A STUDY OF THE POLYMER-CNT INTERACTIONS IN POLYMER/CNT COMPOSITES USING EXPERIMENTAL AND COMPUTATIONAL METHODS

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Jiangsha Meng

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<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>AIREBO</td>
<td>adaptive intermolecular reactive empirical bond order forcefield</td>
</tr>
<tr>
<td>CG (for simulation method)</td>
<td>coarse grain</td>
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<tr>
<td>CG (for energy minimization)</td>
<td>conjugate gradient</td>
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<td>CHARMM</td>
<td>chemistry at Harvard macromolecular mechanics forcefield</td>
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<td>CNT</td>
<td>carbon nanotubes</td>
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<tr>
<td>C-Tubes</td>
<td>Cheaptubes (99 wt%) SWNT/DWNT</td>
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<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>CVFF</td>
<td>consistent valence forcefield</td>
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<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
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<tr>
<td>DMAc</td>
<td>N, N dimethylacetamide</td>
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<td>DMF</td>
<td>N, N dimethylformamide</td>
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<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
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<td>DWNT</td>
<td>double-wall carbon nanotubes</td>
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<td>FEA</td>
<td>finite-element analysis</td>
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<tr>
<td>LJ</td>
<td>Lennard-Jones</td>
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<td>MD</td>
<td>molecular dynamics</td>
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<td>MWNT</td>
<td>multi-wall carbon nanotubes</td>
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<tr>
<td>NVE</td>
<td>microcanonical ensemble</td>
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</table>
NVT  canonical ensemble
PAN  polyacrylonitrile
PBO  polybenzoxazole
PE   polyethylene
PEEK polyether ether ketone
PMMA poly(methyl methacrylate)
PmPV poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene)
PS   polystyrene
P-tubes purified SWNT
PVA  poly(vinyl alcohol)
SAXS small-angle X-ray scattering
SD   steepest descent
SEM  scanning electron microscope
SMD  steered Molecular Dynamics
SP-tubes super-purified SWNT
SWNT single-wall carbon nanotubes
TEM  transmission electron microscopes
TGA  thermogravimetric analysis
UHMWPE ultra-high-molecular-weight polyethylene
WAXD wide-angle X-ray diffraction
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**Figure C.3** SMD snapshots of the maximum h-BN sheets separation during polymer matrix pulling for three different cases: (a₁) Case 1: PE matrix on top of the h-BN stacking with one h-BN layer fixed at the bottom; (a₂) Case 2: PE matrix surrounding the h-BN stacking with one h-BN layer fixed at the bottom; and (a₃) Case 3: PE matrix surrounding the h-BN stacking with four h-BN layers fixed at the bottom. The SMD forces and PMF for all cases are summarized in (b₁) and (b₂), respectively.
ABSTRACT

This dissertation work focuses on research related to understanding and controlling the polymer-carbon nanotube (CNT) interactions during composite fiber processing using both experimental and computational means, in order to achieve consistent formation of the interphase regions for various polymers in the vicinity of CNT. The development of the polymer crystalline interphase is important, since it has been shown to have a significant and positive impact on the mechanical performance of polymer/CNT composites. This is achieved by the improvement of stress transfer mechanisms between the polymer matrix and CNT. The preliminary results (i.e., both experimental and computational) provide insight toward understanding the fundamental mechanisms of polymer-CNT interactions under various processing conditions, as well as the resultant polymer or CNT behaviors and composite fibers performance governed by them.

In this thesis work, the initialization and the development of the interphase region in fibers throughout all processing steps are investigated using full-atomistic molecular dynamics (MD) approach as well as experimental means. SWNT dispersion quality with and without polymers present during sonication process is also investigated experimentally, where the polymer-SWNT interactions are impacted by SWNT dispersion qualities. The resultant morphologies and composite fibers properties are also analyzed.

The effect of laminar-flow rates (used during spinning) on the polymer/SWNT composite fiber properties as well as on the fundamental polymer-SWNT interactions and the resultant chain morphologies near the SWNT surface are studied in detail. Full-atomistic MD simulations are conducted to study the influence of various laminar-flow rates on the chain morphologies in the vicinity of SWNT. By combining results from both experimentation and computation, a better understanding of the spinning parameters on the microscopic fiber properties as well as on the microscopic polymer-SWNT interaction is achieved. In addition, combining interphase mechanical properties obtained from SMD simulations with the experimental fiber properties, SWNT effective contributions in the composite fibers due to the interfacial structures are fundamentally analyzed.
Chapter 1 LITERATURE REVIEW

1.1. INTRODUCTION

One of the major trends in current materials research and technology is to reduce the size of devices and/or systems. For this reason, as the size of the material moving towards nanoscale, unique properties of the materials may be revealed and subsequent applications for these nanomaterials can be achieved.\(^1\) Since the fabrication of nanomaterials as well as devices and systems from these materials involves working with individual atoms or materials (i.e., 1 to 100 nm in size), several challenges arise requiring researchers to foster interdisciplinary collaborations between physicists, chemists, biologists, engineers, and material scientists in order to gain fundamental understanding and progress.\(^1\) Due to the potential game changing applications, nanotechnology has attracted significant amount of attention from the general public, various industries, as well as government funded research labs/centers.\(^1\)

The properties of many nanomaterials have been studied over the past few decades in order to product a new generation of materials that are faster, lighter, stronger, and multifunctional as compared to the current state-of-the-art materials.\(^1,2\) In this chapter of the dissertation, the carbon-based nanomaterials that are used as the enhancement fillers in the polymer matrices for producing composite materials will be reviewed. In addition, various types of morphologies between the matrices and the nano carbon fillers will also be discussed as they pertain to the design of the material and resultant its properties.

1.2. GENERAL PROPERTIES OF CARBON NANOTUBES

The unique geometry and the excellent mechanical, electrical, and thermal properties associated with the carbon nanotubes (CNT) have generated enormous research activities since the discovery of CNT in 1991.\(^3-31\) The superior combination of CNT’s properties makes it an excellent candidate for advanced applications ranging from large-scale structures in aircrafts to micro-scale structures in electronics.\(^16,31-35\) There are typically three kinds of CNT, namely, single-wall carbon nanotubes (SWNT), double-wall carbon nanotubes (DWNT), and multi-wall carbon nanotubes (MWNT). SWNT consist of a single graphene sheet rolled to
form a tube structure with diameters of 1 nm and length in the order of millimeters. DWNT and MWNT consist of two or multiple layers of this tubular structure with inter-layer distance of ~0.32 nm. DWNT and MWNT both have length in the order of millimeters, and with diameters of 2 - 5 nm and 10 - 100 nm, respectively.\textsuperscript{36, 37} Figure 1.1 shows a schematic representation of the structures for SWNT, DWNT, and MWNT.

\textbf{Figure 1.1} Schematic of both isometric and top views along CNT axis for (a) single-wall carbon nanotube (SWNT), (b) double-wall carbon nanotube (DWNT), and (c) multi-wall carbon nanotube.

The electrical conductivity of CNT is measured and predicted to be comparable to copper, silicon, and other metals.\textsuperscript{38-40} For this reason, they are incorporated into various polymer matrices to produce conductive plastics with low percolation thresholds.\textsuperscript{41} CNT also possess outstanding thermal conductivity along the axial direction,\textsuperscript{16} and have been used to produce CNT-based thermally conductive composites.\textsuperscript{34} Another promising implementation of CNT comes from its extraordinary mechanical properties in the axial direction, which makes CNT excellent reinforcement filler in the composite fibers. Table 1.1 summarizes the typical electrical conductivity, thermal conductivity, and mechanical properties reported in the literature for CNT materials.
Table 1.1 Summaries for the electrical and thermal conductivity as well as mechanical properties of SWNT and MWNT from the literature.

<table>
<thead>
<tr>
<th>Properties</th>
<th>CNT Types</th>
<th>Characterization Method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MWNT</td>
<td>SWNT</td>
</tr>
<tr>
<td>Mechanical (Young’s Modulus) (TPa)</td>
<td>0.7 – 1.3[43]</td>
<td>0.9 – 1.9[51]</td>
</tr>
<tr>
<td></td>
<td>1.3 (avg. value) [44]</td>
<td>1.2 (avg. value) [52]</td>
</tr>
<tr>
<td></td>
<td>0.7 – 1.9[45]</td>
<td>0.3 – 1.5[50]</td>
</tr>
<tr>
<td>Electrical Conductivity (S·m⁻¹)</td>
<td>10⁸[48]</td>
<td>10⁸[49]</td>
</tr>
<tr>
<td></td>
<td>0.3×10⁷[56]</td>
<td>10⁸[57]</td>
</tr>
<tr>
<td></td>
<td>10⁷[58]</td>
<td>10⁸[59]</td>
</tr>
<tr>
<td>Thermal Conductivity (W·m⁻¹·K⁻¹)</td>
<td>3180 [48]</td>
<td>3500 [16]</td>
</tr>
<tr>
<td></td>
<td>6600 [60]</td>
<td>~3000 [61]</td>
</tr>
</tbody>
</table>

*Devices were made by first patterning the electrodes with desired device geometry on the substrate and deposit nanotubes on top of the electrodes. Depends on the properties intended to measure (i.e., electrical or thermal conductivity), specific geometry can be designed.

The predicted Young’s modulus of the CNT, in the most simplified condition, is assumed be equal to the in-plane modulus of the graphene sheet (i.e., ~1040 GPa). Most calculations have obtained values in the range of 0.9 – 1.5 TPa. Experimentally, as shown in Table 1.1, the Young’s modulus measured for MWNT and SWNT range from 0.4 to 4.2 TPa and from 0.9 to 1.9 TPa, respectively. The methods used to measure the CNT mechanical properties include thermal vibration, cantilever bending, AFM bending, and Raman spectroscopy. The tensile strength of CNT measured is ranged from 11 to 63 GPa. In general, the widely accepted values for CNT mechanical properties are 1 TPa for Young’s modulus, and 63 GPa for tensile strength. This thesis work mainly focuses on taking advantage of CNT’s excellent mechanical properties to reinforce polymeric fibers.
1.3. CNT/POLYMER COMPOSITE FIBERS

1.3.1 CNT as Enhancement Fillers and Polymers as Matrices

The idea of combining two or more materials with different mechanical characteristics to produce composites with properties from both compounds has been put into application for thousands of years.\textsuperscript{71} To ensure the robustness of the overall composite performance, the interfacial binding between the components is critical, since weak interaction between different parts results in a pre-mature failure of the material without taking full advantages of the individual element properties. One way to improve this interfacial interaction is to enlarge or roughen the surface of the fillers. These treatments lead to larger interfacial area between the matrix and the fillers. For instance, in order to improve the concrete-steel performance, grooves are usually incorporated on the steel-rod surface to increase its contact areas with the concrete matrix.

The same basic composite principle is now being extended to the nano-scale. At this scale, the surface accessible area significantly increases for the fillers as their dimensions decrease. CNT is one of the most excellent filler candidates for making one-dimensional composites (i.e., fibers) due to its nano-size and axial mechanical properties (discussed in Section 1.2). To further illustrate the advantages of using CNT fillers to enhance mechanical performances, a Young’s modulus, tensile strength, and dimensional comparison between CNT and various filler materials that widely used in daily life is shown in Figure 1.2.

Even though CNT have been incorporated into many matrices (e.g., metals\textsuperscript{73} and ceramics\textsuperscript{74}), polymeric materials are considered to be one of the more widely explored. Polymer and materials composite counterparts are of great interest for the development of high-performance fibers for a wide range of applications in textiles (e.g., bulletproof vests, firefighter clothing, building constructions, and cables with tensile applications).\textsuperscript{75} Possessing advantages such as low density, high directional Young’s modulus and strength, and ease of shape processing, high-performance polymeric fibers have served as replacements of metallic materials in many applications that require lightweight.
The first high-performance fiber Kevlar® was developed by Stephanie Kwolek at DuPont in the 1960s. Dyneema® (i.e., ultra-high-molecular-weight polyethylene (UHMWPE)) with similar mechanical performance was developed by Albert Pennings in 1960s and was commercialized by DSM (Netherlands) in the 1990s. Zylon® (polybenzoxazole (PBO)) is currently the world’s strongest synthetic polymer fiber with properties surpassing Kevlar® and Dyneema®. The Young’s modulus of these high-performance fibers range from 60 to 180 GPa, and the tensile strength varies from 1.5 to 5.8 GPa. In addition, most of these fibers are processed using polymer solution spinning methods.

Carbon fibers are another leading high-performance material fabricated from polymer precursors. Polyacrylonitrile (PAN) is currently the most widely-used carbon-fiber precursor due to its combination of tensile properties as well as high carbon yield (typically 50 – 60%). Precursor PAN fibers go through processes of stabilization, carbonization, and graphitization in order to form carbon fibers with graphitic structures. Historically, carbon

5

\textit{Figure 1.2} Comparison of Young’s modulus, tensile strength, and dimensional properties for CNT and other widely-used composite filler materials\textsuperscript{72}
fibers were also fabricated using other polymers (e.g., polyethylene,\textsuperscript{83} cellulose (Rayon\textsuperscript{TM}),\textsuperscript{84} and pitch\textsuperscript{85}). In more recent studies, PAN/CNT composite precursor fibers are also being used to process carbon fibers.\textsuperscript{86-88} This potential next-generation of carbon fibers may exhibit lighter weight and better mechanical performance as compared to the current commercial materials.

1.3.2 Polymer/CNT Composite Fibers with High-concentration of CNT

The general production of polymer/CNT composite fibers has received great research interests in recent years due to their advantages and potentials discussed in Section 1.3.1. Although extensive studies have focused solely on using low concentrations of CNT as enhancement fillers in the CNT/polymer composites,\textsuperscript{21, 81, 89-93} fibers with high CNT content (> 5 wt\%) are also advantageous. These high concentration composites can exhibit enhanced combinations of mechanical, thermal, and electrical properties.\textsuperscript{12, 94-105} The two major approaches are used to produce high content CNT-based fibers include (i) solid-state spinning and (ii) liquid-state spinning. For the solid-state spinning approach, pure CNT yarns can be spun directly from the CNT forest using the ancient yarn spinning techniques.\textsuperscript{94} Additionally, CNT aerogels formed directly inside the hot chemical vapor deposition (CVD) synthesis zone may also be spun into yarns.\textsuperscript{98} For the liquid state spinning approach, one method is to disperse SWNT into strong acids, and subsequently extrude this SWNT dispersion through a small capillary tube into a coagulation bath for the fiber formation.\textsuperscript{105-107} Another method involves dispersing SWNT into surfactants, and subsequently injecting the stable SWNT dispersion into a rotating polymer solution for the fiber formation.\textsuperscript{95} Rotation of the polymer solution may also generate a shear-force field that can act on the composite fibers and potentially aligned the SWNT during the fiber formation.

Although various fabrication methods have been pursued to produce high-content CNT fibers, the mechanical properties of these materials have not approached the theoretical predictions (i.e., 1 TPa for Young’s modulus, and 63 GPa for tensile strength\textsuperscript{13}). In addition, the fiber properties are highly variable. Fibers produced using solid-state spinning approaches have a Young’s modulus varying from 27 GPa\textsuperscript{10} to 357 GPa\textsuperscript{97}, and a tensile strength ranging from 0.2 GPa\textsuperscript{99} to 8.8 GPa\textsuperscript{97}. Similarly, fibers spun using liquid-state spinning methods have a
Young’s modulus from 2 GPa\(^{12}\) to 120 GPa\(^{108}\), and a tensile strength ranging from 0.15 GPa\(^{95}\) to 1.8 GPa\(^{96}\). This drastic difference in fiber performances and low CNT reinforcement efficiencies may be attributed to the inconsistency of controlling processing parameters during fiber preparations.

There are four main factors associated with controlling the effective use of the CNT filler reinforcement in the fibers: (i) CNT dispersion quality, (ii) CNT aspect ratio, (iii) interfacial interaction between filler and matrix, and (iv) CNT orientation. The first two factors can be affected simultaneously by the CNT dispersion process. During the dispersion, a strong external shear stress (i.e., generated by the sonication process) between the tubes surface is needed to break down the aggregates and form a temporary exfoliation state among the tubes. Although the sonication conditions (i.e., ultrasound intensity and frequency, pulsing interval and duration, CNT concentration, external pressure and temperature) can lead to a large variation in CNT dispersion quality, the dispersion quality generally increases as a function of sonication time.\(^{17}\) On the other hand, the bubble implosion occurring (i.e., cavitation) during sonication can also create defective structures on the tube surface and shorten the tubes. This results in lowering CNT aspect ratio as well as introducing edge and end defects in the final product. For this reason, the homogeneity of the resultant CNT bundle exfoliation levels can be very difficult to control in general.\(^{15,103}\) An alternative approach to obtain more uniformed CNT dispersions is by using a polymer-assisted process. With the presence of polymer chains in the vicinity of temporarily exfoliated CNT bundles, chain absorption or wrapping can occur on the CNT surface and prevent the bundle reformation effectively.\(^{17}\) The effectiveness of such polymer-assisted dispersion also depends on the interfacial interactions between the polymer matrices and CNT. This is another important component that can contribute to the global reinforcement efficiency of CNT in the composite fibers.

