is most likely obscured by the fluorine peaks. The C1s scans of the P-SWNTs and F-SWNTs are shown in Figures 3.9 and 3.10, respectively. The C1s scan of the P-SWNTs contains peaks of the sp² carbons at 284.8 eV, oxygen grafted carbons in the form of hydroxyl and carboxyl groups at 286.1 and 288.3 eV, and a π-π* shake-up peak at 290.6 eV [104, 105]. The oxygen grafted carbon states can be formed during the oxidizing acid treatment step in the purification procedure [15].

![C1s Spectra](image)

Figure 3.9: C1s scan by XPS of the P-SWNTs showing the carboxyl and hydroxyl groups created by purification.

The C1s scan of the F-SWNTs also showed sp² carbon at 284.7 eV and oxygen grafted carbons at 285.8 eV, and two peaks characteristic of fluorinated carbon were observed at 287.7 and 289.9 eV [106]. Analysis of the peaks produced elemental
percentages of 54.17% carbon, 43.35% fluorine, and 2.48% oxygen for the F-SWNTs, consistent with a stoichiometry of approximately C₂F [79].

![C₁s Scan by XPS](image)

Figure 3.10: C₁s scan by XPS of the F-SWNTs showing the change in carbon bonding states caused by fluorination.

Raman spectroscopy also demonstrates the significant change to the P-SWNT structure caused by fluorination as seen in Figure 3.11. The radial breathing modes between 200 and 300 cm⁻¹, the disorder mode indicative of defects in the form of sp³ carbon bonding at approximately 1300 cm⁻¹, and the tangential stretching mode indicative of sp² carbon bonding at approximately 1590 cm⁻¹ are monitored for wavenumber shifts to signal interaction between the nanotubes and the polymer or changes to the nanotubes. The Raman features of the nanotubes prior to fluorination were typical of P-SWNTs, but after the fluorination, the bonding states of the carbon atoms have largely changed from sp² to sp³ because the fluorine has bonded to the nanotubes at the unsaturated sidewall
sites [79, 107]. The sp² carbon peak of the graphene π-system at 1592 cm⁻¹ disappeared, leaving a shoulder at 1565 cm⁻¹ due to a disrupted π-conjugation, and the intensity of the disorder mode increased. The latter mode did not shift appreciably because the mass difference between the oxygen functional groups on the sidewalls of the oxidized SWNTs and the fluorine functional groups is not significant. The breathing modes were obscured by the background and showed only two defined peaks.

Figure 3.11: Raman spectra of P-SWNTs and F-SWNTs showing the shift from sp² to sp³ carbon hybridization caused by fluorination.

3.6 Conclusion

The starting materials and processing techniques for the two composite systems used to evaluate the effect of alignment and chemical functionalization with respect to SWNT reinforced polymer composites are described in this chapter. Dispersion is achieved through incipient wetting and shear mixing. In all cases, commercially acquired polymers are compounded with nanotubes or nanofibers to create the composite. After
the common processing steps, the materials used in the alignment study are extruded using SFF techniques to align the fibers whereas the materials used in the chemical functionalization are further characterized. Chapter 4 focuses on the effectiveness of the processing presented here to achieve dispersion as well as aspects of alignment, degradation, and interfacial properties.
CHAPTER FOUR

DISPERSION, ALIGNMENT, DEGRADATION, AND INTERFACIAL PROPERTIES

4.1 Introduction

The mere presence of additives or fillers in polymer matrices does not guarantee mechanical property increases. Among the factors that influence the filler's effect on mechanical properties are dispersion, alignment (in the case of anisotropic fillers), degradation to the host material caused by processing or the addition of fillers, and interfacial properties. Chapter 4 describes these aspects related to the nanofiber and nanotube reinforced polymers processed for the alignment and chemical functionalization studies. Section 4.2 includes the dispersion analysis with emphasis on the effect of purification and functionalization procedures. The next section evaluates the effectiveness of SFF in aligning VGCFs and SWNTs in ABS matrices. Section 4.4 contains a through analysis of possible polymer degradation with respect to bulk thermal degradation, structural degradation, and viscosity degradation, and Section 4.5 discusses the interfacial properties achieved in the composite materials produced for both studies. The chapter ends with a conclusion. The mechanical properties achieved as a result of these composite properties is detailed in the subsequent chapters.

4.2 Dispersion

Mechanical property increases in nanofiber reinforced composites require a high dispersion state though its effect on other multifunctional properties such as electrical conductivity is less understood [108]. Agglomerated fibers cause stress concentrations
and premature failure of the material. To date, the dispersion in nanotube reinforced composite is evaluated mainly by microscopy which can be subjective. Recent developments in rheological methods [109] could provide another evaluation tool and create a more objective standard for dispersion, but it may only be effective at low concentrations as it relies on the observation of network formation which can be observed in very low loadings of nanotubes [1, 2]. In this work, the degree of dispersion achieved is evaluated using fractography where the imaging is performed with a scanning electron microscope (SEM), specifically a Phillips Electroscan XL30 SEM. Through examinations of the exposed surfaces of multiple samples are conducted to determine the macroscopic level of dispersion. The samples are broken at room temperature and in most cases by a tensile test. The MDPE materials are fractured manually. All samples, except the 5 wt.% P-SWNT/HB-ABS samples, are coated with gold to dissipate charge from the SEM’s electron beam. The 5 wt.% P-SWNT/HB-ABS samples possess enough intrinsic conductivity to resist charging during imaging [94].

Previous research by Lozano et al. demonstrates the effect of purification on VGCF dispersion in thermoplastic matrices [83]. In addition to removing soot and impurities, the purification procedure loosens the entanglements between VGCFs in the as-received condition and aids in achieving homogeneous dispersion. Both samples containing VGCFs, the VGCFs are well dispersed, separated from one another, and surrounded by the polymer matrix as shown in Figure 4.1. Also, increasing the VGCF concentration from 5 wt.% to 10wt.% does not diminish the dispersion of VGCFs in the matrix.
Figure 4.1: VGCFs dispersed in ABS matrices. The image on the left is 10 wt.% P-VGCFs/M-ABS, and the image of the right is 5 wt.% P-VGCFs/HB-ABS. Both systems show homogeneity. Adapted from Shofner et al. [100].

Similarly, incipient wetting and purification has an impact on the dispersion of SWNTs in ABS matrices. Both materials experience similar levels of mixing torque, indicating that similar amounts of shear stress are imparted on the SWNT agglomerates, but the composite containing as-received SWNTs did not disperse evenly in the matrix. The SWNT/M-ABS composite has a polka-dot morphology. Tangled masses of nanotubes are surrounded by polymer containing no nanotubes. Few isolated ropes are observed. The purified nanotubes also show entanglement at the exposed surface, but the entanglement is due to the formation of an interconnected network. Electrical conductivity measurements performed on this material by Barrera [94] indicate that the percolation threshold is approximately 1 wt.%, so at a loading of 5 wt.% nanotubes, a percolated network is formed. The network structure is more open and nanotubes are distributed evenly over the entire fracture surface. Since incipient wetting and purification are not studied separately, their independent effects cannot be deduced. Likely, they both contribute to the improved dispersion in a synergistic way. Purification removes metal catalysts and amorphous carbon loosening the entanglement, and incipient
wetting provides the energy necessary to break up the larger structures and keep them separated when they are initially applied to the polymer. The viscosity of the polymer melt during mixing does not allow sufficient diffusion to occur for reagglomeration. The differences in dispersion levels achieved with as-received and purified nanotubes are shown in Figure 4.2. The difference in dispersion level is apparent at multiple magnifications. As-received nanotubes appear as large agglomerated bundles while the P-SWNTs appear entangled but evenly distributed over the entire fracture surface.

Figure 4.2: Dispersion level achieved in composites containing as-received (left) and purified (right) SWNTs. Adapted from Shofner et al. [67], [53].
Unlike the ABS polymers, the lower mixing torque experienced by the MDPE materials and low melt viscosity reduce the amount of shear stress experienced by the melt, allowing the effect of chemical functionalization on dispersion to be studied nearly independently from high shear mixing. The fluorine groups on the nanotube surface create a driving force for better dispersion through repelling other surface fluorine groups [79, 107]. The repulsive force results in a more homogeneous dispersion of f-SWNTs in the polyethylene than the P-SWNTs, as shown in Figure 4.3. The f-SWNTs appear as smaller separated ropes whereas the P-SWNTs are observed as agglomerated bundles separated by regions containing no nanotubes. The smaller ropes behave similarly to a larger concentration of nanotubes. The observation supports the higher torques seen in the f-SWNT composites in Chapter 3. The two solvents used in this work produce the same mixing and dispersion behavior in the P-SWNTs in spite of an increased solubility of P-SWNTs in tertiary butanol.

Figure 4.3: Dispersion of 1.5 wt.% F-SWNTs (left) and 1.5 wt.% P-SWNTs (right) in MDPE. Both samples used isopropanol as the solvent during incipient wetting.
Combining the knowledge gained from analyzing the materials processed for the alignment and chemical functionalization studies, fiber treatment, be it purification or functionalization, can improve dispersion of nanofibers and nanotubes. Conventional shear mixing and purification creates an improved dispersion state of VGCFs and SWNTs in ABS matrices. Direct comparisons can be made between purified and as-received SWNTs from this work. Fluorination also improves dispersion with respect to purification in the absence of high shear forces during processing.

4.3 Nanofiber and Nanotube Alignment

The degree of fiber alignment becomes more critical as the fiber diameter decreases and the tensile strength increases. Smaller amounts of misalignment are acceptable as fiber diameter decreases, tensile strength increases, and concentration by weight remains constant. Using mathematical models such as the Kelly-Tyson [110], this effect becomes apparent when considering individual nanotubes, VGCFs, and conventional PAN carbon fiber of equal aspect ratio. This model calculates composite strength of a unidirectional composite as a function of fiber angle with consideration to three stress states. Which stress state causes failure (fiber strength, shear strength, or matrix strength) depends on the angular orientation of the fibers. Maximum strengthening occurs when the fiber is able to carry the load, and as misorientation increases above a critical point, the composite strength drops dramatically. Figure 4.4 shows this behavior for the SWNT, VGCF, and PAN carbon fiber reinforced HB-ABS with 5 wt.% fiber reinforcement. The fiber properties used in the model are those presented in Table 2.1, and the matrix properties include those contained in Table 3.1 and
a shear modulus of 100 MPa. The critical amount of misorientation predicted by this model is 4.7° for SWNTs whereas the critical misorientation is 25° and 45° for VGCFs and conventional PAN carbon fibers, respectively. The model indicates that achieving optimum strength improvements with SWNTs requires a high degree of alignment, and more latitude is available with VGCFs and conventional carbon fiber.