1.4. POLYMER/CNT INTERFACES AND INTERPHASES

In order to better understand the interfacial interactions between the polymer and CNT within a composite, a localized nano-scale region can be broken down into three domains: (i) bulk, (ii) interface, and (iii) interphase regions (Figure 1.3).\(^{109-111}\) The polymer bulk region (Figure 1.3, Region ①) can be considered as the area that is furthest from the fillers, where the chain
behavior is not affected by the polymer-CNT interactions and exhibits properties indistinguishable from the neat polymer matrix. The interface region (Figure 1.3, Region ②) refers to the domain where polymer chains are directly interacting with the filler particles. In this domain, interfacial electrostatic, π-π stacking, and van der Waals interactions between the polymer and fillers can significantly influence chain behavior, and may noticeably change properties such as thermal stability and crystallization rate.\textsuperscript{112} The unique interphase region (Figure 1.3, Region ③) refers to the zone between the bulk and the filler. The crystallization behavior of the interphase region has been shown to differ from the bulk, and is influenced by the direct polymer-CNT interactions at the interface region.\textsuperscript{112}

Most of the direct interactions between the polymer and CNT at the interface region (Figure 1.3, Region ②) can be summarized into two main categories: (i) non-covalent bonding and (ii) covalent bonding. Non-covalent bonding refers to the absorption and/or wrapping of the polymer chains on the CNT surface due to the van der Waals forces. In this case, no chemical bonding/debonding processes occur and polymer and CNT particles interaction can be described by a Lenoard-Jones potential well. This polymer-CNT interaction at the interface can not only prevent the CNT re-aggregation during dispersion process, but also act as the intermediate layer between the bulk matrix and the filler for more effective stress transfer in the final material. The interfacial strength determined by this polymer-CNT interaction will subsequently translate to the mechanical performance of the end products. The second form of polymer-CNT interfacial interaction is covalent bonding, which is the formation of chemical bonding between the polymer chains and CNT.\textsuperscript{113, 114} Enhancement of polymer-CNT interactions is accomplished by modifying the CNT surface with reactive chemical groups that can form covalent bonds with polymer chains. This functionalization process requires chemical treatment of the CNT and can damage its structure. Although the bonding mechanisms are different in these two approaches, they share the same fundamental goal of improving the interfacial interaction and strength between polymer and CNT.
The interphase region (Figure 1.3, Region ③) is an intermediate layer between the interface and the bulk, which is influenced by the interface region. Although there is no direct polymer-CNT interaction in this region, the polymer chains are still affected (i.e., templated) by the chain behavior at the interface. As a result, they typically behave differently from the bulk. One characteristic of the interphase in the nano-composite with semi-crystalline polymers is that, it is usually composed of aligned crystallites that can be heterogeneously nucleated from the fillers (i.e., polymer crystallites are parallel to the CNT axial direction). These crystalline regions may also have higher chain-packing density (i.e., closer chain packing in unit cells) as compared to crystals in the bulk. Research evidence has also shown that the interphase region can grow and extend for some distance from the fillers (i.e., 2–13 nm), and even become a dominate presence contributing to further improvement in composite properties. Therefore, fundamental understanding of the polymer-CNT interactions at the interface and studying the relationship between various processing factors and the interphase...
growth become critical for consistently producing polymer/CNT composite fibers with excellent performance.

1.5. EFFECTS OF PROCESSING CONDITIONS ON POLYMER/CNT COMPOSITE FIBERS
Several major processing factors pertaining to polymer/CNT composite fibers are considered and studied in this thesis work. Each one of these conditions can significantly influence the four aspects of CNT reinforcement effectiveness (discussed in Section 1.3.2) in the fibers. Specifically, the effect of polymer chain shearing along the fiber axis during and after fiber processing, as well as the influence of the CNT dispersion quality during the spinning dope preparation are studied in depth. The purpose of these studies is to shine light on the fundamental polymer-CNT interaction mechanisms morphology under various spinning conditions.

1.5.1 Axial Shearing Effect on Polymer/CNT Composite Fibers
As mentioned in Section 1.3.2, CNT orientation with respect to the fiber axis is another important factor that influences its reinforcement efficiency in the composite. It has been shown that the Young’s modulus of the composite fibers decreases approximately 80% with a minimal change (i.e., ~ 5°) in the global CNT misalignment angle with respect to the fiber axis. Therefore, the alignment of the CNT needs to be very well-controlled in order to increase its contribution to the composite fiber. In order to achieve good CNT alignment, not only are high-quality CNT dispersions (i.e., no aggregations and high level of exfoliation) necessary, but additional external forces applied along fiber direction is also required. In high-performance polymeric fibers production it is typical to have a hot-drawing process after spinning to increase the global alignment of the polymer chains. This same approach is applied to polymer/CNT composite fibers. Due to the existing polymer-CNT interactions (i.e., non-covalent bonding or covalent bonding) in the composite fibers, both polymer chains and CNT tubes/bundles experience additional interactive forces from one another, which can be used to improve alignment along the fiber direction.

In addition to the hot-drawing process, additional parameters can also be used during fiber spinning to improve polymer/CNT alignment. One such parameter is the incorporation of
flow during spinning processes. By introducing axial laminar flow to act on the spinning dope during fiber gel-formation, an initial draw ratio can be applied to induce chain alignment prior to the post-processing (i.e., hot-drawing). The mechanism of enhancing polymer/CNT alignment using flow can be contributed to the interaction between solvent molecules and polymer. The solvent molecules moving along the flow direction can potentially affect the polymer chain and CNT movement, and direct their mobility. For this reason, the polymer and CNT can be carried by the solvent molecules and aligned along flow direction.

Flow during spinning may have a two-fold effect: (i) chain alignment improvement, and (ii) promotion of polymer extended-chain crystallization behavior. By studying the properties and morphologies of dilute and semi-dilute polymer solution under various flow fields both experimentally and computationally, research has also shown that the bundle-like polymer nuclei that are parallel to the streamlines can be formed. With the additional presence of CNT, polymers were observed experimentally to form specific morphologies on the CNT surface.

![Figure 1.4](image)

**Figure 1.4** (a) TEM image of SWNT periodically patterned with PE lamellae crystals (hybrid “shish-kebab” structure). (b) TEM observation of extended-chain PVA crystals forming in the vicinity of CNT.
One of the commonly observed morphology for flow induced polymer crystals is the hybrid ‘shish-kebab’ structure (Figure 1.4a). While the kebab is composed of folded-chain crystals with local orientation parallel to the CNT axis, the growth of the kebab is actually perpendicular to the CNT axis. This, however, is not ideal for fibers tensile properties. Within the composite, the space between the kebabs can become filled with bulk polymer. Considering that the bulk polymer may not possess a highly ordered structure as compared to the folded-chain ‘kebab’, the polymer-CNT interaction is reduced. The interface between bulk polymer and kebab structure may also contain defects that may eventually cause pre-mature failure of the resultant fibers. Another flow-induced morphology pertaining to the polymer interphase is the formation of extended-chain crystals in the vicinity of CNT (Figure 1.4b).\textsuperscript{79} This type of crystalline interphase has been found more attractive for the improvement of the fiber tensile properties by providing more complete polymer-CNT interaction and more efficient stress transfer from the bulk to CNT.

\textbf{Figure 1.5} Schematic showing the effects of the flow on the polymer-CNT interactions during fiber coagulation. (a) Random distribution of the polymer chains and CNT when the flow is initially applied. (b) Morphology of the polymer chains and CNT after the flow field is developed, where alignment of both components are improved by the force acting in the fiber axial direction. The formation of the extended-chain polymer interphase regions occurs in the vicinity of CNT and is emphasized by the shaded regions (i.e., red color).
Studies have shown that the extension of the polymer chains is determined by temperature, local pressure and the external shear-force.\textsuperscript{129, 130, 128, 131-134} By carefully controlling the parameters applied during the fiber spinning process, a proper combination of the solution temperature, spatial confinement between polymer and CNT caused by CNT dispersion and initial fiber draw ratio, as well as the flow rate is expected to cause the formation of extended-chain polymer interphase morphology. Figure 1.5b illustrates the desired effect of incorporating flow to influence polymer-CNT interaction (during fiber gel-spinning processes). The shaded (i.e., red) regions indicate the extended-chain interphase formed in the vicinity of CNT.

1.5.2 CNT Dispersion Effects on Polymer/CNT Composite Fibers

As discussed, to improve the overall performance as well as the consistency of the composite fibers, the CNT dispersion quality during material processing provides another challenge.\textsuperscript{135} The first (and the most intuitive) cause for this issue is related to the quality of the tubes themselves. Differences in the CNT synthesis procedures/parameters typically results in several inconsistencies with respect to structural aspects for the fillers. For example, small variations in synthesis routes lead to deviation in tube length, chirality distribution, aspect ratio, and morphological consistency. These will then contribute to different electrical, thermal, and mechanical performance for both the as-produced tubes as well as the filled polymeric composite fibers.\textsuperscript{32, 44, 50, 137, 138}

A second factor that also contributes significantly to the irregularity of the CNT dispersion (i.e., formation of aggregations and agglomerations, as well as lack of bundle exfoliation\textsuperscript{33}) within the polymer matrix is the type of dispersion method/parameter used. Interactions between tube bundles are governed by van der Waals (vdW) forces.\textsuperscript{139} Although vdW forces are considered to be weak as compared to primary bonds, due to the large aspect ratio of the tubes and the existence in large bundles. It is a major challenge to fully separate without damaging its pristine structure. One approach for reducing such bundling in a CNT-solvent dispersion is to introduce a strong external shear stress (e.g., generated by sonication processes) between tube surfaces. This mechanism breaks down the aggregates to form a temporary exfoliated state for the tubes in dispersion. This state allows for surface adsorption
of dispersants or polymers, which may subsequently stabilize the dispersed state. However, the bubble implosion process (i.e., cavitation) occurring during sonication can be seen as random and qualitatively depends on conditions such as ultrasound intensity and frequency, pulsing interval and duration, CNT concentration, external pressure, and temperature. For this reason, the homogeneity of the resultant CNT bundle exfoliation levels can be very difficult to control. For composite processing this is disadvantageous, considering homogeneity of the filler is desirable. In particular, for cases of dispersing high-concentrations of CNT (e.g., greater than 5 wt%) tube exfoliation processes may be further limited by the local spatial confinements from other surrounding SWNT bundles and tubes. This lack of control regarding the overall dispersion process for nanotube materials directly affects the ultimate quality of the SWNT distribution in a polymer matrix. This lack of homogeneity for the CNT dispersion will lead to an increase of defective elements (i.e., aggregates and variation in CNT bundle size and length leading to edge/end-defects) and decrease the overall polymer-CNT interactions, which will ultimately lower the mechanical performance of the composite end-product.

Interfacial interaction between a polymer matrix and CNT is an important factor determining the effective utilization of the exceptional mechanical properties of nanotubes within composite fibers. If homogenous polymer/CNT interactions can be achieved throughout the fiber system, then CNT bundle re-aggregation may be prevented by polymer wrapping and crystallization behavior of the polymer chains, as well as the formation of an ordered polymer interphase region between the SWNT and the bulk matrix. The growth of the ordered interphase region is considered to be a major factor for maximizing the mechanical contribution from the CNT, since it leads to a graded-region between the CNT and bulk-polymer matrix to improve stress transfer in the composite. In addition, the mechanical contribution from the ordered interphase region has been shown to be significantly higher than the bulk-polymer (i.e., semi-crystalline) region and further enhances composite fiber performance. As stated, to achieve higher mechanical improvement in the nano-composite requires (i) even distribution of CNT, (ii) exfoliation of the CNT bundles (i.e., no aggregations and
entanglements), and (iii) the formation of a distinct crystalline polymer interphase structure in the fiber. In particular, for the high CNT concentration cases presented in this thesis work, it is most probable that some of the CNT aggregates will not fully exfoliate and interact with the polymer chains due to insufficient polymer/SWNT interactions at various locations. For this reason, high-concentration polymer/CNT dispersion may separate into CNT-rich (i.e., aggregate-CNT interaction dominates) and polymer-rich domains (i.e., inter-chain interaction is preferred), which ultimately acts as defective regions in the fibers and result in early failure at these region boundaries (similar to grain boundaries of polycrystalline materials\(^21\)).

Composite fibers with high SWNT loadings, similar polymer matrices, and fiber-spinning processes have been produced by various research groups. These studies show that the mechanical performances of the final products deviate significantly.\(^80,95,96,142,143\) For instance, the PVA/SWNT fibers (> 60 wt% of SWNT) produced by polymer flow coagulation method have modulus of 7 to 15 GPa and strength of 0.15 GPa;\(^95\) while fibers with similar SWNT loading and spinning approach achieved modulus of 40 to 80 GPa and strength of 0.3 to 1.8 GPa.\(^96,142\) In another case, the PAN/SWNT fibers (1 wt% of SWNT) produced by wet-spinning method was reported to have modulus of 10.3 GPa and strength of 0.56 GPa;\(^143\) and the fibers with the same SWNT loading and similar spinning approach achieved modulus of 28.7 GPa and strength of 1.1 GPa.\(^80\) Therefore, in order to minimize the property deviation, more fundamental understanding regarding the structure-property relationship as a function of changes in processing parameters (i.e., control thereof) is necessary.

The reviews presented in this chapter provide the literature background for the research work that about to discuss in the following chapters. Performing research to try to reach the full potentials of the composite fiber properties by understanding and tailoring the processing parameters discussed in this chapter is the motivation of this dissertation.
1.6. Summaries

In summary, this chapter describes the general aspects of CNT and polymers, and discusses the major factors that influence the mechanical performance of the polymer/CNT composite fibers. This chapter also explains the three distinct regions in polymer/CNT composite fibers (i.e., interface, interphase, and bulk), and discusses the importance of promoting formation of the extended-chain polymer interphase regions for enhancing polymer/CNT composite fibers properties. The effects of various fiber processing conditions on the polymer-CNT interaction within the composite were reviewed, in order to understand the mechanism, morphology, and challenges for improving the growth of the polymer interphase region near CNT surface. Although experimental studies reveal the composite fiber processing-morphology-property relationship at a macroscopic level, due to the limitation of the component sizes as well as the opaque color of the overall composite, better correlation between the conclusions drew experimentally and the polymer-CNT interactions at the nano-scale needs to be built. One approach that can provide accurate micro-level information regardless of the experimental challenges for studying the materials is through computational simulations. For this reason, a combined analysis from both experimentation and computation is proposed and used in this work. By incorporating advantages from both experimental and computational methods, a better understanding of the extended-chain interphase formation during nano-composite fiber processing can be achieved.
Chapter 2 INCORPORATING COMPUTATION FOR CHARACTERIZING POLYMER/NANO CARBON INTERACTION

2.1. INTRODUCTION

Although experimental characterization of the polymer/nano carbon composite materials can be comprehensive at the macroscopic level, the time and cost of experiments, limitation of the testing equipment, inconsistency in specimen preparation, as well as some of the physical traits of the material (e.g., lack of transparency for CNT-based materials) hinder such investigations especially at the microscopic and/or atomic level. Without building fundamental linkage between morphology development and the key composite process conditions and their subsequent influences on the component interactions, control over composite processing parameters will be poor and the consistency of the final product performances will be low. For this reason, researchers have implemented various computational methods for predicting properties of nano carbon-reinforced composites and analyzing the polymer-nano carbon interactions important to its performance. In this way the payload for experimentation can be reduced, and accurate physical insights at the atomic level where experiments are not feasible can also be provided. In this chapter, some of the common modeling techniques used to capture the properties of the CNT and the polymer, as well as their interactions is reviewed. By showing how the results obtained from computational domain complement experiments, a multi-scale linkage for morphology development through processing and its effect on sample performance may be built using combined analysis.

2.2. FRAMEWORK OF MODELING TECHNIQUES

Many modeling approaches have been used to investigate CNT/polymer systems in the past few decades. To date, the applied theoretical studies for simulating such systems can be divided into two major groups: (i) atomistic and (ii) continuum simulation. Atomistic simulation can be sub-divided into three major branches, (a) molecular dynamics (MD), (b)
coarse grain (CG), and (c) density functional theory (DFT). DFT is based on quantum mechanics (i.e., taking electronic structure of atoms into consideration) and is usually computationally expensive and small in model size. Both MD and CG methods are based on the classic Newton’s equations of motion for simulating larger model sizes as well as longer time periods with more accessible computing power requirement. Continuum simulation on the other hand is sub-divided into two main branches, (a) analytical modeling and (b) numerical modeling. Mechanical behavior of the CNT as well as its polymer-based composite materials can be described using both analytical equations and numerical solutions such as finite element analysis (FEA). Researchers have tried to obtain more sophisticated equations to incorporate the lattice structure of the CNT as well as the bonding between the nanotubes and the polymer can be carefully described in continuum simulations.