![Graph showing composite strength as a function of fiber misalignment angle](image)

Figure 4.4: Kelly-Tyson prediction of critical fiber misalignment for individual SWNTs, VGCFs, and PAN carbon fiber. The amount of fiber misorientation increases as fiber diameter increases and fiber strength decreases. Adapted from Barrera [94].

In spite of similar aspect ratios, the SFF processing achieves different degrees of success aligning nanofibers and nanotubes. The alignment of VGCFs in the FDM feedstock and parts are observed in fracture surfaces with SEM imaging. The low ductility of the M-ABS allows the VGCFs to be observed in exposed surfaces. The HB-ABS has higher ductility and plasticity, so the true orientation of the VGCFs is more difficult to observe by fractography. An alternative method is developed to determine the
degree of VGCF alignment caused by EFF. The analysis method used is selective
dissolution of the matrix. VGCF reinforced EFF fibers are subjected to a solvent of the
polymer. The EFF fibers are soaked in chloroform for one minute to etch away a portion
of the ABS and rinsed with water to stop the process. The EFF fiber’s structure is
preserved, and the exposed VGCFs are observed in the resulting material using SEM.
The rigidity of the VGCFs allows them to be studied in this manner because the
nanofibers’ orientation does not change during selective dissolution. FDM feedstock
preparation by the single screw extruder and both SFF processing methods result in
VGCF alignment as seen in Figure 4.5.

Figure 4.5: Alignment of VGCFs in ABS matrices. The arrows indicate the direction of
extrusion. Adapted from Shofner et al. [67, 100].
The FDM feedstock shows a high degree of alignment that is maintained through FDM processing. The FDM part in Figure 4.5 displays VGCFs aligned perpendicular and 10° off of parallel with respect to the testing direction. The different macroscopic alignment provides the opportunity to create parts with tunable multifunctional parts through layer orientation. The EFF fiber also shows VGCFs aligned with the extrusion direction. Porosity seen in this image is the result of the selective dissolution process and is not observed in fracture surface from tensile tests.

The nanotube alignment cannot be observed visually because the nanotubes have a higher flexibility than the VGCFs, so at the exposed surface, the nanotubes fold over and do not retain their as-processed alignment. Therefore, Raman spectroscopy is performed with the instrument described previously in Section 3.5 to study SWNT alignment in the FDM feedstock, FDM and EFF dogbone specimens, and EFF fibers. By computing the ratio of the spectra intensity taken parallel and perpendicular to the extrusion direction, information about the fiber alignment can be obtained [111]. The intensity of the $E_{2g}$ tangential stretching mode peak at approximately 1590 cm$^{-1}$ is used to assess the degree of alignment. Five measurements are made for the FDM parts and EFF fibers produced by the 0.6 mm and 0.3 mm nozzle for a total of fifteen measurements. The average ratio of intensities taken parallel and perpendicular to the EFF fiber axis is 1.49 for samples produced by the 0.6 mm nozzle and 1.64 for samples produced by the 0.3 mm nozzle. The measurements taken on the larger EFF fiber had a smaller degree of scatter than the measurements taken on the smaller EFF fiber as shown in Table 4.1.
Table 4.1: Raman spectroscopy results for SWNT/ABS composite alignment. Adapted from Shofner et al. [67].

<table>
<thead>
<tr>
<th>Nozzle Diameter</th>
<th>Average Ratio</th>
<th>Highest Ratio</th>
<th>Lowest Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 mm (EFF)</td>
<td>1.49</td>
<td>1.58</td>
<td>1.41</td>
</tr>
<tr>
<td>0.3 mm (EFF)</td>
<td>1.64</td>
<td>2.39</td>
<td>1.09</td>
</tr>
<tr>
<td>0.3 mm (FDM)</td>
<td>1.57</td>
<td>2.15</td>
<td>0.85</td>
</tr>
</tbody>
</table>

The differences in measurement variation are related to different degrees of surface roughness in the EFF fibers. The surface roughness is discussed further in the next section concerning degradation. FDM parts show a similar degree of alignment with a ratio of 1.57. The scatter in these measurements is also large, but the surfaces of the material are smooth. The large variation is attributed in this case to the poor dispersion of the as-received SWNTs observed in the fracture surfaces of the FDM parts. These results indicate that some degree of alignment can be attained, but the alignment is not uniform due to manual spooling in both cases, surface roughness in the EFF fibers and poor dispersion in the FDM parts. Even the highest measurement recorded does not indicate a high degree of alignment compared to published work with spun fibers [35, 36, 111]. While better alignment should produce higher property increases, uniform alignment may not always be desirable in SFF applications because fibers bridging across extruded paths can provide increased stability to the part and improved interlayer strength. Therefore, intermediate enhancements in alignment could play a significant role.

4.4 Degradation

To achieve dispersion and alignment in a thermoplastic polymer, processing techniques involving heat and shear forces are generally used. A detrimental result of
these methods can be degradation to the host polymer. In addition, introducing fillers can adversely affect the matrix's physical properties. In this research, both issues are relevant to materials processed for the alignment and functionalization studies because of the multi-step processing protocol used. The M-ABS materials are not tested by the methods described in this section because they do not exhibit any evidence of degradation. The steady state mixing torque measured during compounding remains constant, as shown in Figure 3.5, and the extruded parts have smooth surfaces. However, the surface roughness present in the P-SWNT/HB-ABS composite material following EFF processing warrant further study to determine the cause. The materials in the functionalization study are tested specifically to understand the thermal stability of the fluorine functionalization and how its removal may impact the relationship between the nanotube and the polymer. Thermogravimetric analysis (TGA) and TGA coupled with infrared spectroscopy (TGA-IR) observe bulk thermal degradation in both sets of materials and fluorination stability in the functionalization study materials, respectively. Additionally, polymer structural changes are observed with solid state infrared (IR) spectroscopy for the HB-ABS and MDPE matrix materials. A decreased degradation temperature and changes to absorption bands will indicate material degradation in TGA testing and IR spectroscopy, respectively.

4.4.1 Bulk Thermal Degradation: TGA

As stated above, TGA is used to assess bulk degradation properties of materials and observe the thermal evolution of fluorine functional groups through evolved gas analysis using TGA. TGA uses a microbalance inside a furnace to track the weight loss
of a material as it is heated through a controlled temperature program. The test is conducted in the presence of flowing gas or vacuum, so many degradation patterns may be studied with this versatile technique. TGA experiments with the HB-ABS materials and MDPE materials are conducted using a TA Instruments SDT 2960 device.

Additional TGA-IR decomposition experiments are performed on a TA Instruments Q500 TGA coupled to a Thermo-Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer. In both types of TGA experiments, the tests are performed at a rate of 10\degree C/minute. All materials are tested in an air environment with a flow rate of 100 mL/min to test the thermo-oxidative stability. In addition to these tests, the MDPE materials are tested in a nitrogen environment with a flow rate of 100 mL/min to enable collection of the nanotube residue following the test for further study.

To better understand the decomposition pattern of ABS, the components of ABS, SAN and polybutadiene, are also tested with TGA. As seen in Figure 4.5, the SAN degrades at a higher temperature when incorporated into ABS, but the thermal stability of polybutadiene is lowered when incorporated into ABS. The destabilizing effect of SAN on polybutadiene has also been seen in an inert gas environment using TGA-IR [112].

The degradation of neat ABS in air occurs in two steps as shown in Figure 4.6. The first step consumes approximately 85\% of the weight and occurs between 200\degree C and 500\degree C. The derivative weight loss curve indicates three major peaks centered at 375\degree C, 435\degree C, and 450\degree C. The peaks at 375\degree C and 435\degree C are attributes to the SAN phase and the last peak is associated with the butadiene phase. The second step consumes the remaining material and occurs between 500\degree C and 600\degree C.
Figure 4.6: Thermal decomposition pattern of ABS and its components: SAN and polybutadiene. The degradation temperature of SAN increases when incorporated into ABS, and the polybutadiene's thermal stability is decreased in the presence of SAN.

With the addition of SWNTs and VGCFs, the major degradation steps are similar to those of the neat HB-ABS as shown in Figure 4.7. The steps are unaffected because both the SWNTs and VGCFs show separate degradation from the polymer. The SWNT decomposition is marked by an exothermic event at 550°C, and the VGCFs begins decomposing at 600°C after the polymer is removed. Also, bulk degradation to the
materials induced by EFF processing is not observed in these tests because the samples tested before and after EFF processing show the same behavior. These tests do not provide any evidence of bulk thermal degradation caused by EFF, but IR spectroscopy measurements, described in the following section, are performed to confirm the TGA tests.

Figure 4.7: TGA data of materials before EFF processing (top) and after EFF processing (bottom). The curves are consistent indicating that no thermal degradation occurred. The addition of VGCFs and SWNTs did not drastically change the onset of degradation or the major degradation step. Both nanofibers showed separate degradation behavior following the first degradation step. Adapted from Shofner et al. [67].
Unlike the HB-ABS materials, the MDPE composites show increased thermal stability with respect to the neat polymer in TGA experiments conducted in flowing air as shown in Figure 4.8. The 1.5 wt.% composites are omitted for clarity. The decomposition pattern of polyethylene in the presence of oxygen is complex and occurs in several steps as seen in the shape of the degradation curves. The addition of nanotubes, purified and fluorinated, inhibits oxidation of polyethylene, and the degradation temperature increases with increasing nanotube concentration. Therefore, the F-SWNT composites show lesser increases than their P-SWNT composite counterpart. The maximum improvement is seen with the 5 wt.% P-SWNT/MDPE composite. As shown in Figure 4.8, the temperature at 50% weight remaining increases from approximately 320°C in the neat MDPE up to 470°C in the 5 wt.% P-SWNT/polyethylene composite material.

![TGA graph](image)

Figure 4.8: TGA data in air of neat MDPE and MDPE containing P-SWNTs and F-SWNTs. The curves show improved thermal behavior with nanotubes and do not indicate that any thermo-oxidative degradation is caused by the presence of nanotubes. F-SWNTs increase the thermal degradation temperature to a lesser extent than P-SWNTs due to a lower nanotube content in an equal concentration by weight. Adapted from Shofner et al. [67, 113].
A different behavior is seen in an inert gas environment. While TGA experiments show that the P-SWNTs and the F-SWNTs do not decrease the thermal stability of the polyethylene matrix, smaller increases in the main degradation temperature are observed. Table 4.2 lists the details of each test; each value is the average of two tests. The melting temperature data is taken from the temperature difference data, and the inflection point is taken as the peak of the derivative percent weight loss curve.

Table 4.2: TGA data showing the increase in inflection temperature with increasing nanotube concentration.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Temperature (°C)</th>
<th>Inflection Temperature (°C)</th>
<th>Weight % at 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat MDPE</td>
<td>110.7</td>
<td>470.7</td>
<td>negligible</td>
</tr>
<tr>
<td>1.5 wt% F-SWNT/MDPE</td>
<td>110.7</td>
<td>470.7</td>
<td>negligible</td>
</tr>
<tr>
<td>1.5 wt% P-SWNT/MDPE</td>
<td>110.4</td>
<td>475.9</td>
<td>0.95</td>
</tr>
<tr>
<td>5 wt% F-SWNT/MDPE</td>
<td>110.7</td>
<td>474.7</td>
<td>2.99</td>
</tr>
<tr>
<td>5 wt% P-SWNT/MDPE</td>
<td>109.5</td>
<td>478.8</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Figure 4.9 shows the decomposition curves for the neat MDPE, 5 wt.% F-SWNT/MDPE, and 5 wt.% P-SWNT/MDPE. The 1.5 wt.% SWNT composites are omitted for clarity. The shape of the decomposition curves is similar in all materials, but the composite materials’ curves are shifted to slightly higher temperatures. As with the TGA experiments in air, the 5 wt.% P-SWNT composite material produces the largest change in decomposition behavior by increasing the inflection temperature approximately eight degrees compared to the neat polyethylene. The F-SWNT containing materials produce smaller differences in the thermal behavior than their P-SWNT counterparts because of a lower loading of carbon nanotube component. As mentioned previously in
Section 3.3.2, the F-SWNT composites contain fewer nanotubes than the P-SWNT composites at equal loadings. Because the fluorine is included in the SWNT weight, a lower loading would account for the difference.

![TGA data in nitrogen of the neat MDPE, 5 wt.% F-SWNT/MDPE, and 5 wt.% P-SWNT/MPDE. The addition of F-SWNTs and P-SWNTs does not drastically change the onset of degradation or the major degradation step. The increases in thermal stability are related to nanotube carbon concentration.](image)

4.4.2 Fluorination Stability: TGA-IR

The stability of the fluorine functional group is assessed by analyzing the evolved gases collected during TGA-IR experiments from the 5 wt.% F-SWNT/polyethylene composite. In both the air and nitrogen experiments, the majority of the fluorine functional groups begin to detach as HF at 185°C, above the polymer's melting temperature of approximately 110°C. No significant amount of fluorinated carbon species is present in the evolved gases, suggesting that the nanotube frame does not degrade. HF evolution represents a different defluorination pattern than one observed previously for the F-SWNTs without a polymer matrix [114]. When heated in an argon
atmosphere, the free-standing F-SWNTs decompose in two steps. Between 300 and 560°C CO₂ and COF₂ evolve, and above 560°C CF₄ is observed as the main product. Fluorinated carbon gases indicated that parts of the nanotubes are destroyed, and after heating to 1000°C, the remaining nanotubes are cut into shorter segments with an average length of 40 nm. The shorter lengths would be expected to provide less reinforcement mechanically than the original nanotubes. However, the nanotubes in this work are not found to be shortened after the TGA experiment. The residue from both the P-SWNT and F-SWNT composites are mats of long nanotube ropes as shown in Figure 4.10. Neither sample require gold coating to prevent charging, indicating that the intrinsic nanotube conductivity is restored to the residue from the F-SWNT composite. Previous attempts to image F-SWNTs by SEM required gold coating or environmental mode to compensate for the low conductivity.

Figure 4.10: SEM images of the TGA residue from the 5 wt.% F-SWNT/MDPE (left) and 5 wt.% P-SWNT/MDPE (right) composites. The residue contains nanotubes without altered lengths that have consolidated into a mat of ropes.

The Raman spectrum of the P-SWNT composite TGA residue is identical to the P-SWNTs, but for the F-SWNT composite TGA residue, the disorder peak at 1291 cm⁻¹
is larger as shown in Figure 4.11. The increase in the disorder mode is likely caused by
damage to the nanotubes during defluorination [70, 79]. The presence of a small amount
of fluorinated carbon gases in the TGA-IR experiments support damage.

Figure 4.11: Raman spectra of P-SWNTs and TGA residue from the 5 wt.% F-
SWNT/MDPE and 5 wt.% P-SWNT/MDPE composites. The features of P-SWNTs are
seen in both samples. The F-SWNT composite residue shows an increase in the sp³
carbon peak intensity as compared to the original P-SWNTs. The increase was attributed
to damage.

4.4.3 Fourier Transform Infrared Spectroscopy

Both the HB-ABS and MDPE matrix materials are examined with infrared
spectroscopy, specifically FTIR. Changes in the group positions and intensities are used
to assess any thermo-oxidative degradation or new bonding states. FTIR is performed in
attenuated total reflectance mode using a Thermo-Nicolet Nexus 670 FTIR spectrometer.
Spectra are collected as the sum of 128 scans with a resolution of 4 cm⁻¹. For the HB-
ABS materials, scans are performed on material not incorporated into feedrods and thin
sheets made from EFF fibers by heated compression molding. MDPE materials are
examined after mixing, and the materials are in the form of a thin sheet.

Infrared spectroscopy results of the HB-ABS materials agree with the TGA
measurements. The positions of all ABS bands are constant for all materials before and
after EFF processing, and degradation is not apparent in any of the samples. Since the
EFF processing temperature is above the glass transition temperature for the styrene-
crylonitrile copolymer, the predominant degradation will occur in the polybutadiene
phase [115]. The intensity of the C=C unsaturation band at 965 cm\(^{-1}\) and the 1,2
butadiene terminal C-H band at 910 cm\(^{-1}\) are unaffected and carbonyl (1724 cm\(^{-1}\)) and
hydroxyl groups (3473 cm\(^{-1}\)) do not appear in the spectra as shown in Figure 4.12. These
results coupled with the TGA results suggest that no thermally induced degradation
occurred.

![Infrared Spectra](image)

**Figure 4.12:** Infrared spectra of the neat HB-ABS and 5 wt.% P-SWNT/HB-ABS before
and after EFF processing. No evidence of thermal degradation is observed because no
oxygen groups appear in the spectra and the group positions are unchanged.
The MDPE composites also show no shifts in peak positions, and no new peaks are present in the spectra. The spectra are typical of polyethylene with three main peaks representing CH$_2$ stretching (2916 and 2848 cm$^{-1}$), bending (1473 and 1462 cm$^{-1}$), and rocking (719 and 731 cm$^{-1}$). The similarities between the neat polymer and the composites suggest that the MDPE does not degrade because of the addition of nanotubes or during the partial defluorination caused by mixing.

![Infrared spectra of MDPE and 5 wt.% SWNT composites.](image)

Figure 4.13: Infrared spectra of MDPE and 5 wt.% SWNT composites. No changes in absorption bands are observed in these measurements with the addition of nanotubes discernable.

4.4.4: Melt Fracture of SWNT/HB-ABS composite

In the absence of thermally induced degradation, other possible causes of the rough surfaces in the SWNT/HB-ABS material processed by EFF include phase separation or melt fracture resulting from changes in die swell or excessive shear stresses. Phase separation is eliminated because the SWNT/ABS material can be remolded with
smooth, glossy surfaces following EFF processing. Melt fracture can be caused by a change in the elastic recovery properties of the melt [98, 116]. In this work, the change results from the addition of SWNTs. While both of the filled melts are more brittle in nature than the unfilled ABS, the SWNT reinforced material has the least extensional flow capabilities during manual drawing. Also, the extrusion parameters suggest a higher viscosity of the SWNT/ABS melt as compared to the other material that would likely increase the relaxation time. Attempts to reduce shear stresses in the nozzle through lower extrusion speeds, larger nozzles, and higher extrusion temperatures do not eliminate the irregular surfaces. Extursion speeds are lowered until the material will not flow, and extrusion temperatures are increased until the material becomes discontinuous.

Melt fracture is supported by the parameters required to produce a filament and the alignment behavior. The SWNT/ABS melt is subjected to higher stresses than the unfilled ABS and VGCF/ABS composite, evidenced by higher extrusion forces. Also, the limited alignment of the nanotubes contributes to an increased resistance to flow as compared to the aligned VGCF/ABS melt. Melt fracture is also observed by Haggenmueller et al. in a SWNT/polymer composite fibers and attributed to an increase in melt viscosity [35, 36]. Based on the published work and the behavior of the composite materials studied here, the irregular surfaces are associated with melt fracture. While neither melt fracture resulting from die swell or large shear stress can be eliminated as the cause, the increase in melt viscosity with the addition of nanotubes is the critical factor involved. In a typical ABS polymer, the higher styrene and lower butadiene content can mitigate this effect through lower neat polymer viscosity as is observed in the M-ABS processed by FDM. The ultimate consequence of the melt
fracture is observed in the mechanical testing where the surface roughness decreases the interlayer fusion in the SWNT/ABS parts which in turn affects the tensile strength.