Figure 2.1 Comparison of various modeling techniques in terms of their simulation time scale, simulation size, and the disciplines they belong. The figures also compare some experimental characterization methods to each modeling approach.

For the aforementioned approaches and algorithms, both the methods and simulation scales are different. Depending on the study of interest, the selection of the computational resource...
Figure 2.1 shows a respective timescale versus size of the simulation domains for each modeling methodology, and their corresponding testing approaches with in the experimental domain. In this thesis work, understanding CNT-polymer interaction energy at the atomistic level, as well as the interfacial morphology development of the polymer near CNT is a priority. For this reason, MD simulation approaches are selected. An overview of the full-atomic MD methods as well as the forcefields used for describing the atomic system is provided in the following section.

2.3. MOLECULAR DYNAMICS

2.3.1 Algorithms

MD is a widely used computational approach that simulates groups of atoms and molecules whose movements and interactions are governed by certain energy equations. It is utilized to investigate the atomistic interaction mechanisms that reflect the global physical properties of materials. Aided by statistical mechanics theory, the microscopic properties obtained from MD simulation can be related to the bulk material properties (i.e., mechanical, thermal, and electrical properties).

In MD, atoms are simplified as a point with its atomic mass. Each atom in the system has a specified energy state as well as a moving trajectory that are governed individually by the Newton’s equation of motions. The attractive or repulsive forces between atoms are defined by imposing interaction potentials. At each given time step, the simulation integrates Newton’s equation of motions and updates the trajectories of the particles with three general parameters, (i) positions of atoms \( r_i(t) \), (ii) velocities of atoms \( v_i(t) \), and (iii) accelerations of atoms \( a_i(t) \). Hence, the overall dynamics of the system can be determined.

A commonly used algorithm for integrating equation of motions is Velocity Verlet. The general procedure of Velocity Verlet is given by Equation 2.1.

\[
\text{Step 1: } \quad r(t + \delta t) = r(t) + v(t)\delta t + \frac{\delta t^2}{2} a(t)
\]  

(2.1)
Equation 2.1 is used to calculate new atom positions using the assigned atom positions, velocities, and accelerations.

**Step 2:**
\[ v(t + \frac{\delta t}{2}) = v(t) + \frac{\delta t}{2} a(t) \]  

(2.2)

Equation 2.2 is used to determine new atom velocities at half time steps.

**Step 3:**
\[ a(t + \delta t) = F(t) / m \]  

(2.3)

Equation 2.3 determines new atom accelerations at half time steps.

**Step 4:**
\[ v(t + \delta t) = v(t + \frac{\delta t}{2}) + \frac{\delta t}{2} a(t + \delta t) \]  

(2.4)

Equation 2.4 calculates new atom velocities at full time steps.

The total energy of the system can be described using Hamiltonian \((H)\), which is given by the summation of the system’s kinetic energy \((K)\) and potential energy \((U)\) (Equations 2.5 to 2.7):

\[ H = K + U \]  

(2.5)

Where,

\[ K = \frac{1}{2} \sum_{i=1}^{N} m_i v_i^2 \]  

(2.6)

and

\[ U = \sum_{i=1}^{N} U_i(r_i) \]  

(2.7)

For Equations 2.6 and 2.7, \(N\) is the total number of atoms in the system; \(m_i\) is the atomic mass for each atom; \(v_i\) is the velocity of each atom at a given time step; and \(U_i(r_i)\) is the potential energy of each atom with multiple geometric constraints (e.g., bond stretching \(U(r_{ij})\), bond rotation \(U(\theta_{ijk})\), and bond torsion \(U(\theta_{ijkl})\)) with respect to the forcefield used for the system. The parameters and conditions for these constraints will change.
2.3.2 Forcefield

The usage of the forcefield is essential for MD simulations. If the forcefield is defined and use appropriately in the system, a complete set of material properties can be accurately predicted without having prior sample information. Forcefield expressions are usually derived from the fitting calculations based on real experimental data in order to model the atomic interactions in the computational domain. Many forcefields have been developed over the past few decades to meet different property, application, and accuracy requirements. A proper choice of the forcefield depends on the system of modeling interest. For instance, AIREBO and CVFF have been shown to give good results when simulating carbon-based nano materials; DREIDING and CVFF potentials are used for modeling polymeric materials; and CHARMM potentials are shown to be more suitable for modeling biological materials like proteins and collagen molecules.

One of the simplest but most important components for the forcefield is the pair potentials. It defines the interactions between two adjacent atoms, where the interactive energy solely depends on the distance between the two. Pair potentials are divided into two major categories (i) non-bonded potentials and (ii) bonded potentials. Lennard-Jones (LJ) potential is commonly used to describe the non-bonded interactions between atoms. The general form of the LJ potential is given by Equation 2.8.

\[
\phi_{LJ} = 4\varepsilon_0 \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \]  

(2.8)

In this equation, \(\varepsilon_0\) is the depth of the energy well, and \(\sigma\) is the distance between two atoms when the LJ potential energy is equal to zero (Figure 2.2a). Note that the orders for the first and second terms of this expression are 12 and 6, respectively. This is the most common form for the LJ potential (i.e., 12-6 LJ potential), and it is general used to describe van der Waals interactions. There are also other forms of the LJ potentials with different orders. For example, without considering the electrostatic effect, a 9-6 LJ potential has been reported to be a better fit to describe the hydrogen bonding in the PVA melt system. For certain molecular interaction requirements, LJ functions with various modified parameters can be chosen to fit
experimental data. **Figure 2.2b** shows a comparison between the standard 12-6 LJ and 9-6 LJ functions.

![Comparison between standard 12-6 LJ potential and 9-6 LJ potential with the same set of carbon-carbon interaction parameters.](image)

**Figure 2.2** (a) 12-6 Lennard-Jones (LJ) energy curve based on carbon-carbon interaction parameters. (b) Comparison between standard 12-6 LJ potential and 9-6 LJ potential with the same set of carbon-carbon interaction parameters.

In this thesis work, a consistent-valence forcefield (CVFF) is used for most of the simulation studies since it has been used for both CNT and polymer systems. CVFF has defined atom types for 20 commonly occurring amino acids, most hydrocarbons, and many other organic molecules. The analytical form and its schematic illustration of the energy expression in CVFF are presented in **Figure 2.3**.

The first four terms shown in **Figure 2.3** are usually referred to as the diagonal terms of the forcefield. They are used to represent the energy changes due to the deformation of bond length, angles, torsions, and out-of-plane interactions. More accurate Morse potential (Term 1) is used for bond stretching instead of the common harmonic form. Terms 5 through 9 refer to as the off-diagonal terms, which represent the coupling effects due to the deformations and coordinate changes. The last two terms describe the non-bonded interactions, where standard 12-6 LJ function is used for vdW forces (Term 10) and Coulombic expression is used for electrostatic interactions (Term 11). It needs to point out that the hydrogen bonding is a natural consequence of the standard vdW and electrostatic parameters in CVFF. Therefore,
special hydrogen bond functions do not necessarily improve the accuracy of the CVFF fitting to experimental data.\textsuperscript{192}

\[ E_{\text{CVFF}} = \sum_b D_b [1 - e^{-a(b-b_0)}] + \sum_{\theta} H_{\theta} [1 + s \cos(n\phi)] \]

\[ + \sum_{\phi} \cos \phi(\theta - \theta_0)(\phi - \phi_0) \]

\[ + \sum_{\beta} F_{\beta} (\beta - \beta_0) \]

\[ + \sum_{\gamma} \frac{q_i q_j}{\varepsilon_{ij}} \]

\[ + \sum_{\delta} \frac{(r^+ / r)^2 - 2(r^+ / r)^6}{\varepsilon} \]

\textbf{Figure 2.3.} Analytical form of the energy expression of CVFF and corresponding schematic illustrations.

\section*{2.4. Computational Methods for Investigating the Polymer-CNT Interactions}

As discussed in Chapter 1, it is clear that one key factor for producing desired interphase morphologies and having improved polymer/CNT composite fiber properties is fundamental understanding and control of interfacial polymer-CNT interactions. Therefore, a systematic study of polymer-CNT interactions under different processing conditions is needed. The current experimental approaches being used to characterize these interactions can be divided into three main categories, (i) coupling mechanical testing of polymer/CNT bulk composites
with continuum theories;\textsuperscript{193-198} (ii) using Raman spectroscopy to determine the characteristics of CNT (i.e., diameters and dispersion levels);\textsuperscript{199,202} and (iii) performing CNT pull-out tests from a polymeric substrate using AFM tip to understand the mechanics, fracture, and failure processes at the interface.\textsuperscript{200, 204} However, due to the challenges of the experimental methods discussed at the beginning of this chapter, researchers have also tried to take advantage of computational modeling methods to study the polymer-CNT interaction in simulation settings. In this section, some of the representative studies for simulating the interaction between the CNT and the polymer matrix using both continuum theory and atomistic modeling are summarized.

2.4.1 Continuum Modeling for Studying Polymer-CNT Interactions

The morphology of the polymer-CNT interaction, as shown in Section 1.4 has mainly three different regions (i.e., polymer matrix (bulk), polymer interphase, and polymer-CNT interface). In order for the analytical methods to be valid when studying this system, the traditional microscale rules cannot be directly applied. For instance, the micromechanics equations treat CNT as a solid fiber without considering its lattice structure. In addition, these equations assume perfect bonding between the fillers and the polymer interphase.\textsuperscript{144} In the real situation, however, polymer chains at the interphase region interact with CNT through van der Waals (vdW) forces. Therefore, the perfect bonding assumption is not valid when studying the polymer-CNT interaction.

In order to incorporate these vdW interactions in their analytical model, researchers have suggested many approaches.\textsuperscript{161-163} Some works proposed an imaginary material at the interface region to resolve the perfect bonding issue. However, the property of this material is hard to determine without any experimental basis.\textsuperscript{161} Other works have suggested the incorporation of some imperfection factors at the polymer-CNT interface by changing ratio of the interactive area between the two components. In such cases, the effective Young’s modulus of the CNT decreases as the imperfection of the interface increases.\textsuperscript{162} While this approach can somewhat reflect the ‘real’ interfacial interaction environment by diminishing the effect of complete interactions, the bonding is still considered ‘perfect’ in the areas of interaction. For this reason, model showed higher stress transfer from the matrix to the filler,
which lead to an over prediction of the composite properties. Another widely accepted model that can take the interface debonding and sliding into account is the cohesive zone model. By calculating the total energy of the material through volume integration and movement differentiations in both vertical and tangential direction, the parameter for the vdW force between CNT and polymer matrix can be obtained. The relationship between the shear stress and sliding displacement across the polymer-CNT interface as a function of the volume densities of CNT and polymer was also reported.

Numerical modeling methods employing FEA have also been used to study this interfacial interaction. Compared to analytical models, the polymer interphase is considered more carefully by assigning different properties and thickness as compared to the bulk polymer. Many groups also applied various types of elements in conjunction with LJ potentials to simulate the vdW interactions between the CNT and the interphase. Some of the studies that investigated the polymer-CNT interactions by continuum modeling are summarized in Table 2.1.

Table 2.1 Summary of studies of polymer-CNT interactions using continuum modeling

<table>
<thead>
<tr>
<th>Method</th>
<th>Region</th>
<th>Polymer-CNT Interaction</th>
<th>Interphase Thickness (nm)</th>
<th>Method of Modeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analytical</td>
<td>Interface$^{163}$</td>
<td>vdW</td>
<td>N/A</td>
<td>Cohesive energy</td>
</tr>
<tr>
<td></td>
<td>Interface$^{196}$</td>
<td>vdW</td>
<td>N/A</td>
<td>Elasticity</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{205}$</td>
<td>perfect</td>
<td>0.01</td>
<td>Elasticity</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{161}$</td>
<td>vdW</td>
<td>0.17</td>
<td>Elasticity</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{206}$</td>
<td>vdW</td>
<td>0.17</td>
<td>Joint element</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{165}$</td>
<td>vdW</td>
<td>0.34</td>
<td>Spring</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{155}$</td>
<td>vdW</td>
<td>0.17</td>
<td>Nonlinear spring</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{207}$</td>
<td>perfect</td>
<td>0.15</td>
<td>Solid</td>
</tr>
<tr>
<td></td>
<td>Interphase$^{208}$</td>
<td>vdW</td>
<td>0.38</td>
<td>Truss rod</td>
</tr>
</tbody>
</table>

25
2.4.2 Atomistic Modeling for Studying Polymer-CNT Interactions

Atomistic simulation is another powerful computational technique that has been widely used to study the interactions of particles at the atomic level due to its accuracy as well as flexibility in constructing initial configurations and introducing desired changes into the systems. In addition, the comparable sizes of individual CNT and polymer chains makes it suitable to model nano-composites without sacrificing the result accuracy caused by the dimensioned variation between the components.\textsuperscript{159}

MD Simulation for Polymer-CNT Interactions

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{image}
\caption{MD snapshots of two different polymer chains introduced to a SWNT. (a) Poly(caprolactone) interacting with SWNT freely for 2.4 ns,\textsuperscript{209} and (b) Poly(paraphenylene vinylene) interacting with SWNT freely for 2.4 ns.\textsuperscript{160}}
\end{figure}

Two major types of MD simulations are typically performed to study the polymer-CNT interactions.\textsuperscript{167, 210} These studies include (1) introduction and (2) pull-out of CNT from the polymer matrices. For such simulations, CNT are usually surrounded by polymer chains, which are allowed to freely interact with one another. The polymer-CNT interaction in this case is usually presented in the form of interaction energy $E_{\text{int}}$,\textsuperscript{167, 210} given by Equation 2.9.
\[ E_{\text{int}} = E_{\text{total}} - (E_{\text{CNT}} + E_{\text{polymer}}) \] (2.9)

\( E_{\text{total}} \), \( E_{\text{CNT}} \), and \( E_{\text{polymer}} \) represent the energy of the whole system, the CNT, and the polymer, respectively. Figure 2.4 shows MD snapshots for two different polymer-SWNT introduction simulations reported in the literature.\textsuperscript{160, 209}

For pull-out simulations, similar to CNT straining test in experiments, CNT are drawn computationally from the surrounding polymer matrices. In this case, the polymer-CNT interaction energy is usually presented in the form of interface shear strength,\textsuperscript{211} stress-strain curve,\textsuperscript{212} or effective viscosity.\textsuperscript{213} The typical interface shear strength is calculated based on the total pull-out work \( W_{\text{pull-out}} \), given by Equation 2.10.

\[ \tau_{\text{int}} = \frac{W_{\text{pull-out}}}{\pi r L^2} \] (2.10)

\( \tau_{\text{int}} \), \( r \), and \( L \) are the interfacial shear strength, nanotube external radius, and length of the nanotube, respectively. Figure 2.5 shows snapshots of the CNT pullout process and the typical force-displacement curves reported in the literature.\textsuperscript{214}

Figure 2.5 (a through h) Deformation process of CNT pull-out from polymer matrix and (i) the typical pulling force-displacement curves.\textsuperscript{214}
Coarse Grain Simulation for Polymer-CNT Interactions

Coarse grain simulations are another approach developed to map atomic systems onto other particle systems with coarser resolutions. This technique allows larger systems with longer simulation time periods and less computational efforts to be investigated.\textsuperscript{215-217} CG is mainly used for studying the material bulk properties. This is needed when the desired behavior, property, or response of the composites are both inaccessible to full atomistic MD simulation (nano-scale) and inapplicable to continuum theory (micro-scale). The coarse grain models usually use bead-spring models, where each bead represents a group of atoms (typically the repeat unit of the material) with estimated atomistic information. The neighboring beads are connected by springs, which contain bonding, rotation, as well as torsion information. Other interactions between non-bonded beads, such as van der Waals interaction and hydrogen bonding, are usually modeled by LJ potentials with different parameters. The accuracy and utility of the CG models is typically determined by the parameters associated with their governing potentials. The parameter fitting process for CG is usually conducted by comparing the energy results obtained from CG with the full atomistic MD results. Regardless of how well the fitting is done, CG models normally lose some detailed information in the beads (e.g., dihedral and improper information), which results in inaccuracy of nonlinear stress-strain mechanical behavior of materials.\textsuperscript{144} Since typical polymer behaviors upon tension or compression are nonlinear due to their semi-crystalline nature, CG models used to study polymer mechanical performances should be carefully parameterized.
**Figure 2.6** (a₁) Coarse-grain mapping mechanism for PVA and its application for studying PVA crystallization behavior (a₂) before and after undercooling. (b₁) Coarse-grain mapping for CNT, and (b₂) its derived buckypaper model\(^{164, 165, 218}\)

Since the CG model was developed to investigate the properties of the bulk materials, many studies have been dedicated to understanding the control polymer or CNT properties separately. For example, the bulk properties (e.g., density, glass transition/melting temperature, expansion coefficient, and Young’s modulus/tensile strength) of polyethylene (PE) have been studied comprehensively using CG models.\(^{219, 220}\) CG models for polystyrene (PS) were also developed to study its thermodynamic and chemical properties.\(^{221, 222}\) The crystallization behavior from PVA melt was also studied using CG models.\(^{191, 223}\) The mapping mechanism and configuration of the PVA melt before and after cooling are shown in **Figure 2.6a.** CG models for CNT have also been developed to examine the CNT mechanical properties. These models have been used to characterize its nanindentation response of Buckypaper with SWNT and DWNT (Figure 2.6b).\(^{218}\) The microstructural evolution and
failure mechanism of the CNT networks have also been evaluated by such modeling. Very few studies have focused on investigating the polymer-CNT interactions using CG analysis. This is mainly due to the variation of Lennard-Jones potentials between CG beads of polymer and CNT.\textsuperscript{144} Table 2.2 summarizes typical MD and CG simulation studies used to investigate polymer-CNT interactions.

### Table 2.2 Summary of molecular dynamics and coarse grain studies of polymer-CNT interactions:\textsuperscript{211,225,213,193,210,226,167,142,227}

<table>
<thead>
<tr>
<th>CNT Types</th>
<th>Polymer Matrix</th>
<th>Tube/Bundle Length (nm)</th>
<th>Methods</th>
<th>Major Findings/Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWNT and DWNT\textsuperscript{211}</td>
<td>Polystyrene</td>
<td>2</td>
<td>MD, CNT pullout</td>
<td>Interface shear strength of 160 MPa</td>
</tr>
<tr>
<td>SWNT\textsuperscript{225}</td>
<td>Polyethylene</td>
<td>2</td>
<td>MD, CNT introduction</td>
<td>Introduction of CNT increased PE glass transition temperature</td>
</tr>
<tr>
<td>SWNT\textsuperscript{213}</td>
<td>Polyethylene</td>
<td>5.3</td>
<td>MD, CNT pullout</td>
<td>Shear strength increased 10 times with 1% SWNT-polymer cross-link</td>
</tr>
<tr>
<td>SWNT bundles\textsuperscript{193}</td>
<td>Epoxy</td>
<td>5.1</td>
<td>MD, CNT pullout</td>
<td>Stronger SWNT-epoxy interactions compared to SWNT bundles</td>
</tr>
<tr>
<td>SWNT\textsuperscript{210}</td>
<td>Poly(methyl methacrylate)</td>
<td>5.3</td>
<td>MD, CNT introduction and pullout</td>
<td>Polymer-CNT interaction energy of 0.39 kcal/mol Å²</td>
</tr>
<tr>
<td>SWNT\textsuperscript{226}</td>
<td>Polyethylene with various chain lengths</td>
<td>25 to 75</td>
<td>MD, CNT introduction</td>
<td>Thermal resistance of CNT junctions can be improved by modifying polymer-CNT interface</td>
</tr>
<tr>
<td>SWNT\textsuperscript{167}</td>
<td>Polyphenylacetylene</td>
<td>5.0</td>
<td>MD, CNT introduction</td>
<td>Strongest polymer adhesion happened for armchair CNT</td>
</tr>
<tr>
<td>SWNT\textsuperscript{142}</td>
<td>PmPV</td>
<td>4.1</td>
<td>MD, CNT introduction</td>
<td>Strong non-covalent polymer-CNT interaction</td>
</tr>
<tr>
<td>SWNT\textsuperscript{227}</td>
<td>Polyethylene</td>
<td>5.9</td>
<td>CG, CNT introduction</td>
<td>Angle between two polymer-wrapped SWNT determines the load transfer</td>
</tr>
</tbody>
</table>
The simulation results obtained from various modeling techniques reviewed in this chapter can be drastically different and are dependent on factors such as theoretical assumptions, initial configurations, boundary conditions, and integration methods. Especially for the polymer-nano carbon interaction in composite fiber studies, the translation from the atomic-scale polymer-nano carbon interaction information obtained using MD or CG methods to the macroscopic fiber properties (e.g., mechanical properties, thermal, and electrical conductivities) acquired from experiments or macro-scale simulations using FEM becomes crucial for properly linking the data from different domains to provide deeper understanding of the problem.

2.5. SUMMARIES

In summary, this chapter introduced the framework of some widely used modeling techniques for simulating the interaction between the CNT fillers and the polymer matrix. Since the simulation portion of this thesis work mainly focuses on utilizing MD methods to investigate atomistic interactive morphologies and energy states, the general principles, algorithms, and various forcefields used in full-atomistic MD simulation has been discussed in details. Some of the polymer-CNT interaction studies in the literature using both continuum modeling and atomistic modeling were summarized. This literature review to emphasize the need of using computational means to study the discussed interaction problems to improve understanding and complement the results obtain from experimentation.
Chapter 3 BUILDING LINKAGE BETWEEN EXPERIMENTATION AND COMPUTATION

3.1. INTRODUCTION

As reviewed and discussed in Chapter 1 and Chapter 2, experimental and computational methods have several drawbacks when implemented independently in order to analyze composite materials in nano-scale. In particular for the polymer/CNT composite fiber systems studied in this work, some of the macroscopic fiber properties such as mechanical and electrical behavior, fiber dimensions and orientations, and CNT distribution network in the matrix can be obtained more conveniently and accurately using experimental methods. However, other microscopic properties such as polymer-CNT interaction energies, polymer chain morphologies on the CNT surface under different conditions, adhesion strength between nanotube bundles, and interphase are more suitable for computational approaches. However, the properties obtained from each domain can only provide partial information about the whole system. For this reason, a joint approach is needed to truly integrate the experimental and computational results in order to provide a complete picture of and to better characterize the nano-composite fiber systems of interest. This combined method is also crucial for engineering the desired polymer morphology in this work (i.e., the interphase region) by understanding and subsequently controlling the fundamental polymer-CNT interactions at the atomic level.

In this chapter, the theoretical foundation for connecting experimentation and computation is discussed. Possible linkages and methodologies used specifically for the composite fiber system studied in this work are also presented. Key objectives of this dissertation using both methods are also listed in detail. The chapters associated with the research performed for each objective are also included.
3.2. LINKING EXPERIMENTATION WITH NUMERICAL SIMULATION

3.2.1 Statistical Mechanics for Proper Linkage

The joint approach used in this work is to combine experimental analysis (i.e., tensile testing, SEM imaging, X-ray scattering, thermal analysis) with full-atomistic MD simulations. Therefore, connections between experiments and MD simulations need to be explained in details. The goal of MD is to obtain macroscopic properties of a system (e.g., system temperature, mechanical properties, and mechanism of conformational changes) through microscopic simulations. In order for the microscopic information obtained to correctly reflect the macro-scale properties, statistical mechanics approaches are introduced. In statistical mechanics, rigorous mathematical expressions that relate the macroscopic properties of materials to the distribution and motion of the atoms and molecules are provided. MD simulation evaluates these expressions by solving Newton’s equation of motion.

It is given in modern statistical mechanics that the average of a system is defined as an ensemble average (i.e., collection of all possible systems with identical macroscopic state but different microscopic states) shown in Equation 3.1.

\[
< A >_{\text{ensemble}} = \int dp^N \int dr^N A(p^N, r^N) \rho(p^N, r^N)
\]  

(3.1)

In Equation 3.1, \( N \) is the fixed number of atoms in the system. \( A(p^N, r^N) \) is the observable of interest and is given as a function of momentum \( p \) and positions \( r \) of the system. \( \rho(p^N, r^N) \) is the probability density of the system also given as a function of \( p \) and \( r \). Averaging this ensemble is extremely difficult because it requires a complete calculation of all possible microscopic states of the system. For this reason, time averaging is used instead for system averaging in MD. Equation 3.2 shows the typical expression of time averaging used in MD.

\[
< A >_{\text{time}} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau A(p^N(t), r^N(t)) dt \approx \frac{1}{M} \sum_{t=1}^M A(p^N(t), r^N(t))
\]  

(3.2)
In Equation 3.2, $\tau$ is the simulation time. $M$ is the number of time steps. $A(p^N(t), r^N(t))$ is the observable value at a given simulation time $t$. As compared to Equation 3.1, this expression makes the macroscopic properties of interest time-dependent (i.e., $<A>_{\text{time}}$) instead of state-dependent (i.e., $<A>_{\text{ensemble}}$) by shifting the integration method from all possible system macroscopic states to simulation time. Although this integration allows MD to obtain properties at a reasonable simulation time scale without fully exploring the possibility of all microscopic states, the accuracy of MD simulation depends on the $<A>_{\text{time}}$ obtained as compared to $<A>_{\text{ensemble}}$. In addition, since the averaging method used in experiment is similar to average ensembles used in statistical mechanics (i.e., the number of trials in this context), the relationship between $<A>_{\text{ensemble}}$ and $<A>_{\text{time}}$ also becomes crucial for properly linking experimental results with MD data.

This connection is given by ergodic hypothesis, one of the most fundamental axioms of statistical mechanics (Equation 3.3).

$$<A>_{\text{ensemble}} = <A>_{\text{time}} \quad \text{(3.3)}$$

This hypothesis states that over long periods of simulation time, the time that system spent in some microstates with the same energy equals to the volume of this region. Simply put, if allowing the system to evolve for long enough time, the system will eventually pass through all possible microstates and exhibit macroscopic properties. For this reason, in order for MD simulation to determine macroscopic properties of the system, the simulation should generate enough representative conformations of the system so that this equality is satisfied. It is also worth mentioned that the microstates which are close to the system equilibrium have more likelihood to be visited. This indicates that Equation 3.3 is more likely to be satisfied when system reaches equilibrium. Therefore, ergodic hypothesis not only allows MD simulations to capture the macroscopic properties of the system using reasonable amount of computation resources, but also provides theoretical foundation for properly linking MD and experiments in analysis.

Since this research work centers around fabricating and analyzing polymer/nanotubes composite fibers to understand the fundamental polymer-CNT interactions for interphase formation, some of the most important macroscopic properties of the fibers need to be
properly connected with the MD results from simulation. For this reason, the following sections focus on the methodologies used to bridge the fiber properties obtained from each domain.

3.2.2 Fiber Processing Condition Linkages

Undercooling process for Initiating Polymer Interphase Formation

One of the goals in this thesis work is to control fiber processing conditions for initiating the polymer interphase formation. While the mechanism for the continuous crystal growth at the nuclei surfaces (i.e., known as the secondary nucleation where more and more chains join the initial nucleus) is governed by Lauritzen-Hoffman theory and will not be the discussed focus here, the initialization of the polymer nuclei (i.e., primary nucleation) is crucial for initiating the interphase growth in the first place. The difficulty of initiating the primary nucleation process is higher than initiating the secondary nucleation, due to the reduction of the specific area (i.e., surface area of the crystal divided by its volume) on the crystal surface. For this reason, understanding and controlling primary nucleation of the polymer chains become important in this work. In order for the polymer chains to initiate primary nucleation, the Gibbs free energy barrier needs to be overcome. The critical size of the nucleus required for them to be stable depends on this free energy barrier. An illustration of the Gibbs free energy as a function of nucleus size is given in Figure 3.1a.

![Figure 3.1](image)

**Figure 3.1.** (a) Schematic of the variation in Gibbs free energy as a function of polymer nucleus size. The critical free energy barrier needs to be crossed for the nucleus to be stable. (b) Schematic of the critical nucleus size as well as the critical free energy barrier decrease as the undercooling increase.
A mathematical expression for describing the formation of the initial nucleus using Gibbs free energy is given by Equation 3.4: \[ \Delta G = \frac{4}{3} \pi r^3 \Delta G_e + 4 \pi r^2 \gamma^* \] (3.4)

In Equation 3.4, $\Delta G$ is the Gibbs free energy of the nucleus as function of its radius $r$. $\Delta G_e$ is the free energy of crystallization/unit volume. The specific surface free energy is given by $\gamma^*$. Since the representative curve for this expression, shown in Figure 3.1a, has an initial increase in the free energy and a subsequent drop afterwards, the critical value of $r^*$ and $\Delta G^*$ can be obtained by taking the first derivative of the curve expression and equating it with zero. The final expression of the critical points are given in Equation 3.5 and 3.6:

\[ r^* = \frac{2\sigma}{\Delta G_e} = \frac{2\sigma T_m^*}{\Delta H_f^* \Delta T_c} \] (3.5)

\[ \Delta G^* = \frac{16\pi \sigma^3}{3\Delta G_e^2} = \frac{16\pi \sigma^3 T_m^*}{3\Delta H_f^* \Delta T_c^2} \] (3.6)

In the above expression, $\sigma$ is the surface energy, $T_m^*$ is the equilibrium melting point of the polymer. $\Delta H_f$ is the change in enthalpy of the system, and $\Delta T_c$ is the undercooling of the system. From these two expressions, it is found that the critical polymer nucleus size $r^*$ and the critical free energy $\Delta G^*$ both depend on the undercooling $\Delta T_c$. When plotting these relationships, a clear trend is observed. As shown in Figure 3.1b, as the degree of undercooling increases, the energy barrier needed to be overcome as well as the minimum size needed for nucleus to be stable is decreased. This suggests that the control of the undercooling process is beneficial to the initialization of the polymer nucleus and can be applied directly to the fiber fabrication process.

As related to this work, the undercooling process is applied experimentally to the spinning dope of the composite fibers in order to initiate the nucleation of the polymer interphase in the vicinity of CNT. The degree of undercooling is accurately measured by a thermal couple, and the temperature control is performed using the digital hot plate. The polymer morphologies
near the CNT surface within the composite fibers spun from the dopes with and without the undercooling process are subsequently examined using SEM. For comparison, a similar undercooling procedure is performed in the computational domain by constructing polymer/nanotubes scenarios that corresponds to the experimental conditions and performing a Nose-Hoover thermostat on the system. The final configurations of the polymer chains near CNT surface with and without the undercooling process can be visualized using molecular visualization software.

Dispersion Study for Optimizing CNT Distribution in Composite Fibers

Quantifying the effects of the CNT dispersions in the composites is another area of interest in this work and can be investigated using both experimental and computational perspectives. For experimental analysis, the bundle size of the nanotubes can be analyzed using various methods. The dispersion quality of CNT in spinning dope preparation can be indirectly measured using X-ray scattering techniques. By fitting certain portions of the resultant scattering profile using theoretical expressions, the nanotube bundle size can be obtained. The CNT dispersion quality in the composite fibers can also be studied by examining the distribution of CNT network within the fiber after removing (i.e., burning off) the polymer regions using TGA and measuring the residual CNT bundle sizes via SEM. These experimental studies provide information regarding the processing-structure relationship during fiber fabrication process. However, only the initial input conditions (i.e., dispersion conditions and material used) and the final output results (i.e., CNT bundle size and distribution morphology) can be observed using experimental approach. The roles that each component (i.e., polymer and CNT) plays during dispersion (in-situ) and the resultant quality difference due to different polymer-CNT interaction cannot be analyzed quantitatively. For this reason, various simulation scenarios that mimic the statuses of different dispersion stages are necessary to provide quantitative and morphological evidence for supporting experimental observations.

For the computational portion of this study, individual nanotube/nanotube bundles are created with polymer chains allocated in various spatial positions to simulate different dispersion
quality and confinement states observed from experimental domain. The interaction energy between the polymer chains and nanotubes can be monitored and plotted as a function of simulation time. The chain morphologies can also be analyzed through visualization software package to show the effects of different dispersion and confinement conditions. This provides quantitative and morphological evidences of the interactive behavior between polymer chain and nanotubes, which complement the experimental data.

**Laminar Flow Optimization for Creating Extended Chain Morphology**

This work utilizes a laminar-flow gel-spinning apparatus for fabricating composite fibers. The laminar-flow effect during the fiber spinning process not only affects the alignment of the polymer chains and the nanotubes, but also provides unique external forces that can potentially extend the polymer chains on the CNT surface. For this reason, understanding and optimization of the laminar-flow is necessary. In experiments, the laminar-flow is created by pumping the coagulation solvent (i.e., methanol) into a glass tube using a step-wise pump. The efficiency of the pump can be accurately controlled in order to adjust the laminar-flow speed. Fibers produced by using various laminar-flow rates are characterized and compared to investigate the effect of it on the fiber structure and the final mechanical performance. However, although a connection between the laminar-flow used and the final fiber properties can be made, information about the polymer-CNT interaction process under the effect of the laminar-flow is lost. For this reason, MD simulation is also used to explore this fundamental interaction with various laminar-flow rates.

By constructing polymer/CNT/solvent systems correspond to the experimental conditions and subsequently applying acceleration forces to the solvent molecules, laminar-flow with speeds comparable to experiments can be created in MD simulation. By changing the magnitudes of such acceleration, different laminar-flow rates can be achieved and used to study the polymer-CNT interactions. The conformational changes of the polymer chains under various laminar-flow rates can be analyzed from morphological and energetic points of view. Final system conformations obtained from different laminar-flow speeds can be used to relate to the findings in experiments. The snapshots of the chain morphological evolution under flow
conditions can also provide unique insight for visualizing and better understanding the interphase formation mechanism during fiber spinning, which cannot be captured from experimental domain.