4.5 Interfacial Properties

In addition to alignment and dispersion, the polymer matrix and reinforcement should be bridged by an interfacial region to enable load transfer and in turn increase mechanical properties. The interfacial region becomes particularly important with nanosize reinforcements because the surface area to volume ratio of reinforcements is inversely proportional to fiber radius by the following estimation:

$$\frac{S}{V} = \frac{2R\pi L}{\pi R^2 L} = 2/R [27]$$

Where $S$ = fiber surface area (neglecting fiber ends)

$V$ = fiber volume

$R$ = fiber radius

$L$ = Fiber length

Using this approximation, conventional carbon fibers have a surface to volume ratio of 4000 cm$^2$/cm$^3$, using a radius of 5 μm. The ratio for VGCFs increases two orders of magnitude with respect to conventional carbon fiber if the fiber radius is 50 nm. In the case of nanotubes, the surface area to volume ratio increases to 4,000,000 cm$^2$/cm$^3$ and 40,000,000 cm$^2$/cm$^3$ for SWNT ropes (5 nm radius) and individual SWNTs (0.5 nm radius), respectively. The increasing surface area of the reinforcement increases the interfacial area and the importance of a strong interface for mechanical property improvements. This section evaluates the interaction between the fibers and the matrix achieved in the composites processed for the alignment and functionalization studies.
using SEM imaging, thermogravimetric analysis (TGA), infrared spectroscopy (IR), and Raman spectroscopy. Each of these techniques offers a different insight into the interface. Imaging allows for visual confirmation of an interaction, but it cannot define the type of interface: mechanical or chemical. TGA and IR can establish a chemical interface by observation of changed degradation behavior and observation of changed or new absorption bands, respectively. Raman spectroscopy is used to monitor changes in the nanotube surface caused by the presence of a surrounding polymer matrix and chemical functionalization.

4.5.1 P-VGCF/ABS Composites

The cleaning procedure used prior to mixing on the VGCFs produces surface functionalization of the fiber [84], but in this instance, the functionalization does not promote interfacial bonding, evidenced by clean surfaces and troughs around the base of the fiber seen in Figure 4.14. The separate degradation pattern of the VGCFs in the TGA measurements described in Section 4.4.1 and the absence of shifted bands in the IR spectrum shown in Figure 4.15 provide further evidence that the VGCFs and the polymer are not interacting chemically. Both ABS matrices show the same level of interaction with VGCFs. The functional groups produced by the cleaning procedure are not created specifically for use with ABS, so different functionalization practices tailored for the nanofiber/polymer combination should improve the interface [109, 117].
Figure 4.14: P-VGCF/HB-ABS composite fracture surface. Limited interfacial bonding is present in both ABS composite materials containing VGCFs.

Figure 4.15: IR spectra of the neat HB-ABS and 5 wt.% P-VGCF/HB-ABS. No chemical bonding is observed in the spectra.

4.5.2 SWNT/ABS Composites

Visual observation of the fiber matrix interface in Figure 4.16 indicates that the interaction between SWNTs and both ABS matrices is improved with respect to the VGCF composites. While the surfaces of the exposed nanotubes are clean and smooth as with the VGCF composites, the matrix is attached to the base of the fiber. However, the
TGA and infrared spectroscopy do not indicate any direct chemical bond has formed between the nanotubes and the matrix. An explanation of the improved interface is provided by Yang et al. [118]. In that work, thermal analysis studies suggest an interaction between the butadiene domains and the SWNTs. This interaction could originate from the presence of unsaturated bonds in the polybutadiene phase that would be attracted by hydrogen bonding to the pi bonds of the nanotube, similar to attractions between nanotubes and conjugated polymers [119, 120].

![Image](image.jpg)

Figure 4.16: P-SWNT/HB-ABS composite fracture surface. Some level of interaction is indicated by the deformed polymer clinging to the base of the exposed nanotube.

As with the TGA and IR spectroscopy, Raman spectroscopy of the nanotubes and the composites does not suggest a strong chemical interaction. Figures 4.17 and 4.18 show similar nanotube spectral features regardless of the presence of a polymer matrix. The spectra in Figure 4.17 are typical for both types of nanotubes, but they are not measurements of the exact batch of nanotubes used. The shifts in the sp² peaks and the shift in the radial breathing mode for the P-SWNTs inside of and outside of ABS are
within the resolution of the spectrometer, so they are not considered significant. The difference in the position of the radial breathing mode for the as-received SWNTs is nearly 4 cm\(^{-1}\), but it is likely attributed to batch to batch differences. Between the two sets of composites, two changes are seen. The position of the sp\(^2\) peak is different by 2 cm\(^{-1}\), and, a peak at 1003 cm\(^{-1}\) is present in the SWNT/M-ABS composite. The difference in the sp\(^2\) peak is similar to the shift seen in the nanotubes outside of a polymer matrix, and the peak at 1003 cm\(^{-1}\) represents sp\(^3\) carbon that is removed by the purification procedure. Based on this data and the TGA, IR spectroscopy, and SEM data, the interaction between the polymer and the nanotubes is not derived from a direct chemical bond but could originate from attraction between the unsaturated bonds in the polybutadiene phase and the pi bonds in the nanotubes.

![Raman spectra](image)

Figure 4.17: Raman spectra of SWNTs produced by the dual laser vaporization technique from Tubes@Rice. As-received SWNTs are shown in (a), and P-SWNTs are shown in (b). Small shifts within the resolution of the spectrometer are observed, and a change in the distribution of nanotubes occurs following purification as evidenced by changes to the radial breathing modes. All measurements are made with a 780 nm laser on the same spectrometer used in this thesis. Adapted from Chiang et al. [20].
Figure 4.18: Raman spectra of the SWNT/ABS composites following SFF processing. Results are consistent with Figure 4.17.

4.5.3 SWNT/MDPE Composites

Differences between the P-SWNT and F-SWNT composites are evident when observing the nanotubes by Raman spectroscopy at each processing step. P-SWNT composites show no remarkable changes in the Raman spectrum as shown in Figure 4.19. The nanotubes are unaffected by the presence of the polymer matrix though an upshift of 3 to 4 cm\(^{-1}\) in three of the dominant radial breathing modes is observed. The shift in breathing modes is not considered significant because previous work has shown that both the radial breathing modes and the tangential stretching modes experience an upshift when loaded by hydrostatic compressive pressure [121]. Like the tangential stretching mode, the disorder mode remains unchanged by the presence of polyethylene.
Figure 4.19: Raman spectra of P-SWNTs and a P-SWNT/MDPE composite. No compressive stresses are imposed upon them by the surrounding polymer matrix because no significant shifts are observed.

In contrast, the F-SWNTs display a substantial interaction with the polyethylene matrix that is observed by Raman spectroscopy. The F-SWNT composites demonstrate dramatic changes through the processing as shown in Figure 4.20. The Raman features of the nanotubes prior to fluorination are typical of P-SWNTs, but after the fluorination, the bonding states of the carbon atoms have largely changed from sp² to sp³ because the fluorine is bonded to the nanotubes at the unsaturated sidewall sites [79, 107]. The sp² carbon peak of the graphene π-system at 1592 cm⁻¹ disappears, leaving a shoulder at 1565 cm⁻¹ due to a disrupted π-conjugation, and the intensity of the disorder mode increases. The latter mode does not shift appreciably because the mass difference between the oxygen functional groups on the sidewalls of the oxidized SWNTs and the fluorine functional groups is not significant. The breathing modes are obscured by the background and show only two defined peaks. After compounding with the
polyethylene, these breathing modes do not change relative to the F-SWNTs, but changes to the disorder mode and tangential mode suggest two events occurred: partial fluorine loss and subsequent direct covalent bonding between the nanotube and the polymer.

Figure 4.20: Raman spectra of P-SWNTs, F-SWNTs, and F-SWNT/MDPE composite. The addition of fluorine to the nanotube sidewalls reduces the intensity of the sp$^2$ C=C stretching mode and increased the intensity of the sp$^3$ C-C stretching mode. After mixing, some of the fluorine is removed from the nanotubes, and the nanotubes covalently bonded to the polymer as evidenced by the return of the sp$^2$ peak at 1592 cm$^{-1}$ and the shift in the sp$^3$ stretching mode, respectively.

Partial defluorination is supported by the return of the sp$^2$ peak at 1592 cm$^{-1}$. The position of this peak indicates that some of the fluorine functional groups had detached from the nanotube sidewalls. Complete defluorination is unlikely because large background scattering is still present in the Raman spectrum, and the intensity of the sp$^3$ peak is still small compared to P-SWNT/polyethylene composite material as shown in Figure 4.19. Based on the current knowledge, two scenarios are possible explanations for the partial fluorine loss. First, certain sizes or chiralities of nanotubes could lose their
fluorine functional groups. SWNTs produced by the HiPco process contain nanotubes of many different diameters indicated in the Raman spectrum by the radial breathing mode frequencies, so defluorination of nanotubes with certain size or shape characteristics is not improbable. Computational and experimental results have shown that the formation and stability of the C-F bond is related to nanotube characteristics. Chiang et al. [85] determines that the fluorination reaction is also dependent on nanotube diameter. As the nanotube diameter decreases, the fluorination process occurs at lower temperatures and shorter times because the higher curvature of the smaller diameter nanotubes makes them more reactive. Computational results by Bettinger et al. [122] and Kudin et al. [123] find that the C-F bond dissociation energy and nanotube diameter are inversely related. Jaffe [124] adds to this result by investigating the effect of chirality. His work suggests that zig-zag nanotubes form stronger bonds with fluorine. Experimental research performed by Pulikkathara et al. [82] concerning composites containing F-SWNTs exposed to radiation shows a higher stability for larger diameter nanotubes. Research is continuing to investigate the mechanism observed there. Combined, these studies do not identify the mechanism seen here, but they do provide the possibility of preferred defluorination based on nanotube size or shape.

The second explanation for the partial defluorination observed following mixing is defluorination of the outside surfaces of the nanotube ropes. Even though fluorination disrupts larger ropes, the nanotubes are still contained in ropes as seen in Figure 4.3. Since the defluorination product is HF and the hydrogen is removed from the polymer chain, fluorine species in close contact with the polymer chain would be the most likely to be removed. Polymer chains do not penetrate the SWNT ropes, so internal surfaces
are not in proximity to the polymer. The loss of fluorine at the outside surface would explain the partial defluorination and not preclude the earlier explanation because nanotube surfaces of certain curvature and chirality exposed to the polymer could also be losing fluorine while the functionalization on the corresponding surfaces internal to the rope may not be affected.