### 3.2.3 Mechanical Properties of Composite Fibers

The mechanical performance of the composite fibers is another area of focus in this work. Not only because CNT is used as the strengthening filler in the matrix to enhance fiber properties, but also since the relationship between the morphology and structure of polymer and CNT can be further understood by performing mechanical analysis. Therefore, mechanical analysis is performed in both experiments and simulations to better understand the strengthening mechanism of composite fibers. A proper connection between these two domains can be made by examining the mechanical contribution from the CNT in the composite fiber using rule-of-mixture analysis (Equations 3.7 and 3.8).

\[
Y_{\text{composite}} = V_{\text{matrix}} Y_{\text{matrix}} + V_{\text{CNT}} Y_{\text{CNT}} + V_{\text{interphase}} Y_{\text{interphase}} 
\]

\[
\sigma_{\text{composite}} = V_{\text{matrix}} \sigma_{\text{matrix}} + V_{\text{CNT}} \sigma_{\text{CNT}} + V_{\text{interphase}} \sigma_{\text{interphase}} 
\]

In these two expressions, the effective Young’s modulus and tensile strength of CNT (i.e., \(Y_{\text{CNT}}\) and \(\sigma_{\text{CNT}}\) respectively) are the analysis of interest. \(Y_{\text{composite}}\), \(Y_{\text{matrix}}\) and \(Y_{\text{interphase}}\) are the Young’s modulus of the composite fibers, polymer bulk and interphase region, respectively. \(\sigma_{\text{composite}}\), \(\sigma_{\text{matrix}}\), \(\sigma_{\text{interphase}}\) are the tensile strength of the composite fibers, polymer bulk and interphase region, respectively. \(V_{\text{matrix}}\), \(V_{\text{CNT}}\), and \(V_{\text{interphase}}\) are the volume fraction of the matrix region, the CNT, and the interphase region, respectively. \(V_{\text{CNT}}\) can be calculated based on the final concentration of the nanotubes with respect to the polymer content. Since the thickness of the interphase region coated around the CNT bundle can be measured from SEM imaging in experiments, \(V_{\text{interphase}}\) can be approximated by assuming perfect coating on all CNT bundles. \(V_{\text{matrix}}\) can be calculated after the obtaining values for \(V_{\text{CNT}}\) and \(V_{\text{interphase}}\). In addition, the Young’s modulus and tensile strength of the control and composite fibers can be obtained by performing tensile testing in experiments. The control fiber properties are used as
Therefore, in order to accurately approximate \( Y_{CNT} \) and \( \sigma_{CNT} \), proper evaluation for the mechanical properties of the polymer interphase are necessary.

In typical experimental analysis, due to the difficulty of measuring the interphase-CNT interfacial strength, the polymer interphase region is assumed to be the 100% crystalline region with perfectly aligned polymer chains in the fiber direction. This assumption provides mechanical properties of the interphase equate to an ideal polymer crystalline structure with properties directly governed the carbon-carbon bonds in the polymer backbone with perfect inter-chain interaction without considering any entanglements. For this reason, the interphase properties are usually over predicted, which results in the under prediction of the CNT effective properties.

As compared to experiments, more accurate predictions of the interphase-CNT adhesion strength can be quantitatively studied by conducting pulling tests in simulations. By obtaining interphase morphology near the CNT surface either from the laminar-flow studies mentioned in Section 3.2.2 or from the free interaction of a pre-built configuration with interphase region present, interfacial adhesion strength between the interphase and the nanotubes can be obtained in MD. The pulling forces measured from the interphase can be converted into the Young’s modulus and tensile strength of the interphase, and subsequently replace the \( Y_{interphase} \) and \( \sigma_{interphase} \) terms in Equations 3.7 and 3.8. This way more accurate prediction of the nanotube effective properties can be achieved.

### 3.2.4 Crystallization Behavior of Polymer Chains

Another area for building linkages in this work is by looking at the difference in crystallization behavior of the polymer from both perspectives. From an experimental point of view, different polymer crystal structures can be studied by using X-ray diffraction technique. Information such as crystal size, crystallinity, and orientation can be obtained from the diffraction patterns. Although this information can provide insight towards further explaining various fiber strengthening mechanism in the nano-scale, the fundamental inter-chain interaction that affects the crystallization behavior and the stress transfer mechanism within the crystal unit cell is still lacking. For this reason, simulations that can provide information
about the unit cell structure as well as the inter-chain interaction are needed. In the simulation, hypothetical polymer unit cells can be built to conduct virtual X-ray diffraction using certain algorithm to acquire simulated X-ray patterns. Reasonable unit cells hypothesis can be determined by matching the simulated curves with the experimental observations. Subsequently, the chain packing and interaction information within unit cells can be studied in details.

3.3. SUMMARY AND OBJECTIVES

In summary, this chapter discusses the theoretical foundations for building proper linkages between experimentation and computation. Regarding the specific research work related to this dissertation, this chapter also provides detailed methodologies for studying some key fiber spinning parameters using both experimental and computational methods. By coupling results from both domains, stronger understanding toward the fundamental polymer-CNT interactions under various fiber-processing conditions may to be realized. The key objectives of this dissertation are listed below. The chapters corresponding to the research performed in relation to each of the objectives is also included.

- To study the undercooling effect during fiber spinning dope preparation process on the initiation of the interphase formation as well as the interphase development process (Chapter 4)
- To characterize the dispersion quality of the nanotubes during sonication process as well as after fiber spinning (Chapter 5)
- To investigate the effect of various laminar-flow rates on the fundamental polymer-CNT interaction and the chain morphologies, as well as on the resultant fiber performance (Chapter 6)
- To study the mechanical contribution from the nanotubes and the interphase region within composite fibers. (Chapter 7)
- To study the interfacial adhesion strength between the interphase region and the CNT surface. (Chapter 7)
Chapter 4 FORMATION OF CRYSTALLINE INTERPHASE IN THE POLYMER/CNT COMPOSITE FIBERS

4.1. INTRODUCTION
As discussed in the previous chapters, the development of the polymer interphase in the vicinity of CNT plays a key role toward enhancement of the polymer-CNT interaction in the composite fiber. Previous experimental studies have shown the evidence of interphase growth in polymer/CNT composite fibers with low CNT content.\(^{79,92}\) In this chapter, an experimental processing approach toward polymer interphase development in the polymer/CNT composite fibers with high CNT loading is discussed. Based on the thermodynamic behavior of the polymer chains under various temperature conditions, an undercooling process is introduced during spinning dope preparation to promote the growth of a crystalline polymer interphase. The final fiber samples with and without the existence of the polymer interphase region are characterized. The difference in polymer crystal structures between the bulk polymer matrix and the confined interphase region is also studied using WAXD. Combined unit cell simulations based on the experimental observation are also performed to offer a more quantitative analysis and be coupled to the empirical data. In addition, full-atomistic MD studies of the undercooling process during dope preparation as well as the growth mechanism of the interphase region due to the bulk-interphase interaction are conducted.

4.2. METHODS

4.2.1 Materials
PVA (molecular weight 325,000 g mol\(^{-1}\), Mowiol 235) was obtained from Kuraray America Incorporation. SWNT (purity > 90 wt%, ash < 1.5 wt%) was obtained from Cheaptubes Incorporation. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich and used as-received.
4.2.2 Solution Preparation

SWNT is dispersed in DMSO solvent (at a concentration of 21 mg of SWNT mL$^{-1}$ of DMSO) using a bath sonicator (FS30 manufactured by Fisher Scientific) for a period of 48 h. After sonication, the PVA powder and additional DMSO solvent are added into the dispersion to achieve a final PVA concentration of 5 wt% in DMSO and SWNT concentration of 10 wt% with respect to solid content of PVA in the solution. The mixture is subsequently heated and homogenized (T10 ULTRA-TURRAX manufactured by IKA) for 20 h in order to further disperse SWNT and completely dissolve all PVA. Two different solution batches are prepared by using separate heat treatments during homogenization: (i) the first batch of solution (S-A) is homogenized under a constant hot plate temperature of 120 °C (i.e., solution temperature of 60 °C); and (ii) the second batch of solution (S-B) is homogenized using a hot plate temperature 160 °C (i.e., solution temperature of 90 °C) for the first 2 h and subsequently cool down to 120 °C. The change in temperature used for the S-B solution induces PVA crystallization during homogenization. The overall thermal processes performed on the S-A and S-B are illustrated in **Figure 4.1**

![Figure 4.1](image)

**Figure 4.1** Illustration of the general spinning dope preparation processes of S-A and S-B, where additional undercooling procedure (indicating in green line) is added to S-B from a higher hot plate temperature compared to S-A.
4.2.3 SWNT Dispersions

The nanotube dispersions are studied by electron microscopy in order to determine the length distribution of the SWNT after sonication. For image characterization, diluted droplets of the dispersions are dried on silicon and imaged by SEM. Images are analyzed using the software package Image J (version 1.44o). It is found that after 48 h of bath sonication the SWNT length varied considerably. The average SWNT length distribution based on more than 100 measurements of distinct tubes/bundles is 1.5 ± 1.1 μm. The bundle size within the composite fibers measured from the SEM images is 5.9 – 14.7 nm.

4.2.4 Fiber Preparation

Rotation of a cylindrical stir-bar in a flat bottom flask is used to create laminar-flow. The gap size between the cylinder and flask is 10 mm. The rotational speed of the stir-bar ranges from 50 RPM to 100 RPM. A methanol spinning bath is used and maintained at 0 °C for the purpose of gelation. By using a glass syringe (Thermo Scientific HPLC 100 μL), the PVA/SWNT solutions are injected at a speed of 10 μL s⁻¹ through a 22-gauge blunt tip needle into the cold methanol (0 °C) subjected to laminar-flow. The as-spun fibers are further immersed in cold methanol for 1 h before being drawn on a hot-plate. Two hot-drawing stages are used at temperatures of 90 °C and 160 °C, respectively. The drawn fibers are subsequently cut into specimens for tensile tests. The final fibers processed from the S-A and S-B spinning dopes are referred to as F-A and F-B fibers, respectively. The specific gel-spinning and hot-drawing parameters used for the F-A and F-B composite fibers are listed in Table 4.1.
Table 4.1 Processing parameters for PVA control and PVA/SWNT composite fibers.

<table>
<thead>
<tr>
<th>Fabrication Parameters/ Drawing conditions</th>
<th>F-A</th>
<th>F-B</th>
<th>Control Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sonication Parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time [h]</td>
<td>48</td>
<td>48</td>
<td>--</td>
</tr>
<tr>
<td>Bath Temperature [°C]</td>
<td>50</td>
<td>50</td>
<td>--</td>
</tr>
<tr>
<td>Homogenization Parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time [h]</td>
<td>20</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Hot Plate Temperature [°C]</td>
<td>T₀: 120 (first 2h)</td>
<td>T₀: 120 (after 2h)</td>
<td>PVA was dissolved by mechanically stirring on 120 °C hot plate</td>
</tr>
<tr>
<td>Laminar-Flow Spinning</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Needles Gauge/diameter [mm]</td>
<td>22/0.394</td>
<td>22/0.394</td>
<td>22/0.394</td>
</tr>
<tr>
<td>Gelation Temperature [°C]</td>
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<td>5 - 8</td>
<td>5 - 8</td>
</tr>
<tr>
<td>Syringe Push Speed [μL s⁻¹]</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Take-up Speed [RPM]</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Hot Drawing Process</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-spun Draw Ratio</td>
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<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Coagulation Time [h]</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Drawing Temperatures [°C]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st stage</td>
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<td>90</td>
<td>90</td>
</tr>
<tr>
<td>2nd stage</td>
<td>160</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>Draw Ratio</td>
<td></td>
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</tr>
<tr>
<td>1st stage</td>
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<td>9.0</td>
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<tr>
<td>2nd stage</td>
<td>2.2</td>
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<td>1.7</td>
</tr>
</tbody>
</table>

4.2.5 Sample Characterization

Scanning electron microscopy (SEM) is performed using a Supra-25 (operating voltage 5 kV, manufactured by Zeiss). SEM samples are placed on carbon tape and sputter coated with platinum for imaging. WAXD patterns are obtained on multi-filament fiber bundles for samples using Rigaku MicroMax-002 Microfocus X-ray Generator and Rigaku RAPID II (operating voltage at 40 kV, current at 30 mA, CuKα, λ = 0.1541 nm) both manufactured by Rigaku Americas Corporation.
4.2.6 Unit Cell Simulation and MD Configuration

In order to capture the effects of temperature treatments for dope preparation on the S-A and S-B preparation process, PVA/SWNT systems with similar solid content ratio as compared to experimental parameters (i.e., 10 wt% SWNT loading) are constructed in the computational domain. The as-built configuration for the undercooling study is shown in Figure 4.2a and 4.2b. The size of the SWNT bundle and the PVA matrix is selected such that nanotubes is ~10 wt% with respect to the content of polymer. For computational efficiency purpose, the diameter of the nanotubes is chosen to be close to the minimum bundle size measured from SEM images within the composite fibers (i.e., 5.9 to 14.7 nm) while having the complete hexagonal bundle surface for the surrounding polymer chains to interact with. For this reason, a 7-tube hexagonal (10, 10) SWNT bundle with diameter of 5.2 nm is used in the system. 36 PVA chains with 200 monomers on each chain are used to fully surround the SWNT bundle with two polymer layers (i.e., 14 chains for the inner layer and 22 chains for the outer layer). The length of the SWNT bundle is adjusted to 6.4 nm so that the nanotubes is ~10 wt% with respect to the polymer content. Before performing temperature treatments, the initial system is minimized using the conjugate gradient (CG) algorithm with a maximum moving distance constraint of 0.01 Å for each atom in a single iteration. This is followed by another minimization process with steepest descent (SD) algorithm. A NVE ensemble with maximum moving distance constraint of 0.05 Å for each atom in a single iteration is then performed for 0.1 ns to achieve a relaxed conformation. Based on the experimental procedures, two different temperature treatments are selected for the computational studies. Both procedures are graphically represented in Figure 4.2b.

The total simulation time for each case is intentionally kept the same (i.e., 2.6 ns), since the solution processing time for both solutions in experiment is similar (i.e., 24 hours). Although the simulation time is still several orders shorter than the real processing time, both cases are run until the total free energy of the system reached its minimum value. This ensures the steady-state chain morphologies are achieved and the energy values are comparable. The aim of this study is to provide understanding regarding baseline polymer-SWNT energetic interactions and resultant polymer matrix morphology under the influence of the undercooling. For this reason, solvent atoms are not added to the system for both cases.
Figure 4.2 (a₁) Top and (a₂) side views of the as-built PVA/SWNT bundle system for undercooling studies. System contains one 7-hexagonal (10, 10) SWNT bundle (diameter: 5.2 nm, length: 6.4 nm), and 36 bulk-conformation PVA chains fully surrounding the nanotube bundle (14 chains for inner circle and 22 chains for outer circle). (b) Systems heating procedures with and without the undercooling treatment are graphically plotted. Green curve and notations describe the procedure with undercooling. Red curve and notations demonstrate the procedure without undercooling. Black notations show the processes shared by both cases.

Understanding the development of the polymer interphase region is also of interest. It has been discussed previously that the interphase polymer chains not only possess more extended chain morphology due to the epitaxial interactions with the SWNT, but the region itself can also grow to reach certain thickness. The polymer interphase region thickens as more chains are added to this ordered region driven by both templating and crystallization processes. This thickening process is very difficult to observe experimentally in-situ. Instead, typical characterization of the interphase size can be estimated using experimental characterization tools like electron microscopy, X-ray diffraction, or thermal analysis. For this reason, the formation of the interphase is investigated using full-atomistic MD approach. Due
to computational limitations in terms of system size and simulation time, only the initial addition for a monolayer of PVA chains from a bulk-conformation to an interphase conformation is examined. As shown in Figure 4.3a1 and 4.3a2, a thin layer (i.e., thickness ~ 1.17 nm) of the extended PVA chains is put around the 7-tube hexagonal (10, 10) SWNT bundle (length: 49.2 nm, diameter: 5.2 nm) to create the initial interphase region (i.e., indicating in red color). The length of the bundle is selected such that it contains 200 repeat units of SWNT, which is sufficiently long for the PVA chains with 200 monomers to interact and form various morphologies on top. Outside of the interphase region, 12 bulk-PVA chains are allocated around the interphase to represent the bulk. The number of the bulk-PVA chains is selected so that the whole interphase/SWNT region can be fully covered by one layer of polymer matrix.

To explore the development of the interphase region at areas further away from the bundle and the thin layer of extended PVA, another system with extra surrounding PVA chains is built (Figure 4.3b1 and 4.3b2). In this configuration, 20 additional PVA chains are allocated to circle the as-built 12 PVA chains near the interphase region from the previous case. The number of additional PVA chains is chosen to fully surround the existed PVA/SWNT system.

Before performing temperature treatments, the initial systems are minimized using the conjugate gradient (CG) algorithm with a maximum moving distance constraint of 0.01 Å for each atom in a single iteration. This is followed by another minimization process with steepest descent (SD) algorithm. NVE ensemble with maximum moving distance constraint of 0.05 Å for each atom in a single iteration is then performed for 0.1 ns to achieve relaxed conformations. The systems are then held at 60 °C using NVT ensemble to allow free interaction for 100 ps. The interaction energies between the three components (i.e., bulk, interphase, and SWNT) are monitored and recorded.
Figure 4.3 (a₁) Top and (a₂) side views of the as-built configuration for the interphase development study, respectively. System contains one 7-hexagonal (10, 10) SWNT bundle (diameter: 5.2 nm, length: 49.2 nm), and PVA chains fully surrounding the nanotube bundle (20 chains for interphase region with extended morphology and 12 surrounding bulk-conformation chains). In order to explore the interphase development situations at regions further away from the bundle and interphase regions, another system with thicker bulk-conformation region is built. Top and side views of the as-built configuration are given in (b₁) and (b₂), respectively. In addition to the first system, this system contains additional 20 bulk-conformation PVA chains to surround the existed PVA/SWNT bundle system. The thin interphase region with extended chain morphology was highlighted in red color.

4.3. RESULTS AND DISCUSSION

4.3.1 Fiber Morphologies

As discussed in regards to solution preparation (Section 4.2.2), two solutions S-A and S-B are made using different solution temperature conditions to promote interfacial crystal formation on the SWNT during spinning. After tensile testing, the fractured ends for each set of samples are saved and sputter coated with platinum for SEM imaging. SEM micrographs of the fractured ends of the F-A and F-B composite fibers are shown in Figure 4.4.
Figure 4.4 Scanning electron microscopy (SEM) images of fiber fracture surfaces for (a) the F-A fiber and (b) high-magnification of F-A fiber showing no evidence of interphase PVA structure around SWNT (see arrow), (c) the F-B fiber and (d) high-magnification of the F-B fiber showing distinct PVA interphase structure around the SWNT (see arrow).\cite{141}

For F-A fibers (Figures 4.4a and 4.4b), no interfacial coating of PVA is observed around the SWNT bundles at the fractured surface. In contrast, very distinct interfacial crystallization of PVA is observed for F-B fibers (Figures 4.4c and 4.4d). The thickness of the interfacial coating $b$ can be calculated using Equation 4.1:

$$b = \frac{D_{\text{coating}} - D_{\text{SWNT}}}{2}$$  \hspace{1cm} (4.1)

$D_{\text{coating}}$ is the average total thickness of the coated SWNT bundle, and $D_{\text{SWNT}}$ is the average diameter of the SWNT bundle. Both $D_{\text{coating}}$ and $D_{\text{SWNT}}$ can be obtained experimentally from microscopy analysis. Based on experimental analysis, $D_{\text{coating}}$ is measured to be $\sim 26.7 \pm 5.8$ nm, while $D_{\text{SWNT}}$ is determined to be $\sim 10.3 \pm 4.4$ nm. Based on this calculation, the average thickness $b$ of the interfacial coating is calculated to be $\sim 8.2 \pm 5.1$ nm.
4.3.2 WAXD Analysis and Unit Cell Simulation

To understand the structural make-up of the observed interfacial regions as well as the overall fibers, WAXD analysis is performed. Experimental WAXD data for F-A and F-B composite fibers are shown in Figure 4.5a, respectively.

Figure 4.5 (a) Wide-angle X-ray diffraction (WAXD) data for the F-A fibers shows a major crystallization reflection for the (101) plane, followed by the simulated WAXD pattern for the proposed PVA unit cell arrangement with major (101) reflection. The experimental WAXD pattern of F-B fibers shows a major crystallization reflection for the (001) plane, followed by the simulated WAXD pattern for the proposed PVA unit cell arrangement with major (001) reflection. Crystal structure comparison of the F-A and F-B fibers: (b1) unit cell arrangement for the F-A fibers (i.e., Bunn unit cell) in a-c projection, and (b2) in a-b projection. (c1) Unit cell structure for the F-B fibers constructed using the simulated WAXD pattern results in a-c projection (c2) in a-b projection.141

Interestingly, compared to the F-A fibers WAXD pattern, the main crystallization plane of the F-B fibers shifts from the most common (101) plane at 2θ = 19.3° (i.e., main crystallization plane for the F-A fibers and typical for PVA) to (001) plane at 2θ = 16.7° (Figure 4.5a). This change of the predominant crystallization plane has never been reported previously. This (001)
major crystallization plane is associated with more adjacent chain packing as compared to the (101) plane. Crystal sizes \( L \) for the F-A and F-B fibers corresponding to their predominant crystallization planes are calculated based on the diffraction peak full-width at maximum \( B \) at 2θ angle using Scherrer’s equation. The calculated crystal sizes for the predominant crystallization planes for the F-A and F-B fibers are 4.48 nm (101) and 8.18 nm (001), respectively. Noticeably, the crystal size with respect to the (001) plane for the F-B fibers is very similar to the average thickness of the interfacial coating (\( \sim 8.2 \pm 5.1 \) nm) measured from the SEM images (Figure 4.4d). This indicates that the F-B fibers consists of mostly interphase polymer considering that the (001) crystallization plane is predominant. This (001) plane is associated with crystal growth such that the chain axis is parallel to the fiber axis. This change in crystallization for the PVA in the F-B fibers is due to the effect of SWNT templating.

Table 4.2 Parameters used to reconstruct the Bunn’s as well as build a proposed PVA unit cells as it corresponds to this work

<table>
<thead>
<tr>
<th>Unit Cell Type</th>
<th>Lattice Parameters</th>
<th>Spatial Parameters [Cartesian, Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Symmetry a [Å] b [Å] c [Å] β</td>
<td>C (H₂) a:1.484 a:2.163 a:3.522 a:2.085</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b:0.630 b:1.890 b:1.890 b:1.890</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c:4.441 c:3.901 c:4.309 c:2.480</td>
</tr>
<tr>
<td>Bunn(^234)</td>
<td>P₂/m 7.81 2.52 5.51 91°42’</td>
<td>Proposed cell for F-B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a:1.108 a:1.907 a:2.879 a:2.430</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b:0.630 b:1.890 b:1.890 b:1.890</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c:2.652 c:2.652 c:3.891 c:1.441</td>
</tr>
</tbody>
</table>

WAXD simulation analysis is used to better understand the crystallization and strengthening mechanism of the interphase structure in the F-B fibers. The F-A fibers with main crystallization plane (101) is built (Figures 4.5b) based on the typical PVA unit cell proposed by Bunn.\(^234\) A new PVA unit cell based on Bunn’s structure is also proposed to describe the
crystal formation in the F-B fibers exhibiting a major crystallization plane of (001) (Figure 4.5c). The detailed parameters of the typical and the proposed PVA unit cell structures are listed in Table 4.2. These two built unit cells are subjected to X-ray diffraction simulation using algorithms. The simulated WAXD curves are compared with the experimental data and shown in Figure 4.5a. Both experimental and simulated curves are in good agreement in terms of their major crystallization peaks. This confirms the unique arrangement of the PVA chains for the fibers containing interphase polymers (i.e., F-B) as well as the ability for SWNT to template interfacial morphology development.

4.3.3 Undercooling Effects on Polymer-SWNT Interaction

In order to investigate the undercooling effects on the polymer-SWNT interactions during spinning dope processing, two scenarios (i.e., one with undercooling and one without) are created in the simulation domain. The detailed modeling procedures and the concepts beyond initial configuration are discussed in Section 4.2.6. The polymer chains conformational results as well as the polymer-SWNT interaction energy results are shown in Figure 4.6. In order obtain a complete picture of how PVA chains interact with the nanotube bundle under different temperature procedure, multiple snapshots for each case around the SWNT bundle surface are captured and shown in Figures 4.6a and 4.6b. Conformations from different view angles for the same system are noted as i, ii, and iii. Due to the crowding of the polymer chains in both cases, no distinct morphological differences on the bundle surfaces are observed. Both systems possess similar folded-chain PVA conformation on the nanotube surface, and similar polymer crystalline regions further away from the bundle. The PVA-SWNT bundle interaction energies normalized by bundle area for both cases are plotted in Figure 4.6c. When combining system temperature profiles (Figure 4.6d) to analyze the polymer-SWNT interaction development, it is found that there is an energy switch-over after the undercooling process is finished (i.e., simulation time = 1.4 ns). Prior to the switch point, the undercooling case has a slightly lower interaction energy compared to the no-undercooling case. After the switch point, the interaction energy of the no-undercooling case becomes lower than the undercooling case. Although the interaction energy magnitudes for both cases are similar throughout the heating and cooling process, the energy switch-over
point still suggests a somewhat favorable interaction between the matrix and the bundle due to the undercooling effect. It is recognized that the development of the polymer interphase region still depends on other factors such as laminar-flow rate, CNT dispersion quality, and polymer/SWNT types. This energy comparison, however, indicates that the undercooling process is beneficial to the initialization of the interphase formation by promoting interaction between the polymer and the nanotubes.

**Figure 4.6** Snapshots of final configurations for cases without (a) and with (b) the undercooling process. Multiple views of the PVA chains morphology around the SWNT bundle (i,ii,iii notations) are provided for each case. (c) The PVA-SWNT interaction energies normalized by the SWNT bundle area for both undercooling and no-undercooling cases. The correspondent system temperature profiles for each case are plotted in (d).

The PVA-SWNT interaction energy range to initialize such interphase formation is obtained from both cases in Figure 4.6c. By normalizing the energy data using nanotube bundle area, the interaction energy is ranging from -37.1 Kcal/mol-nm² (no-undercooling case) to -34.9
Kcal/mol-nm$^2$ (undercooling case). It is also recognized that there are still other factors (e.g., solvent effects, polymer density, and degree of polymerization of the chains, etc.) need to be considered to achieve more accurate results. The values obtained in this work, however, still provide a quantitative baseline for initiating the formation of the PVA interphase.

4.3.4 Interphase Growth Simulation

After investigating the effects of undercooling on the polymer/SWNT system, another important factor that needs to be studied is the development mechanism of the interphase region. As discussed in the previous sections, the templating effect of the SWNT can result in the PVA chains initially forming a thin interphase layer around the tube. This extended chain like interfacial interaction is also observed in the previous undercooling effect. As discussed, other processing parameters also play a role in the formation of this morphology (e.g., confinement, flow during spinning, and post processing conditions). In addition, the combined epitaxial and curved effects of the nanotube surface, the chain morphology of the interphase can be more extended compared to the bulk region. This initial thin layer of interphase can potentially induce more polymer chains from the bulk to be drawn to this region and mimic the extended-chain conformation. For this reason, the transformation process and the interactive mechanism between the SWNT, the interphase, and the bulk should be studied. Detailed modeling procedures as well as the concepts beyond initial configuration are discussed in Section 4.2.6. The evolution of chain addition from the bulk-conformation to the interphase-conformation is illustrated using the time elapsed snapshots from the simulation (Figure 4.7a).

As shown in Figure 4.7a, the interphase-matrix interaction causes the bulk-conformation polymer chains to slowly transform into the interphase region. Instead of forming folded-chain crystals on top of the interphase, the bulk chains are affected by the extended morphology of the interphase, and form similar extended configuration after certain simulation time. This observation is confirmed by plotting the interphase-bulk interaction energy normalized by bundle area (Figure 4.7d). As the simulation continues, interaction between the interphase and the bulk becomes lower (i.e., stronger interphase-bulk interaction) and reaches a stable value of -14.0 Kcal/mol-nm$^2$. When comparing this value with the
SWNT-bulk interaction value (-0.4 Kcal/mol·nm²) presented in Figure 4.7c, it is noted that the bundle has very little interaction with the bulk-conformation polymer chains. This finding suggests that the transformation of the bulk-conformation chains to the interphase-conformation chains is mainly caused by the thin layer of the extended interphase region initially formed. The role of the nanotubes bundle plays in this process is to provide the template for the initial interphase region to form. In addition, it is also noted that the SWNT-interphase interaction energy value (Figure 4.7b, -34.0 Kcal/mol·nm²) is very similar to the value obtained from the undercooling simulations (-37.1 to -34.9 Kcal/mol·nm²). This further confirms the possibility of initiating the polymer interphase formation on the nanotube surface using thermal treatment.

Figure 4.7 (a) Evolution of the interphase growth, where the bulk-conformation polymer chains interacted with the interphase region and transformed into extended morphology. The original interphase region is highlighted in red color. The interaction energy curves for (b) SWNT-interphase, (c) SWNT-bulk, and (d) interphase-bulk interactions were also plotted.
It is mentioned before that the interphase growth can only reach certain thickness. As the interphase thickness increases, the curvature effect that confines the growth of the bulk-conformation chains along interphase chain direction becomes weaker. This results in a natural transition from the interphase to the semi-crystalline bulk region without the chain orientations parallel to the interphase chain. For this reason, the interphase development mechanism with surrounding of thicker bulk-conformation matrix needs to be studied.

The detailed modeling procedure is given in Section 4.2.6. Additional layer of the bulk-conformation PVA chains are allocated around the as-built configuration from previous case. The evolution of chain interaction between the bulk-conformation and the interphase-conformation is illustrated using the time elapsed snapshots from the simulation (Figure 4.8a).

As shown in Figure 4.8a, although the inner bulk-conformation layer (i.e., chains that are close to the bundle/interphase region) still transforms into extended-chain morphology similar to the previous case, the outer bulk layer (i.e., the additional chains that are further away from the bulk/interphase region) does not join the transformation and forms a somewhat amorphous region instead. This indicates that the templating effects of the bundle and the thin interphase themselves are relatively weak compared to the bulk-bulk interaction. In order to have more bulk-conformation chains to join the development of the interphase with extended morphology, additional conditions such as the spatial confinements of nanotube bundles, the laminar-flow during fiber spinning, and the hot-drawing process after spinning are needed.

The normalized interaction energies of SWNT-interphase, SWNT-bulk and interphase-bulk are plotted in Figures 4.8b, 4.8c, and 4.8d, respectively. The SWNT-interphase interaction energy value (-34 Kcal/mol-nm$^2$) is very similar to the value obtained from the previous case. This further confirms that there is no additional effect from the nanotubes bundle on the interphase development rather than providing the templating surface for the initialization of the interphase. Compared to the previous case, delays in the energy decay for both SWNT-bulk and interphase-bulk interactions are also noticed. In addition, a slightly weaker SWNT-bulk interaction energy (-0.33 Kcal/mol-nm$^2$) comparing to the previous case is also noticed. These observations might due to the outer bulk-conformation chains that potentially...
disrupt the inner chains to join the interphase, and hence hinder the interphase development process.

Figure 4.8 (a) Evolution of the interphase growth for the thick matrix case, where only the bulk-conformation polymer chains near the interphase transforms into extended morphology, and bulk-conformation chains further away from the interphase forms amorphous region by themselves. The original interphase region is highlighted in red color. The interaction energy curves for (b) SWNT-interphase, (c) SWNT-bulk, and (d) interphase-bulk interactions are also plotted.
4.4. CONCLUSION

In order to study the effect of thermal undercooling process on the polymer interphase initiation during spinning dope preparation, two sets of PVA/SWNT composite fibers with and without the undercooling procedure are produced. The introduction of undercooling process results in a successful formation of the interphase region in PVA/SWNT composite fibers. WAXD analysis shows that the composite fiber with the presence of polymer interphase has a different crystallization behavior compared to the one without the interphase region. The unit cell WAXD simulations suggest a closer distance and stronger hydrogen bonding between two adjacent PVA chains for the interphase case.

Full-atomistic MD simulations are conducted to investigate the polymer-SWNT interaction under the effect of undercooling. The development of the interphase (i.e., the transformation of the bulk polymer chains to the interphase region with extended morphology) is also studied by allowing bulk-conformation PVA chains to freely interact with the interphase region. Results showed that it is possible for the bulk-conformation chains to join the interphase and form more extended chain morphology. The nanotubes bundle is mainly responsible for the initialization of the polymer interphase; and the initial interphase region is responsible for the development of itself. Once the thin layer of interphase formed in the vicinity of the CNT, the interphase-bulk interaction will cause more chains from the bulk to join the interphase region. This finding is confirmed by plotting the interaction energies between the three components in the system (i.e., bulk, interphase, and nanotubes).