The suggested direct bonding between the carbon atoms on the polymer and the nanotube at the exposed surface is supported by the shift in the disorder mode from 1295 to 1305 cm\(^{-1}\). Carbon is lighter than fluorine, so the sp\(^3\) peak is observed to shift to a higher frequency. The opportunity for the bond to form may occur when the fluorine group is detached from the nanotube. Liberated fluorine atoms can attack the polymer and scavenge hydrogen to form HF gas. If hydrogen is removed from the chain, the open radical site on the polymer can form a covalent bond with the radical site on the nanotube where the fluorine group was, creating a sp\(^3\) carbon-carbon bond.

![Diagram](image)

Figure 4.21: Defluorination scheme to cause direct covalent bonding between SWNTs and the polymer matrix. Liberated fluorine extracts hydrogen from the polymer chain to form HF. The resulting radical sites on the nanotube and the polymer can form a direct bond.
4.6 Conclusions

Four issues that impact the mechanical properties of the composite are detailed in this chapter: dispersion, alignment, degradation, and interfacial properties. Purification, functionalization, incipient wetting, and high shear processing are shown to affect the dispersion behavior of VGCFs and SWNTs. For VGCFs, the combination of purification/functionalization and high shear processing achieve dispersion as shown previously by Lozano [83]. Purification is also helpful in dispersing nanotubes, and it should be coupled with incipient wetting and high shear forces. However, when the nanotubes are fluorinated, high shear forces are not required to create desirable dispersion because the fluorine functional groups repel each other. Incipient wetting is used with the functionalized nanotubes, but the necessity of cooperation between incipient wetting and functionalization is not established here. In addition to achieving dispersion, the processing techniques are also effective in achieving aligned VGCFs and preferentially oriented SWNTs. SEM imaging confirms the alignment condition of the VGCFs. The conventional extrusion step and the SFF processing induce alignment of VGCFs in ABS matrices. Lesser alignment is seen with SWNTs, but fiber drawing is expected to improve the alignment. Like degradation, interfacial properties are different for VGCFs and SWNTs. The VGCFs show limited interaction with both ABS matrices as evidenced by troughs at the base of exposed fibers and clean fiber surfaces, but the SWNTs have ABS polymer clinging to the base of the fiber. Attractive hydrogen bonding between the nanotubes and the butadiene phase is a possible explanation for the interaction. Similarly, partial defluorination encourages an interaction between F-SWNTs and an MDPE matrix not seen with the P-SWNTs and the MDPE matrix. Fluorine from the F-
SWNTs removes hydrogen from the MDPE chain creating an opportunity for direct covalent bonding between the fiber and the matrix.
CHAPTER FIVE
MECHANICAL PROPERTIES

5.1 Introduction

The ultimate test of the effectiveness of the processing techniques used in this thesis is demonstrating changes in mechanical properties caused by the addition of nanotubes. Key issues observed in these tests include the effect of fiber treatment, the differences in attainable properties using SWNTs and VGCFs, and the comparison between isotropic orientation and anisotropic orientation. These issues are assessed from mechanical property changes in static tensile testing. The materials processed for the functionalization study are not tested with static tensile testing because the low molecular weight of the MDPE led to an intrinsic brittleness that did not allow for meaningful testing. These materials are tested with DMA, and these results are contained with those for the ABS composites in Chapter 6. Details and results of the tensile testing are contained in Section 5.2. To provide more insight on the tensile test results, four micromechanical models are compared to the experimental data in Section 5.3. The chapter ends with a conclusion and is followed by DMA results in Chapter 6 and an overall concluding chapter.

5.2 Tensile Testing

The M-ABS and HB-ABS samples are tested using slightly different protocols in order to be consistent with earlier work and due to chronology, so relative property increases are compared between the FDM and EFF samples as opposed to property
values. Actual, measured values are compared between FDM sample sets because they are tested using the same parameters. Also, the FDM and EFF processes induce orientation effects in the neat polymer as well as the composites, requiring that neat polymer samples are made for each build style and geometry to compare to the filled samples and to account for changes in the neat polymer properties. As seen in Table 3.4, the only exception made is the straight bar samples; however, these samples are used primarily as an evaluation tool for fill and fusion with build style. Generally, as the number of layers with an orientation of close to 0° increased, the tensile strength and modulus increased. In both the FDM and EFF samples, the samples with a build style of 0x0 have tensile strength values closest to those of the neat ABS polymers as shown in Figure 5.1.

Figure 5.1: Tensile strength values for neat polymer samples made by EFF and FDM. As the extruded paths in the layer are aligned with the long axis of the part, the tensile strength increases.
Tensile tests are conducted on the FDM samples using an MTS 858 Mini Bionix Testing System, and the EFF samples are tested using an Instron 4505 Universal Testing System. The tests are performed based on the ASTM D638 standard at test speeds of 25.4 mm/min and 12.5 mm/min for the M-ABS and HB-ABS samples, respectively. At least four samples of each type are tested. Five EFF fibers of each material are also tested using a test speed of 100 mm/min and a grip distance of 100 mm. T-tests are used to determine if the property changes in all tests are statistically significant using a significance level of 0.05, and a two-tailed distribution. Equal and unequal variance conditions are applied according to the results of an F-test with a significance level of 0.05. Tensile strength values are calculated from the highest load experienced during testing and the original cross sectional area of the part. Tensile modulus measurements are taken from the initial slope of the stress/strain curve. The straight bar samples processed by FDM and the Type V dogbones processed by FDM and EFF are tested with plastic tabs adhered onto the ends of the test specimen, and the 90°/0° and 10°/90° dogbone specimens are put into direct contact with the grips. Care is taken in the placement and orientation of the samples to better understand effects associated with the orientation of the SFF build processes (top and bottom orientations) and positioning of the samples in the grips.

5.2.1 FDM Samples

All four sets of tensile samples show improved mechanical properties with the addition of VGCFs and SWNTs. The straight bar samples showed only increased strength in one set of composite samples, but all three sets of dogbone shape tensile
specimens show increased tensile strength and modulus. However, the elongation to
failure decreased for the composite specimens as shown in Figure 5.2.

![Graph showing strain to failure for different layers and compositions](image)

Figure 5.2: Strain to failure data of FDM parts. Composite parts show decreased strain to
failure due to limited load transfer and decreased fusion, both intralayer and interlayer.
Error bars indicate one standard deviation.

The data of neat ABS in all shapes has a higher degree of scatter than the
composite materials. The composite materials are more consistent but fracture at a lower
level of strain. The more brittle behavior results from low resistance to fiber pull-out, as
discussed in Section 4.5, and decreased interlayer and intralayer fusion during FDM
processing. Decreased interlayer fusion occurs for two reasons. First, variations in
feedstock diameter arise because of manual take-up from the extruder. Second, the
composite feedstock shows less swelling, so fusion inside layers (intralayer) and between
layers (interlayer) is decreased. The amount of intralayer voids tends to increase as the
layer alignment angle decreases. Therefore, the samples built with a 0X0 orientation
have the highest amount of intralayer void space. The variation in interlayer fusion is
shown in Figure 5.3 with the six layer dogbone samples. Observation of the fracture surfaces for straight bar and dogbone samples of the neat ABS show better fusion through the cross section with respect to the composite samples. All specimens with VGCFs possess decreased interlayer fusion and increased intralayer voids, but the level of interlayer fusion varies between sample sets due to variations in feedstock diameter.

Figure 5.3: Differences in interlayer fusion between the neat M-ABS (left) and VGCF/M-ABS composite (right). The samples shown have 6 layers and are built with a 10X90 layer orientation. The decreased swelling of the filled material caused decreased interlayer fusion and intralayer voids. Adapted from Shofner et al. [100].

Independent of differences between neat and filled samples, the straight bar tensile samples do not effectively measure the strength of the materials because all of the samples fracture at the grips, but they are interesting from the standpoint of layer alignment. While the neat ABS samples show a relatively consistent tensile strength, the VGCF/ABS samples have more significant scatter in the data. The error is attributed to the increased intralayer voids. Of the three part build strategies, the 45°/45° samples show the only statistically significant increase in tensile strength with an average improvement of 15%. By skewing the layer orientation with respect to the testing
direction, less intralayer voids occur in the cross section of the part. The decreased void density results in a stronger part.

Conversely, the first set of dogbones, built with a 90X0 pattern over nine layers, shows statistically significant increases in strength and modulus with the addition of P-VGCFs and SWNTs as shown in Figure 5.4. The strength increases are similar in spite of different compositions; however, the modulus improvements are starkly different. The higher modulus with the VGCFs composites is attributed to a higher level of dispersion, better alignment, and a larger concentration of filler than the SWNT composite as discussed in Chapter 3. Since these parts have four of its layers aligned with the long axis of the part (0°), the fracture surface in all samples shows intralayer voids, so the next set of samples is designed to increase the filled space in the cross section.

The third set of tensile samples is also made in a dogbone shape. These samples have a layer stacking sequence of 10°/90°. The top layer is skewed to reduce the intralayer void density while aligning the fibers close to the testing direction. The fracture surfaces of these parts shown in Figure 5.3 demonstrate an improvement, but it is not consistent. The error in the data is larger than that of the straight bar samples, and the neat ABS samples show a lower spread in the data with respect to the filled samples. The persisting trend indicates that the interlayer fusion in the VGCF/ABS samples is worse than the interlayer fusion in the ABS samples. Despite the reduced fusion, the VGCF/ABS samples possess an average tensile strength of 24.4 MPa, 29% higher than the neat ABS.
Figure 5.4: Tensile strength (top) and tensile modulus (bottom) values of neat M-ABS and composites. Nanotubes and nanofiber increased tensile strength and modulus, but each are influences by different aspects of the parts. Tensile strength improvements are more pronounced when all the VGCFs are aligned with the long axis of the part, and tensile modulus improvements are more dependent on level of interlayer fusion and intralayer void density. Error bars represent one standard deviation.