In the next chapter, another important processing parameter – the dispersion quality of the SWNT – is studied in details using both experimental and computational methods. The inconsistency of the SWNT dispersion quality and its effects on the composite fiber performances, as well as on the morphologies of the polymer chains due to different polymer-SWNT interactions is investigated.
Chapter 5 EFFECT OF CNT DISPERSION QUALITY ON POLYMER/CNT COMPOSITE FIBERS WITH HIGH CNT LOADING

5.1. INTRODUCTION

As mentioned in the previous chapters, the dispersion of the nanotubes remains a major challenge that prevents researchers from fully realizing the potential of the tubes in composite materials. In this work, the dispersion quality associated with bundle size distribution of various CNT types during the spinning dope preparations is experimentally studied. Since polymer-assisted dispersion has been shown to be beneficial for cases with low CNT concentration, the possibility of using polymer to improve dispersion with high CNT loadings are also explored. In addition, polymer/CNT composite fibers using the optimized dispersion parameters from these studies are fabricated to incorporate the effect of fiber processing into this problem. The consistency of the CNT dispersion quality within the composite fibers is examined using thermal charring process and SEM. The overall fiber performance as well as the mechanical contributions from CNT are also investigated using tensile testing and theoretical analysis, respectively.

Polymer-CNT interactions in various confinement conditions during spinning dope preparation and fiber spinning process are also studied computationally. Since the confinement conditions (i.e., related to the CNT distribution and degree of tubes/bundles exfoliation) in the spinning dope can directly relate to the CNT dispersion quality to polymer crowding, the representation of these effects in the computational domain are examined. This provides a way to assess the change in CNT bundles sizes and their accessible surface areas to the polymer matrices. For this reason, representative scenarios regarding the SWNT dispersion conditions with different bundle sizes and polymer chain allocations are considered here. This study provides insights related to promoting extended-chain polymer-CNT interphase formation from the viewpoint of controlling SWNT dispersion.
5.2. METHODS

The goal of this work is to study the dispersion status of the CNT during dope preparation and fiber spinning processes. To study CNT dispersion as it relates to dope preparation study, it is ideal to use an in-situ light-scattering approach that can reveal the bundle size as a function of sonication time. To this end, small-angle X-ray scattering (SAXS) is used. However, liquid CNT suspensions only provide weak signals (i.e., signal-to-noise ratio) for the CNT bundles under SAXS due to the interference of the solvents. This provides a challenge for distinguishing and obtaining valid information about the CNT bundle size within the dispersed solvents. For this reason, the CNT dispersions at various sonication times are casted and dried into films to perform solid-state SAXS analysis. In addition, to incorporate the dispersion effects from the fiber spinning process, polymer/CNT composite fibers with optimized CNT dispersion parameters (i.e., combination of sonication time, nanotube type, and polymer assisted effects that provides the average smallest bundle size after dispersing the tubes) based on the solid-state SAXS studies are then fabricated and characterized.

5.2.1 Materials

PVA (molecular weight 325,000 g mol\(^{-1}\), Mowiol 235) was obtained from Kuraray America Incorporation. PAN-co-MAA (molecular weight 513,000 g·mol\(^{-1}\)) was obtained from Japan Exlan Company. Three types of CNT were used in this work (i) SWNT/DWNT powder obtained from Cheaptubes Inc. (C-tubess, purity: > 99wt%, density: 0.23-0.25 g/cm\(^3\)), (ii) Purified SWNT powder (P-tubes, purity: 94.5wt%, density: 0.12 g/cm\(^3\)) and (iii) SuperPurified SWNT powder (SP-tubes, purity: 98.9wt%, density: 0.14 g/cm\(^3\)) purchased from Continental Carbon Nanotechnologies, Inc.. N,N-Dimethylacetamide (DMAc) was purchased from Sigma-Aldrich and used as-received. Dimethyl sulfoxide (DMSO) was purchased from Sigma-Aldrich and used as-received.

5.2.2 Dope and Film Preparation

It was determined from the previous study that no distinct tube debundling occurred prior to 36 hours of sonication time.\(^{233}\) For sonication times exceeding 60 hours, CNT dispersions reached steady-state, and no further exfoliation or reduction of tube dimension (in terms of
length and diameter) was observed. For this reason, the sonication times chosen in this work are 36, 48, and 60 hours.

CNT dispersion states with and without the presence of polymer chains are considered in this work. For cases without polymer, all CNT are sonicated using a bath sonicator (FS30 manufactured by Fisher Scientific) in the solvents for 36, 48, and 60 hours. The concentrations for the CNT are determined to be 3.3 mg/mL and 5.5 mg/mL in DMAc and DMSO, respectively. For cases with polymers, two kinds of polymer powders (i.e., PAN and PVA) with 1:1 weight ratio of the CNT are first dissolved in their respective solvents (i.e., DMAc for PAN, DMSO for PVA). CNT powders are then sonicated in these polymer solutions to achieve suspensions with concentrations of 3.3 mg/mL and 5.5 mg/mL in DMAc and DMSO, respectively. It is determined from CNT dispersion studies without the assistance of polymers that 48 hours is the optimum sonication time that provides minimum nanotube bundle size. For this reason, SWNT are sonicated in the polymer solutions for 48 hours prior to film casting. For all cases, once the targeted sonication times are reached, small portion of the solutions are taken out and casted into films on glass slides. All films are dried at room temperature in air for one week.

5.2.3 Fiber Preparation

CNT are dispersed in a pre-dissolved PAN/DMAc solution (25.5 mg of PAN ml⁻¹ of DMAc, 1:1 weight ratio of CNT and PAN) for 48 hours. After sonication, additional PAN powder and DMAc solvent are added into the dispersion to achieve a final PAN concentration of 7 wt% in DMAc and CNT concentration of 10 wt% with respect to solid content of PAN in the solution. The mixture is subsequently homogenized (T10 ULTRA-TURRAX manufactured by IKA) under a constant solution temperature of 90 °C for the first two hours and subsequently cooled down to 60 °C, and further mixed until the PAN/CNT dope appears optically homogeneous for spinning.

A laminar flow in a glass tube is created using a metering pump (Q3, FMI Fluid Metering, Inc.) and connected to a cold methanol source (5 to 8 °C). The flow-rate is accurately controlled by adjusting the speed of the metering pump which ranged from 0 to 2000 ml/min. A pump speed of 200 ml/min is used for all spinning processes presented in this work.
The PAN/SWNT solution is injected at a speed of 0.30 mL/min through a 22-gauge blunt tip needle into the center of the cold methanol flow. The as-spun fibers are collected and further coagulated in methanol for an additional ~12 hours before being hot-drawn. For post-processing of the fibers hot-drawing stages are used at temperatures of 90 and 160 °C, respectively. The drawn fibers are subsequently cut into specimens for characterization. The fiber spinning parameters are summarized in Table 5.1.

Table 5.1 Processing parameters for the spinning and hot-drawing of the PAN control and PAN/SWNT composite fibers using the laminar-flow gel-spinning process.

<table>
<thead>
<tr>
<th>Fabrication Parameters/ Drawing conditions</th>
<th>Control</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sonication</strong></td>
<td>Time (h)</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>--</td>
</tr>
<tr>
<td><strong>Homogenization</strong></td>
<td>Time (h)</td>
<td>PAN was dissolved by mechanically stirring on</td>
</tr>
<tr>
<td></td>
<td>Hot Plate Temperature (°C)</td>
<td>100 °C hot plate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Laminar-Flow Spinning</strong></td>
<td>Needle Gauge/diameter (mm)</td>
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</tr>
<tr>
<td></td>
<td>Gelation Temperature (°C)</td>
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</tr>
<tr>
<td></td>
<td>Solution Injection Speed (ml/min)</td>
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</tr>
<tr>
<td></td>
<td>Pump Speed (ml/min)</td>
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</tr>
<tr>
<td></td>
<td>Fiber Take-up Speed (m/min)</td>
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<tr>
<td><strong>Hot Drawing Process</strong></td>
<td>As-spun Draw Ratio</td>
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</tr>
<tr>
<td></td>
<td>Coagulation Time (h)</td>
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</tr>
<tr>
<td></td>
<td>Drawing Temperatures (°C)</td>
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<td>2nd stage</td>
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<tr>
<td></td>
<td>Draw Ratio</td>
<td>1st stage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd stage</td>
</tr>
</tbody>
</table>
5.2.4 Sample Characterization

Thermogravimetric analysis (TGA) is performed on a TGA-Q50 (manufactured by TA Instruments). Scanning electron microscopy (SEM) is performed on a Supra-25 (operating voltage 5 kV, manufactured by Zeiss). Tensile tests are performed using a dynamic mechanical analyzer G2-RSA model (manufactured by TA Instruments) with gauge length of 15 mm and strain rate of 0.07 mm·s⁻¹. Wide-angle X-ray diffraction (WAXD) patterns are collected on multi-filament bundles using a Rigaku RAPID II (operating voltage at 40 kV, current at 30 mA, CuKα, λ = 0.1541 nm) equipped with curved detector manufactured by Rigaku Americas Corporation. Small-angle X-ray Scattering (SAXS) patterns are collected using Rigaku MicroMax 007HF (operating voltage at 40 kV, current at 30 mA).

5.2.5 CNT Dispersion Simulation

Full atomistic MD simulations are performed using the software package LAMMPS (http://lammps.sandia.gov/). The consistent valence force field (CVFF) is used to describe the system potential energy for both polymer and SWNT. While more accurate potentials are available for the modeling of both polymers and carbon-carbon interactions (e.g., ReaxFF, AIREBO, or LCBOPII), the CVFF potential is adequate to capture polymer-nanotube interactions under equilibrium conditions via a classical LJ interaction. The CVFF potential has also been shown to accurately reflect the conformation of short polymer chains. Three polymer chains are used for each simulation case and each consisted of 50 monomers with atactic stereo configurational arrangement. The SWNT samples used in the experimental work have an average diameter of 1-2 nm. For this reason, for simulation studies SWNT with three different diameters 1 nm, 1.5 nm, and 2 nm are built into the model to represent the lower bound, average value, and upper bound of the real tube diameter used. All tubes with different diameters have the same length of 12.3 nm and armchair chirality, or (8, 8), (11, 11) and (15, 15) corresponding to diameters of 1 nm, 1.5 nm, and 2 nm, respectively.

SWNT bundles are constructed by arranging individual adjacent tubes into a bundle form. The bundle geometry is optimized by using steepest descent minimization functions with cutoff distance of 0.8 nm for the carbon-carbon LJ interaction. Four variations of SWNT bundles are considered in the analysis. (i) a larger bundle of diameter 8.9 nm (consisting of 19
tubes with 1.5 nm tubes); (ii) three small bundles of diameter 3.7 nm (five - 1 nm tubes); (iii) 5.2 nm (four - 1.5 nm tubes); and (iv) 5.7 nm (four - 2 nm tubes). As the aim of this study is to understand the baseline PAN-SWNT energetic interactions, no solvent molecules are used in any simulations. All simulations are performed using the constant volume and temperature canonical ensemble (NVT), with periodic boundary conditions. The equations of motion are integrated using velocity verlet algorithm with an integration time step of 1 fs, and the temperature was controlled by a Nose-Hoover thermostat. All systems are equilibrated at 300 K (using a damping constant of 2.0) for 2 ns to stabilize the interactions, confirmed by energy convergence. For analysis, polymer-SWNT interaction energies are extracted indirectly from the simulation data and CVFF potential, where interaction energy equals to the total system energy subtracted by the energies from SWNT and polymer separately. It should be noted that the reported energy curves are the average values of three runs for each simulation scenario. All simulations are conducted using Dell Precision Tower 7910 workstation.

5.3. RESULTS AND DISCUSSIONS

5.3.1 CNT Dispersions Analysis

One commonly used technique to study features with sizes on the order of 1 nm to hundreds of nm is SAXS. The scattering patterns from SAXS can provide information about sizes, ordering, and shape of the particles or pores within a matrix material or medium. Figure 5.1 shows a representative SAXS pattern, which can be divided into two distinct regions. By curve fitting the region of interest using different laws, specific particle information can be obtained. The criteria of separating two regions is given by Equation 5.1 and Equation 5.2.  

\[ Q_i R_g < 1.3 \]  \hspace{1cm} (5.1)

\[ Q_i = \frac{1}{R_g} \sqrt{\frac{3d}{2}} \]  \hspace{1cm} (5.2)

\( Q_i \) is the critical scattering vector value that separates the regions, \( R_g \) is the radius of gyration of particles, and \( d \) is the dimension of the material. The region that meets the criteria in Equation 5.1 can be used to calculate \( R_g \) using Guinier’s law. The other half of the curve can
be used to provide information pertaining to the interfaces between the particles and the matrix based on Porod’s law. The general expression of Guinier’s Law and Porod’s law are given by Equation 5.3 and Equation 5.4, respectively:

\[
I(q) = I_o \exp(-q^2 R_g^2 / 3) \quad (5.3)
\]

\[
I(q) = I_e 2\pi \rho^2 S / q^4 \quad (5.4)
\]

In Equation 5.3, \(I(q)\) and \(I_o\) are the total scattered intensity and scattered intensity not related to the shape of the particles, respectively. In Equation 5.4, \(I_e\) is a scattered intensity constant, \(\rho\) is the difference in electron density between particles and matrix, and \(S\) is the surface area of the dispersed particles.

**Figure 5.1** Representative small-angle X-ray scattering (SAXS) pattern. The curve can be divided into two regions by a critical scattering vector \(Q_1\). Region \(q < Q_1\) contains information about particle size (i.e., Guinier’s Law) and form, and region \(q > Q_1\) contains information about particle surface structure (i.e., Porod’s Law).\(^{238}\)
The goal of this dispersion study is to determine the bundle size distribution of the tubes. For this reason, Guinier’s law is used to calculate the average dimensions of the bundles. The SAXS pattern region for Guinier’s law is determined by using Equation 5.1 and Equation 5.2. For fillers with rod shape (i.e., CNT in this work) the modified Guinier’s Law is given by Equation 5.5:

\[
I(q) = I_0 \exp\left(-q^2 R_g^2 / 4 \right) / (2qH)
\]  

(5.5)

In this function, the radius of gyration of the rod-shape material is given by Equation 5.6:

\[
R_g^2 = \frac{R^2}{2} + \frac{H^2}{3}
\]  

(5.6)

\(R\) is the radius of the tube, and \(H\) is half length of the tube. According to the experimental observation, the aspect ratio of the nanotubes varies significantly ranging from 10 to 1000. For this reason, three aspect ratio values for the modified Guinier’s law (i.e., \(H/R=10, 100, \) and 1000) are used to curve-fit the SAXS patterns. The SAXS patterns for the dried dispersions are obtained by randomly sampling five different areas within each film and averaging the scattering intensities.

For pure solvent dispersions, the SWNT bundle size as a function of sonication time and as a function of various tube types are shown in Figures 5.2a1 and 5.2a2, respectively. Error bars in the plot represents the standard deviation due to the change of aspect ratio from Guinier’s law (Equation 5.5). The SAXS profiles and the quantitative summary of the SWNT bundle size for each case are given in Appendix A (Figure A.1 and Table A.1). It is observed in Figure 5.2a1 that the bundle sizes for all types of tubes reached minimum values at sonication time of 48 hours in general. Bundle size distributions also start to increase after 60 hours of sonication. This is due to increased shortening of the tubes results in a mobility increase for the tubes. This additional movement may potentially lead to the rebundling of the tubes with similar mobility and aspect ratio. At lower sonication time (i.e., 36 hours), due to the insufficient dispersion time given to the systems, bundle sizes in all cases are larger than the ones after 48 hours of sonication. For this reason, 48 hours is determined to be the optimum sonication time in this study.
Figure 5.2. Summary of SWNT bundle sizes as a function of (a₁) sonication time or (a₂) tube types (i.e., C-tubes, P-tubes, and SP-tubes) in different solvents without the presence of polymers. Regardless of the solvent used, 48 hours of sonication is found to give minimum bundle sizes for all nanotube types; and the C-tubes are found to have the smallest average bundle size among all tube types after sonication. PVA and PAN assisted dispersions are subsequently conducted using 48 hours of sonication time for the C-tubes. Representative SWNT scattering profiles obtained by subtracting a control PVA film pattern from the composite data using different correction factors (i.e., \( \text{cf} = 0.4 \) to 1) with respect to the control film intensities are shown in (b₁). The polymer-assisted SWNT bundle sizes distributions determined for both PVA and PAN cases are plotted in (b₂). The correction factor plays a role in this calculation (b₂) and it related to the scatter behavior of residual polymer and solvent in the dried composite dispersions.

As shown in Figure 5.2a₂, SWNT bundle size as a function of nanotube types is also summarized. It is found that, regardless of the solvent media used, C-tubes samples (i.e., nanotubes purchased from Cheaptubes. Inc.) exhibit the smallest bundle size distribution
among the three cases. The bundle size range determined for the C-tubes for 38 to 60 hours of sonication is 7.0 to 12.4 nm. It is worth mentioning that the SWNT dispersion procedure used to produce the PVA/SWNT composite fibers in Chapter 4 is similar to this dispersion study (i.e., sonicating SWNT in DMSO for 48 hours without polymer assistance). The nanotubes used in that work were also obtained from the same company but with a lower purity (i.e., 90 wt% purity as compared to 99 wt% purity for this dispersion study). The bundle size within the composite fibers measured from the SEM images is 5.9 to 14.7 nm, which is in good agreement with the dispersion study results presented here. For this reason, the C-tubes are found to be the most effective nanotube in this dispersion process, and is subsequently used for the polymer-assisted dispersion study.