To produce a compromise to the issues of interlayer and intralayer fusion and part strength, the fourth set of tensile samples are fabricated using optimized build parameters and with all layers are aligned with the long axis of the part (0X0) [103]. Three materials are used to make this set of samples: P-ABS, M-ABS, and VGCF/M-ABS. The P-ABS is added to evaluate the practical similarity of M-ABS and P-ABS. These samples have
higher tensile strengths as compared to the straight bar and other dogbone specimens and less scatter in the data of the filled samples. The two ABS materials test similarly, and the measured properties are not statistically different from each other. Their average tensile strength and modulus differ by only 1.3 MPa (5%) and 10 MPa (2%), respectively. As with the previous two sets of data, the VGCF/ABS material has an increased tensile strength. The VGCF/ABS composite displays an average strength of 37.4 MPa and an average modulus of 0.79 GPa representing respective increases of 39% and 60%, respectively, when compared to the neat ABS tensile samples of the same shape. The tensile strength measured is the highest of all the three dogbone sample sets, but the tensile modulus is still less than that observed in the 10X90 parts because the level of fusion is decreased in the 0X0 parts. The tensile test results suggest that tensile strength is highly dependent on fiber alignment condition relative to the testing direction, but tensile modulus is more dependent on the level of interlayer fusion and intralayer voids.

In spite of imperfect fusion, these results compare favorably to other types of reinforcements studied with FDM. Previous work with glass fiber shows an increase of 19% in the tensile strength at a similar concentration. A compatibilizer is required to obtain further property increases in the glass fiber/ABS composite [56]. However, the mechanical measurements do not coincide with those predicted by the rule of mixtures (ROM). As the name suggests, the ROM calculation predicts the strength of composite materials as the sum of the property values of each component multiplied by its volume fraction. Using the tensile strength and modulus measurements from the fourth set of tensile samples for the M-ABS and the tensile strength and modulus values from
previously published data for the VGCFs [30], the composite material should have a
tensile strength and modulus of approximately 200 MPa and 24 GPa, respectively. These
values are respectively one and two orders of magnitude larger than the experimental
results. ROM models generally give higher than reasonable results for discontinuously
reinforced composites because they are designed for continuously reinforced composites
with an ideal fiber/matrix interface, but the magnitude of the discrepancy indicates that
load transfer between the matrix and the fiber is not occurring to an appreciable extent.
From the SEM images, TGA, and IR data presented in Chapter 4, the interaction is poor
between the VGCFs and the ABS interface, indicating the degree of load transfer is not
optimized, but useful increases in mechanical properties are possible without a perfect
interface.

5.2.2 Isotropic and EFF Samples

An added level of understanding is incorporated into the research concerning the
HB-ABS materials. Isotropically and preferentially oriented samples are produced with
this matrix to understand the effect of fiber alignment in this system. Isotropically
oriented samples are cut from the compression molded sheet using a die in the shape of
an ASTM D638 Type V sample and EFF samples are deposited in that shape. Example
fracture surfaces of these materials are shown in Figure 5.5. The EFF parts have the
same build style as the fourth set of FDM samples, 5 layers and a 0X0 build style. As
with the FDM work, the introduction of P-VGCFs and P-SWNTs increased the
mechanical properties. However, surface roughness caused by melt fracture, which is
unique to the SWNT/HB-ABS composite, also plays a part in the attainable properties of
the SWNT composite (Section 4.4.3).
Figure 5.5: Fracture surfaces of isotropic (left) and anisotropic (right) neat HB-ABS and HB-ABS composite samples. The fracture morphology is consistent within a given material system; neat HB-ABS (top), P-VGCF/HB-ABS (middle), and P-SWNT/HB-ABS (bottom); in spite of different fiber alignment conditions and EFF processing. Adapted from Shofner et al. [67].

The fracture surfaces of the isotropic and anisotropic samples have self-consistent morphologies as shown in Figure 5.5. The neat HB-ABS samples show a flat fracture surface and a smaller cross sectional area at fracture than the composites, indicating the neat polymers increased capability to yield and deform plastically. Both composite materials show a rougher fracture surface than the neat HB-ABS, providing a more
tortuous path for crack propagation. Unlike the FDM samples, the composite samples show a low intralayer void density even with a 0X0 build style because the nanotube and nanofiber filled samples did not show decreased swelling. Interlayer fusion of the composite samples is similar to the FDM samples and decreased when compared to the neat HB-ABS. Between the two types of composite samples, the fusion is further decreased in the P-SWNT/HB-ABS composite due to surface roughness.

The mechanical test results of the dogbone tensile samples cut from sheet, the dogbone tensile samples processed by EFF, and the EFF fibers demonstrated the important role of interlayer fusion as shown in Figure 5.6. All values given are averages with one standard deviation, and percent differences are given for statistically significant changes. Prior to EFF processing and with isotropic fiber orientation, the nanofiber and nanotube reinforced materials possess increased tensile strength and modulus with respect to the neat HB-ABS. EFF processing affects the mechanical properties through incomplete interlayer fusion. The P-VGCF/HB-ABS composite and the P-SWNT/HB-ABS composite dogbones processed by EFF possess similar tensile strength and increased tensile modulus compared to the neat HB-ABS EFF dogbones in spite of improved fiber alignment. The mechanical properties of EFF fibers containing SWNTs show different results while the EFF fibers containing P-VGCFs display the same trend as the EFF parts. The VGCF filled EFF fiber possesses similar strength and a modulus increased by 44% compared to the neat HB-ABS. The P-SWNT filled composite demonstrates improvements of 31% and 93% in tensile strength and modulus, respectively. Examining relative increases to mitigate the effect of strain rate and sample geometry, the relative increases in properties are larger than those of the material
possessing isotropic fiber orientation despite irregular surfaces in the case of the SWNT/ABS material. Since the modulus and strength increase in the P-SWNT/HB-ABS EFF fiber as opposed to only the modulus in the dogbone sample, the effect of the rough surfaces is apparent. The rough surfaces on the extruded surfaces inhibit the interlayer bonding in the dogbone samples resulting in decreased load transfer, tensile strength, and tensile modulus. EFF fiber tests produce results more indicative of the material’s properties and less influenced by the processing.

Strain to failure is decreased by the addition of nanofibers and melt fracture as can be seen in the differences in cross sectional area of the tensile samples in Figure 5.5 and the data in Figure 5.7. Both P-VGCFs and P-SWNTs reduce the amount of strain to failure though the addition of fibers alone does not decrease the ability of the material to yield. All isotropic samples show a distinct yield point, and the neat HB-ABS and P-VGCF/HB-ABS samples processed by EFF also show a yield point. The surface roughness caused by EFF induces premature failure of the P-SWNT samples. The ABS samples cut from sheet and EFF fibers possess strain to failure values of approximately 200% while the EFF dogbone parts show strain to failure of 125%. With the addition of VGCFs, the elongation is reduced to 128%, 38%, and 28% in the samples possessing isotropic fiber orientation, EFF parts, and EFF fibers, respectively. The P-SWNTs show further reductions in elongation. The elongation of samples possessing isotropic orientation, EFF dogbones, and EFF fibers is 102%, 12%, and 3%, respectively. Clearly, the surface roughness has an effect on the ductility of the composite because material not processed by EFF display similar strain to failure values as the VGCF reinforced material.
Figure 5.6: Tensile strength and modulus values for the isotropic parts, EFF parts, and EFF fibers. The tensile strength and modulus of the materials prior to EFF processing was improved with the addition of nanofibers and nanotubes. The imperfect interlayer bonding affected the strength and modulus in EFF parts while the EFF fibers of oriented P-SWNT in HB-ABS possessed higher tensile strength and modulus than all other materials. Error bars represent one standard deviation. Adapted from Shofner et al. [67].
Figure 5.7: Strain to failure data of the materials before and after EFF processing. The addition of nanofibers decrease the strain to failure values in all three sets of samples tested. The surface roughness of the EFF parts and EFF fibers further decrease the amount of strain to failure of the SWNT reinforced samples. Error bars represent one standard deviation. Adapted from Shofner et al. [67].

The addition of nanofibers produced mechanical property improvements, enhancing SFF technology. As expected, the SWNTs provided more reinforcement than the VGCFs, and alignment was beneficial to the strength and modulus. However as with the M-ABS composites, the results do not agree with ROM projections which indicate order of magnitude improvements based on the properties of the nanofibers. Factors causing this discrepancy included polymer matrix/nanofiber bonding, nanofiber alignment, surface morphology after EFF, and surface morphology of the nanofibers. In the VGCF composite material, the largest factor influencing the mechanical properties was the limited interaction between the polymer and the nanofiber. The cleaning procedure used prior to mixing on the VGCFs has produced surface functionalization of the fiber [84], but in this instance, the functionalization did not promote interfacial
bonding, evidenced by clean surfaces and troughs around the base of the fiber. The limited fiber/matrix interaction observed in SEM images indicated that a large degree of load transfer from the polymer to the nanofiber did not occur, so additional stiffness resulted from the fibers acting as restrictions to the chains. The separate degradation behavior for the VGCFs in the TGA measurements and the absence of shifted bands in the IR spectrum provided further evidence that the VGCFs and the polymer were not interacting chemically. Different functionalization practices tailored for the nanofiber/polymer combination should increase properties further [109, 117]. The SWNTs used were not chemically altered to create surface functionalization, and their surfaces appeared smooth and clean in the tensile specimen fracture surface images. However, some polymer appeared attached to the base of the fiber indicating that a degree of interfacial interaction occurred between the SWNTs and the ABS. The interaction is explored further for this material through thermal analysis by Yang et al. [118]. Functionalization specific to the SWNT/polymer combination will be the next step in increasing the matrix/fiber bonding. The SWNTs also displayed limited alignment. Order of magnitude increases in mechanical properties will require a high degree of alignment because the aspect ratios of SWNTs are large. The surface roughness specific to the SWNT/ABS material decreased the interlayer bonding and consequently the tensile properties. Finally, SWNTs should be used as individual nanotubes instead of ropes because inter-tube sliding decreases the strength of the composite [24, 94].
5.3 Micromechanical Modeling

In order to better understand the true nature of the reinforcement provided by SWNTs and VGCFs, micromechanical models are used for comparison with the experimental data. Micromechanical models assume knowledge of the independent properties of the fiber and the matrix as well as the location and orientation of the fibers in the matrix. In this work, four models are evaluated. The first model is the ROM which is mentioned in the previous sections as a rudimentary comparison. The ROM calculates the composite’s modulus as the weighted average of the fiber’s and matrix’s properties using the volume concentration of each component. It does not consider fiber/matrix interactions, and the values calculated are generally much higher than actual values. The second model, Krenchel [125], is similar to ROM, but it adds a level of complexity by incorporating an efficiency factor. The efficiency factor is determined by the fiber alignment and the stress direction, so the composite modulus is the sum of the matrix property multiplied by the volume fraction of matrix and the fiber property multiplied by the volume fraction of fibers and an efficiency factor. For a three dimensional isotropic fiber orientation, the efficiency factor is 0.2, and that value is used in the comparison presented here. As with ROM, Krenchel does not consider fiber/matrix interactions and generally predicts higher values than the actual values.

The other two models take the fiber dimensions into consideration and assume that the composite material is macroscopically homogeneous and isotropic. The third model used in this thesis, proposed by Tandon and Weng [126], considers changes to the average stress experienced by the matrix as the result of reinforcing fibers. The modulus is a function of fiber concentration and fiber aspect ratio. The fourth model, formulated
by Weng and Sun [127] builds upon the composite cylinder model of Christensen and Waals [128]. The model divides the composite into representative volume elements. The building blocks of the composite are cylinders which contain one fiber at its center and the remaining volume is a sheath of matrix. Christensen and Waals' model neglects the fiber ends and is better suited for continuous fibers. Weng and Sun is designed specifically for discontinuous fibers. It replaces the discontinuous fiber with an idealized fiber that contains the fiber plus the matrix directly above it and beneath it in the composite cylinder. The modulus of the idealized fiber is intermediate to those of the fiber and matrix, and it is determined from a ROM relation. The model also makes the following assumptions (taken directly from [127]):

a. “Both the fiber and the matrix are isotropic and linearly elastic.”

b. “The unidirectional fiber composite is linearly elastic and free of voids.”

c. “Bonding between the fiber and the matrix is perfect.”

d. “The fiber/fiber interaction is neglected.”

e. “The load carrying capacity of the fiber is full.”

The values used in the models are contained in Table 5.1. Values are obtained from the literature where possible and estimated or calculated from the given knowledge when unavailable. Three conditions are modeled: VGCF reinforced HB-ABS, individual SWNT reinforced HB-ABS, and SWNT rope reinforced HB-ABS. The results are presented separately in Figures 5.8, 5.9, and 5.10.
Table 5.1: Material parameters used in micromechanical models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Source</th>
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<tr>
<td>Individual SWNT Diameter</td>
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<td>[15]</td>
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<tr>
<td>Individual SWNT Length</td>
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<td>[129]</td>
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<tr>
<td>Individual SWNT Density</td>
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<td>Calculated</td>
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<td>Elastic Modulus of Individual SWNTs and SWNT ropes</td>
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<td>[21, 22]</td>
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<td>Shear Modulus of Individual SWNTs</td>
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<td>[24]</td>
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<td>Poisson’s Ratio of Individual SWNT</td>
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</tr>
<tr>
<td>SWNT Rope Diameter</td>
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<tr>
<td>SWNT Rope Length</td>
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<td>[13]</td>
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<td>Shear Modulus of SWNT Rope</td>
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<td>[24]</td>
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<td>VGCF Length</td>
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<td>Poisson’s Ratio for Polymer</td>
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<td>[131]</td>
</tr>
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In the cases of VGCF (Figure 5.8) and individual SWNT reinforced HB-ABS (Figure 5.9), the ROM, Krenchel, and Tandon and Weng models overestimate the composite modulus by at least an order of magnitude, and these models predict that less reinforcement is provided by the VGCFs than by the individual SWNTs based on the intrinsic fiber properties. However, the model that is based on composite cylinders, Weng and Sun, predicts the same amount of reinforcement for VGCFs and individual SWNTs at volume concentrations less than 10%. These values are closer to those experimentally measured but lower. The composite modulus obtained from the two models differs from experiment by 13% and 18% for the VGCF and individual SWNT
composite, respectively. At low concentrations, the similar aspect ratio of the fibers and polymer properties obscure the differences in fiber properties.

Figure 5.8: Micromechanical models of composite modulus for VGCF/HB-ABS. The composite cylinder model shows the closest agreement with experimental data.

Figure 5.9: Micromechanical models of composite modulus for individual SWNT/HB-ABS composites. Weng and Sun provides the most accurate approximation to experiment, but it does not distinguish between VGCFs and individual SWNTs.
Since the SWNTs used in this research are in the form of ropes, an additional set of moduli are calculated to consider the diminished shear modulus of ropes. From Figure 5.10, ROM and Krenchel models are the same as those for the individual SWNTs because the nanotube modulus is unchanged from the individual SWNT. The Weng and Sun model is also not significantly affected at this range of concentrations. The modulus value predicted corresponds to those measured experimentally within 18%. This amount of error is similar to that for the individual SWNT, but the composite modulus predicted by the Tandon and Weng model is lowered substantially with respect to the values in Figures 5.8 and 5.9. When a more realistic value for the shear modulus is used, the model agrees with 14% of the measured values as opposed over an order of magnitude with individual nanotubes.

![Graph](https://via.placeholder.com/150)

**Figure 5.10:** Micromechanical models of composite modulus for SWNT rope/HB-ABS composites. ROM, Krenchel, and composite models correspond to individual SWNT reinforcement, but the reduced shear modulus impacts the Tandon and Weng calculation.
Clearly, the interface plays a critical role in the mechanical properties of nanofiber and nanotube composites. The limited interaction seen with the VGCF composite prevents it from being accurately modeled by Krenchel and Tandon and Weng. Also, the combination of imperfect fiber/matrix interface and inter-rope sliding causes discrepancies for modeling the SWNT composite using the properties of an individual nanotube.

5.4 Conclusion

The mechanical properties of nanofiber and nanotube reinforced parts are improved when compared to the neat polymer for both sets of ABS composites, and SFF is capable of manipulating the nanofibers to exploit their anisotropic properties and increase the mechanical properties with respect to isotropic composite materials. Tensile strength improvements in the P-SWNT/HB-ABS EFF fibers are observed in spite of surface defects, and tensile modulus improvements are observed in all filled materials. When both VGCFs and SWNTs are purified and present in the same concentration, SWNTs provide more reinforcement in when oriented isotropically and anisotropically. ROM models reflect these differences between VGCFs and SWNTs, but the actual values predicted do not correspond well to experimental data. Other models that consider fiber aspect ratio and the fiber/matrix interface do not show large differences in the reinforcement capabilities of the two fibers in spite of differences in their properties or differences in fiber/matrix interaction described in Chapter 4. From the experimental data and the modeling data, the load transfer capacity of SWNTs is severely diminished
when the SWNTs are in the form of ropes due to sliding of individual nanotubes inside of the rope.
CHAPTER SIX

DYNAMIC MECHANICAL ANALYSIS

6.1 Introduction

As opposed to static tensile testing which provides information on the elastic and plastic deformation behavior of materials, DMA includes the elastic (time independent) and viscous (time dependent) response of material. These responses are represented by storage modulus (E') and loss modulus (E'"), respectively. The ratio of these two responses, tan delta, represents the mechanical damping of the system [132]. In the case of polymers, DMA is a particularly useful testing method because these responses can be used to observe thermodynamic transitions such as glass transition temperature (T_g), adding another level of understanding to the effect of reinforcements on the polymer matrix. For composite materials, observations of changes to E' and tan delta are sensitive to the fiber/matrix interface [133, 134]. A simultaneous increase in E' and decrease in tan delta with respect to the neat polymer indicate the presence of a load transferring interface because the stiffness is increased and the damping is decreased. In this thesis, DMA is performed on each of the three materials systems studied: M-ABS composites, HB-ABS composites, and MDPE composites. Storage modulus, tan delta, and T_g are used to compare the composites to the corresponding neat polymer. T_g is assigned to the peak value in the tan delta. The methods and results are presented in Sections 6.2, 6.3, and 6.4, respectively. The chapter ends with a conclusion and is followed by an overall concluding chapter.
6.2 M-ABS Materials

This testing was not performed by the author but was included in Shofner et al. [100] as part of the comprehensive study of nanofiber reinforced polymers processed by FDM. The author would like to acknowledge Mary Carmen Villarreal for performing the measurements while she was a student advised by Dr. Karen Lozano at University of Texas Pan American. The DMA analysis is included here for completeness.

After tensile testing, some of VGCF composite material from the third sample set is fashioned into thin sheet using heated compression molding. The traces of material are oriented along the long axis of the sample before compression molding, but the sample preparation method may decrease the degree of fiber alignment. Rectangular shaped samples with nominal cross-sectional dimensions of 12 mm wide and 1.5 mm thick are cut from the sheet and tested a 2980 DMA from TA Instruments. The tests are performed in single cantilever mode at a frequency of 1 Hz. The samples were heated from approximately 30 to 150°C at a rate of 5°C per minute.

As with the tensile tests, the DMA results indicate an increase in mechanical properties. Two unfilled samples and six filled samples are tested using the procedure described previously. The VGCF reinforced ABS possess a storage modulus 68% greater on average than the unfilled ABS at 40°C as shown in Figure 6.1. The results cannot be directly correlated to the tensile results for two reasons. First, the samples used to make the DMA samples have 3 layers oriented perpendicular to the long axis of the part, so only one half of the fibers could be aligned. Second, heated compression molding possibly compromises the degree of fiber alignment, but this increased value for storage modulus corroborates the increased stiffness obtained in the tensile tests.
Figure 6.1: Storage modulus of neat M-ABS and 10 wt.% P-VGCF/M-ABS. The addition of VGCFs increases the storage modulus by an average of 68%. Adapted from Shofner et al. [100].

Conversely, the weak interface described in Chapter 4 and the deviation from micromechanical models in Chapter 5 is represented in the DMA measurements by the similar tan delta curves of the neat M-ABS and the VGCF/M-ABS composite as shown in Figure 6.2. The $T_g$ of the SAN phase occurs at a slightly higher temperature. In addition, the value of tan delta is lower for the composite material, suggesting that some interaction is occurring because the damping is reduced, but the magnitude of the changes does not indicate a substantial interaction.

Figure 6.2: Tan delta curves of neat M-ABS and 10 wt.% P-VGCF/M-ABS. Small changes in the magnitude tan delta and $T_g$ are observed with the addition of VGCFs.
6.3 HB-ABS Materials

To more thoroughly investigate the possible interaction between the P-SWNTs and the polybutadiene phase of ABS, two DMA studies are performed. The first study is similar to that described in the previous section with the M-ABS materials. Rectangular samples with nominal cross-sectional dimensions of 12 mm wide and 1.5 mm thick are cut from a compression molded sheet. These samples are tested in single cantilever mode using a 2980 DMA from TA Instruments. The temperature ranged from 40°C to 130°C and two frequencies, 1 and 10 Hz, are used. Data is taken during isothermal steps that occur at ten degree intervals so that the different frequency measurements can be compared directly. However, this temperature range allows only the glass transition behavior of the SAN component to be observed, so the second study is aimed at capturing the glass transition temperature of the polybutadiene phase, which occurs at approximately -85°C. A different instrument, Perkin Elmer Diamond DMA, with subambient capabilities is used for this purpose. The samples are tested in a tension clamp and have nominal cross-sectional dimensions of 8 mm wide and 0.5 mm thick. Tests are conducted at a frequency of 1 Hz and in the temperature range of -120 to 120°C. The heating rate used is 5°C/min. In both studies, each material is tested twice. Since the geometry of the samples is different between the two studies, only relative changes are compared between studies.

Examining the storage modulus measured in the first DMA study, the differences in VGCF and SWNT reinforcement is evident. At temperatures between 40°C and the glass transition temperature of SAN, both types of nanofibers show improved stiffness, but similar to the tensile tests, the SWNTs provide greater increases as shown in Figure
6.3. At 40°C and 1 Hz frequency, E' is improved 29% in the VGCF composite and 52% in the SWNT composite. While the values of E' decrease for all materials with increasing temperature, the relative improvement in E' with respect to neat HB-ABS increases to a maximum of 35% and 96% at 100°C for the VGCF and SWNT composite.

Changing the frequency provides more insight into the interaction between the polymer and the fibers. Increasing the frequency to 10 Hz raises E' for all the materials, but the relative increases at lower temperatures are not significantly changed. E' at 40°C is increased 28% for the VGCF/HB-ABS materials and 51% for the SWNT/HB-ABS material. However, E' shows a different behavior at higher temperatures. At 100°C, the stiffness is improved 29% and 68% for the VGCF and SWNT reinforced materials which is less than the improvements seen at 1 Hz.

![Image of storage modulus vs temperature](image)

Figure 6.3: Storage modulus measurements for the HB-ABS materials at a frequency of 1 Hz. Both VGCFs and SWNTs increase the storage modulus of HB-ABS.

The changes in properties with frequency are best illustrated by Figure 6.4 which shows the tan delta curves for the three materials at 1 Hz and 10 Hz. At 1 Hz, T_g of the SAN copolymer in ABS is increased with the addition of nanofibers and nanotubes
causing the maximum improvements in $E'$ and 1 Hz. From the peaks in the curves, $T_g$ for the HB-ABS, VGCF/HB-ABS, and SWNT/HB-ABS occurs at approximately 100°C, 105°C, and 110°C, respectively, but when the measurement frequency is 10 Hz, the $T_g$ for all materials occurs at approximately 110°C, explaining the discrepancy between measurements at 100°C for the two different frequencies. At the lower frequency, the increased stiffness of the nanotubes and nanofibers reduces the mobility of the surrounding polymer, resulting in an increased $T_g$ of the SAN phase, but at higher frequencies, the matrix feels the effect of the fibers to a lesser extent because it is intrinsically stiffer. The comparison of these results to those obtained for the M-ABS materials suggests that the fiber/matrix interaction is stronger for the HB-ABS composites. Larger changes in $T_g$ are seen though similar decreases in the overall values of tan delta before $T_g$ are also observed.

Figure 6.4: Tan delta curves for the HB-ABS materials at 1 Hz (solid lines) and 10 Hz (dashed lines). The increase in $T_g$ seen with the addition of nanotubes and nanofibers at 1 Hz is not seen at 10 Hz due to the increased stiffness of the matrix.
The second DMA study demonstrates the same general behavior at temperatures at and above 40°C as the first DMA study as shown in Figure 6.5. At 40°C, the SWNT composite experiences a 61% increase in \( E' \), and the VGCF composite shows an increase of 23% in \( E' \). The amount of reinforcement increases with temperature. Comparing the values of \( E' \) at 100°C, the SWNT composite shows greater reinforcement than the VGCF composite. The addition of VGCFs increases \( E' \) by 59%, respectively, and the SWNT composite shows an improvement of 261%. The subambient measurements show a nearly constant increase in \( E' \) for both composite systems in the temperature range of -60 to 40°C, but at lower temperatures, the reinforcement decreases.

![Graph showing storage modulus vs. temperature for different materials](image)

**Figure 6.5:** Storage modulus curves for the HB-ABS materials at 1 Hz from -120 to 120°C. SWNTs and VGCFs provide reinforcement to HB-ABS at all temperatures measured.

The tan delta curves, used to assign \( T_g \), corroborate the \( T_g \) for the SAN phase measured in the first DMA study as shown in Figure 6.6. The SWNT composite shows a higher \( T_g \) at a measurement frequency of 1 Hz, but the \( T_g \) of polybutadiene does not change in spite of nanotube or nanofiber reinforcement. Decreases are seen in both types
of composites, but the decreases are greater in the SWNT composites, suggesting a better interface is present.

![Graph showing Tan delta curves for HB-ABS materials.]

**Figure 6.6:** Tan delta curves for the HB-ABS materials. The glass transition of polybutadiene is unchanged with the addition of nanotubes and nanofibers, but the glass transition of SAN is increased when reinforced by SWNTs and VGCFs.

### 6.4 MDPE Materials

The DMA measurements performed on the MDPE materials are the only values used to evaluate the change in mechanical properties because of the intrinsic brittleness of the MDPE, and this trait of the matrix polymer limited the temperature range tested. DMA measurements are performed using a Perkin-Elmer Diamond DMA system. All tests are conducted in tension mode on film samples with an approximate width of 8 mm and thickness 0.25 mm at a frequency of 1 Hz over a temperature range of 20 to -40°C.

Unlike the results of the TGA experiments, the results of the DMA measurements demonstrate a property improvement with the addition of fluorine functionalization. The differences in storage modulus values provides further evidence of an improved interaction between the F-SWNTs and the polyethylene when compared to the P-SWNTs.
and the polyethylene. As shown in Figure 6.7, all composite materials except the 5 wt.% F-SWNT/polyethylene composite show a similar storage modulus at 15°C. The 5 wt.% F-SWNT/polyethylene shows distinct improvement over the neat polyethylene with an average increase of 44%. The changes in the storage modulus of the other three composite materials cannot be separated from the error bars. The enhancement is constant to -40°C as shown in Figure 6.8.

![Graph showing storage moduli for different compositions](image)

Figure 6.7: Storage Modulus at 15°C for neat MDPE and MDPE composites. The 5 wt.% F-SWNT/MDPE composite shows improved mechanical properties when compared to the neat MDPE. All of the other composite materials show no distinct difference at this temperature.

![Graph showing temperature vs. storage modulus](image)

Figure 6.8: Storage modulus of the neat MPDE, 5 wt.% F-SWNT/MPDE, and 5 wt.% P-SWNT/MDPE. The addition of F-SWNTs increases storage modulus whereas the addition of P-SWNT provides less mechanical reinforcement at this concentration.
The behavior of tan delta supports the conclusion that the interfacial load transfer is greater in the F-SWNT composite. The damping ability of the polymer is decreased with increasing F-SWNT concentration as shown in Figure 6.9. 1.5 wt.% P-SWNT also decreases tan delta, but as the concentration increases to 5 wt.%, the value is approximately the same as the neat MDPE. This trend is also seen in the storage modulus data in Figure 6.6. Likely, it is due to decreased dispersion as the P-SWNT concentration increases [36, 135].

Figure 6.9: Tan delta values at 15°C for neat MDPE and MDPE composites. The bold lines indicate the upper and lower bounds of the polymer values. The F-SWNT composites show decreased damping with increasing concentration, but the P-SWNT composites show a saturation behavior.

### 6.5 Conclusion

DMA testing shows similar results to the tensile testing for the alignment study. SWNTs provide more reinforcement than VGCFs to the matrix independent of fiber orientation. Glass transition is also affected to a greater extent at low frequencies, but as frequency is increased, T_g of the composites matches that of the neat polymer. Decreases
in tan delta indicate less mechanical damping and a increased interaction between
SWNTs and the HB-ABS matrix as compared to the VGCFs.

Functionalization is shown to improve interfacial characteristics further in the
second study. Increases in E' and decreases in tan delta indicate that functionalized
nanotubes provide more reinforcement to the matrix than purified nanotubes through
better fiber/matrix interaction. A monotonic change in properties is not seen with P-
SWNTs, and the results suggest that dispersion is impacted as concentration increases.
CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The desirable mechanical properties of SWNTs are combined with novel manufacturing techniques and chemical functionalization of the nanotube surface to create thermoplastic composites materials with improved mechanical properties. SFF and functionalization are used to create prescribed fiber alignment and improved interfacial characteristics, respectively. The use of SFF techniques creates the opportunity for direct production of functional parts containing aligned nanotubes as well as the exciting possibility of tunable multifunctional properties through changes to the layer orientation within the part. Tensile strength and modulus improvements are attained, and preferential orientation of SWNTs by SFF shows mechanical property improvements with respect to the neat polymer and isotropically oriented composites. Comparison composites containing VGCFs also show promising alignment capabilities and mechanical properties, but differences in intrinsic properties and interfacial properties show reduced mechanical property improvements with respect to SWNTs.

Separately, chemical functionalization provides a means to disrupt the larger rope structure and create an opportunity for direct covalent bonding between the nanotubes and the matrix. Both effects improve the interfacial characteristics and mechanical properties of the functionalized nanotube composite with respect to the corresponding purified nanotube composite. These results show the versatility of covalent functionalization to act as a temporary dispersing agent, a removable cross-linking agent, or possibly a method to sort nanotubes by size.
From these results, several future research topics arise.

- Combine SFF or conventional extrusion with chemical functionalization and use the processing technique to simultaneously align SWNTs and remove the functionalization.

- Examine the thermal stability and changes to the decomposition patterns of other types of covalent functionalization that would produce more inert by-products.

- Perform comparison studies on composites containing SWNTs with a narrow distribution of diameters to more fully understand if the defluorination caused by processing is diameter-dependent.

- Prepare composites with higher loadings of F-SWNT to allow elemental analysis of the composites following processing for quantification of the fluorine loss.
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