For the polymer-assisted dispersions, the optimum sonication time and nanotube types determined from the previous studies are used with the addition of polymer. Detailed film preparation procedure for the polymer-CNT dispersions is given in Section 5.2.2. Control films for the two polymers, PVA and PAN, are also casted to obtain SAXS background patterns. Correction factors ranging from 0.4 to 1 are applied on these patterns as a multiplier when correct for background scatter based on the previous studies. The SAXS data for the obtained dried polymer-CNT dispersion films is background corrected using the control data to obtain signals from SWNT bundles. Figure 5.2.b1 plots four representative SWNT bundle patterns after background subtraction using different correction factors. The curve-fitting results using from this data is summarized in Figure 5.2.b2. It is found that the SWNT bundle size for the PAN based samples is stable at ~6.1 nm regardless of the correction factor. However, for PVA samples, the fitted bundle size values obtained are significantly affected by the correction factor applied, and ranged from 5.0 to 11.3 nm. This issue is due to the residual DMSO solvent present in the dried films leading to additional background absorption as observed from SAXS. Based on Figure 5.2.b2, the bundle diameter calculations become more stable as a more appropriate background correction factor is obtained (i.e., 0.6 and 0.4).

SWNT bundle sizes of the C-tubes sample at 48-hour sonication with and without polymer are also compared to understand the effect of the polymer during dispersion. Without polymers present, the average bundle sizes of the C-tubes after 48 hours of sonication are
found to be 7.0 and 8.4 nm in DMSO and DMAc, respectively. With the introduction of polymers, the bundle sizes after same amount of sonication time are found to be 5.0–11.3 and ~6.1 nm for DMSO/PVA and DMAc/PAN samples, respectively. Although the effect of the polymer is somewhat uncertain for PVA case due to the influence of the residual solvent, a decrease in the nanotube bundle size is confirmed for PAN case. This indicates that the introduction of the polymer is indeed beneficial to the SWNT dispersions even at high SWNT concentration. Polymer chains have the ability to introduce polymer-SWNT interactions and to somewhat stabilized the suspension and prevent the temporary dispersed SWNT from rebundling.

5.3.2 Composite Fibers Analysis

As discussed, the nanotubes dispersion quality is not only affected by the spinning dope preparation, but it also depends on various parameters of the fiber spinning process. Spinning factors such as the solvent exchange process (i.e., poor solvent molecules exchange with good solvent molecules in the spinning dope that cause fibers gelation), heat exchange process (i.e., temperature difference between the spinning dope and the coagulation bath), laminar flow conditions, and hot-drawing process can significantly affect the nanotube dispersion. For this reason, the connection between fiber processing and SWNT dispersion quality needs to be studied. It is determined from the spinning dope studies above that PAN and C-tubes with 48 hours of polymer-assisted sonication provide the smallest bundle size. Therefore, PAN and C-tubes are selected to fabricate composite fibers to investigate the effect of fiber spinning process on the nanotubes distribution in the fiber, the fundamental PAN-SWNT interactions, and the resultant fiber performance.

Three sets of composite fibers spun from three batches with similar optimized dispersion parameters are produced and examined. Detailed spinning dope and fiber preparation procedures are given in Section 5.2.3. It is expected that the final SWNT distribution within the composite fiber would have a certain degree of quality variation due to fiber processing factors. To investigate and assess the structural contributions of the SWNT (i.e., dispersion distribution) in the composite fibers made from similar spinning procedure, a thermal charring
treatment is performed. The goal of the charring process is to remove all PAN domains in order to visualize the arrangement/distribution of the SWNT alter in the fibers.

It is found using initial TGA analysis that the degradation temperature of the as-received SWNT powder was determined to be ~500 °C in air and > 900 °C in nitrogen, while the degradation temperature of the as-received PAN powder was found to be ~200 °C in air and ~250 °C in nitrogen. For this reason, all fibers are heated in nitrogen environment from 25 to 900 °C at 5 °C/min to completely remove the PAN regions. The TGA curves for SWNT, PAN, and PAN/SWNT composite fibers are given in Appendix A (Figure A.2). The charred composite fibers are observed using SEM analysis. The overall fiber morphology before and after thermal-charring are also shown in Appendix A (Figure A.3). After thermal-charring, F-1 fibers exhibit large voids due to the burn-out of PAN-rich regions (Figure 5.3a). For F-2 fibers, although no distinct regions of separation are observed, medium sized voids as well as several SWNT aggregations/entanglements (Figure 5.3b) are also found. F-3 fibers (Figure 5.3c) exhibit a much more homogenous distribution of the SWNT throughout the fiber. There is also no evidence of large void structures arising from polymer-rich regions or SWNT aggregates throughout the fiber.

The variation of the nanotubes distribution in these three sets of composite fibers using similar fiber spinning process indicates that the levels of polymer-nanotubes interactions are very sensitive to the spinning conditions. The large voids observed from F-1 fibers might due to the weak PAN-SWNT interaction caused by the fiber spinning process, which results in separation of the mixture into PAN-rich and SWNT-rich domains. Similar to F-1 fibers, the presence of SWNT aggregates in F-2 fibers also suggests an inhomogeneous interaction between PAN and SWNT during the fiber formation process. F-3 fibers may possess a better PAN-SWNT interaction compared to both F-1 and F-2 fibers, since the nanotubes are more evenly distributed in the fibers.
Figure 5.3 SEM images of the PAN/SWNT composites fiber after charring. (a₁) Cross-section of the F-1 composite fiber showing the presence of large void defects and a magnified image (a₂) shows the presence of more voids in the fiber. The void structure captured in the charred fibers are due to the burn out of PAN during charring as well as voids that may have been present upon drying out of the solvent during fiber processing. (b₁) Shows the F-2 composite fibers which exhibits both medium-sized voids (i.e., as compared to the F-1 fiber) and SWNT aggregates. At higher magnification (b₂) the highly entangled SWNT agglomerates can be clearly visualized. (c₁) and (c₂) show a more uniform distribution of SWNT and presence of small voids for the F-3 composite fiber.

Representative stress-strain curves for the three batches (F-1, F-2, and F-3) of PAN/SWNT composite fibers are shown in Figure 5.4. Although all sets of fibers are produced by using similar laminar-flow gel-spinning procedure, due to noticeable changes in the SWNT dispersion quality within the fibers, differences in their Young’s modulus and tensile strength properties are observed. Comparing the mechanical performance for all composite fibers, an increase in the Young’s modulus following the ratio of 1:1.4:2.5, as well as an increase in tensile strength according to the ratio of 1:1.9:3.2 are found for the F-1, F-2, and F-3 composite fibers, which also corresponded to increases in the dispersion quality. This further confirms that, although the SWNT dispersion quality is optimized in the spinning dope.
preparation stage, the SWNT distributions in the final composite fibers and their resultant mechanical properties are still drastically influenced by the overall fiber spinning conditions.

![Figure 5.4](image)

**Figure 5.4** (a) Typical stress-strain curves, (b) Young’s modulus and tensile strength for three sets of PAN/SWNT composite fibers produced by the same gel-spinning procedure. Compared to the first set of composite fibers (F-1) with the lowest mechanical performance, the second set (F-2) and the third set (F-3) has an intermediate and highest mechanical improvement on both modulus and strength, respectively.

In order to analyze the stiffness contributions from the SWNT in the composites, the theoretical rule-of-mixture treatment (Equation 5.7) is used to calculate the effective modulus contribution of SWNT in all composite fibers.

\[
E_c = \left( E_{SWNT-eff} - E_{PAN-eff} \right) V_f + E_{PAN-eff}
\]

(5.7)

\( V_f \) is the volume fraction of SWNT in the composite fibers, and \( E_{PAN-eff} \) and \( E_{SWNT-eff} \) are the effective Young’s modulus of the PAN and the SWNT, respectively.

PAN orientation is assessed by WAXD analysis, and the effective Young’s modulus values for PAN (\( E_{PAN-eff} \)) is determined from Equation 5.8 to 5.10. Representative WAXD profiles for F-1, F-2, and F-3 are plotted in Appendix A (Figure A.4). All parameters as well as the calculated \( E_{PAN-eff} \) values are listed in Table 5.2.
According to these contribution calculations, the effective modulus of SWNT \( E_{SWNT-eff} \) improves as the SWNT dispersion quality increases. This correlation indicates a better stress transfer from the PAN matrix to the tubes as the nanotubes dispersion quality improved. In addition, the increase in effective modulus can also be contributed to the increase in fiber orientation shown in Table 5.2. The highest effective contribution of SWNT \( (E_{SWNT-eff} = 197 \text{ GPa}) \) is found in F-3 fibers, which exhibits the most uniform SWNT dispersion. This theoretical treatment also supports that notion that PAN-SWNT interactions improve with dispersion quality.\(^{241}\)

Both the experimental and theoretical analysis show that the composite properties increase as the SWNT dispersion improves. To understand the fundamental issues relating processing approaches to the final fiber structure and ultimate properties, the molecular interactions between the PAN and SWNT are also explored computationally. In this work, the computational models are defined taking both the experimental and theoretical results into consideration in order to assess a best possible representation of the PAN-SWNT molecular interactions observed the composite fiber. For model simplification, PAN-SWNT interactions are assumed to occur in two experimentally recognized combinations (i) individual SWNT to PAN chains, and (ii) SWNT bundles to PAN chains.\(^{242,246}\) Similarly, studies have also been

\[
\frac{1}{E_{PAN-eff}} = \frac{1}{E_1} + \left( \frac{1}{G_{12}} - \frac{2\nu_{12}}{E_1} - \frac{2}{E_2} \right) \langle \cos^2 \theta \rangle + \left( \frac{1}{E_1} + \frac{1}{E_2} - \frac{1}{G_{12}} + \frac{2\nu_{12}}{E_1} \right) \langle \cos^4 \theta \rangle
\]  

(5.8)

Where

\[
\langle \cos^2 \theta \rangle = \frac{\int_0^{\frac{\pi}{2}} I(\theta) \cos^2 \theta \sin \theta \, d\theta}{\int_0^{\frac{\pi}{2}} I(\theta) \sin \theta \, d\theta}
\]

(5.9)

\[
\langle \cos^4 \theta \rangle = \frac{\int_0^{\frac{\pi}{2}} I(\theta) \cos^4 \theta \sin \theta \, d\theta}{\int_0^{\frac{\pi}{2}} I(\theta) \sin \theta \, d\theta}
\]

(5.10)

According to these contribution calculations, the effective modulus of SWNT \( (E_{SWNT-eff}) \) improves as the SWNT dispersion quality increases. This correlation indicates a better stress transfer from the PAN matrix to the tubes as the nanotubes dispersion quality improved. In addition, the increase in effective modulus can also be contributed to the increase in fiber orientation shown in Table 5.2. The highest effective contribution of SWNT \( (E_{SWNT-eff} = 197 \text{ GPa}) \) is found in F-3 fibers, which exhibits the most uniform SWNT dispersion. This theoretical treatment also supports that notion that PAN-SWNT interactions improve with dispersion quality.\(^{241}\)

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performed from a computational viewpoint in order to obtain molecular level information or to study conditions that are not accessible experimentally.\(^{145, 155, 157, 160, 247, 248}\)

**Table 5.2 Parameters used for calculating the effective Young’s modulus and orientation factor (f) of PAN, as well as the effective Young’s modulus of contribution of SWNT in all three composite fibers.**

<table>
<thead>
<tr>
<th>Parameters for Calculating ( f_{\text{PAN}} ) and ( E_{\text{PAN-eff}} )</th>
<th>( F-1 )</th>
<th>( F-2 )</th>
<th>( F-3 )</th>
</tr>
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<tbody>
<tr>
<td>( E_1 ) (GPa)</td>
<td>22.1</td>
<td>22.1</td>
<td>22.1</td>
</tr>
<tr>
<td>( E_2 ) (GPa)(^{249})</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>( \nu_{12} )</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>( G_{12} ) (GPa)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(&lt;\cos^2\theta_{110}&gt;)</td>
<td>0.06</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>(&lt;\cos^4\theta_{110}&gt;)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>( \rho_1 ) (°)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \rho_2 ) (°)</td>
<td>59.1</td>
<td>59.1</td>
<td>59.1</td>
</tr>
<tr>
<td>( f )</td>
<td><strong>0.75</strong></td>
<td><strong>0.77</strong></td>
<td><strong>0.79</strong></td>
</tr>
<tr>
<td>( E_{\text{PAN-eff}} ) (GPa)</td>
<td>7.3</td>
<td>7.3</td>
<td>8.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters for Calculating ( E_{\text{SWNT-eff}} )</th>
<th>( E_c ) (GPa)</th>
<th>( V_f )</th>
<th>( E_{\text{SWNT-eff}} ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_c ) (GPa)</td>
<td>12.8 ± 0.9</td>
<td>0.128</td>
<td><strong>50.4</strong></td>
</tr>
<tr>
<td>( V_f )</td>
<td>18.4 ± 2.2</td>
<td>0.128</td>
<td>94.2</td>
</tr>
<tr>
<td>( E_{\text{SWNT-eff}} ) (GPa)</td>
<td>32.4 ± 3.8</td>
<td>0.128</td>
<td>197.4</td>
</tr>
</tbody>
</table>

**5.3.3 Computational Analysis**

To evaluate these molecular effects, the interaction energy between the PAN chains and SWNT is studied in four scenarios (Figure 5.5). These scenarios include two surface effects (i) PAN chain interactions with a SWNT bundle, as well as two confined effects (ii) PAN chain interactions with individual (exfoliated) SWNT. The confined effects provide
a snapshot evaluation of molecular interactions, which are more likely to occur in a composite material, where the polymer is actually surrounded (i.e., confined) by the SWNT with various levels of dispersions (i.e., exfoliated/bundles of SWNT). For all simulations, no solvent molecules are included in the models. It is acknowledged that the values of interaction energies may change with the solvent presence. However, the changing energy trends from case to case should remain the same since the same solvent effect would be equally imposed on all cases.

The two scenarios exploring the basic surface PAN-SWNT molecular interactions are shown in Figures 5.5a and 5.5b. Three PAN chains are located near the surface of an individual SWNT (case 1, Figure 5.5a1) and a SWNT bundle (case 2, Figure 5.5b1). Both systems are allowed to freely interact at 300 K for 2 ns while the interaction energies are recorded. The PAN-SWNT and PAN-PAN interaction energies per PAN monomer for each case are also recorded (Figures 5.5e1 and 5.5e2). As shown in the simulation results, the PAN-PAN interaction is predominant in case 1 and resulted in a local PAN rich region near the SWNT surface. For case 2, an improvement of the PAN-SWNT interaction and a decrease in PAN-PAN interaction energy is observed. This is due to the increase in available graphitic surface. Therefore, the polymer chains to have more opportunity to interact with the SWNT bundle. These simple surface studies show that the PAN chains prefer chain-to-chain interactions. However, increasing the presence of SWNT in the near vicinity can reduce PAN chains self-interactions slightly.

In experiments, nanotubes are dispersed in the spinning dope in quiescent state with the assistance of PAN. The SWNT bundle size can be somewhat stabilized after sonication process as discussed in Section 5.4.1. However, additional PAN powder is adding to the dispersion to achieve the final spinning dope. The introduction of additional PAN-PAN interaction might disrupt the temporary SWNT dispersion state, and potentially cause the small bundles to form bigger bundles. In addition, the good and bad solvent exchange processing as well as the interference of the laminar-flow during fiber gel-spinning can also affect the SWNT debundling and rebundling process. For these reasons, the change in
available graphitic surface of the SWNT bundle is drastically influenced by the fiber spinning process, which resulted in the various SWNT morphologies observed in experiments.

Another factor that affects the PAN-SWNT interaction and the resultant chain morphology is the physical confinement effect between these two components. To study these confinement effects on the PAN-SWNT interactions, two other scenarios with three PAN chains surrounded by dispersed SWNT bundles (case 3, Figure 5.5c₁) or exfoliated tubes (case 4, Figure 5.5d₁) are also studied. Similar to the surface studies, all systems are allowed to freely interact at 300 K for 2 ns while the interaction energies are recorded. For case 3 (Figures 5.5c₁ and 5.5c₂) the PAN chains are confined by dispersed SWNT bundles, and the PAN-SWNT interaction level is slightly improved compared to case 2. For case 4 (Figures 5.5d₁ and 5.5d₂), as the dispersion level increases to full exfoliation of the individual SWNT, the highest PAN-SWNT bonding energy and the lowest PAN-PAN interaction energy of all cases (Figures 5.5e₁ and 5.5e₂) are observed. Morphologically, it is observed that the PAN extended-chain conformation becomes more pronounced as the SWNT dispersion more towards uniformity.

The simulation results suggest that, as SWNT exfoliation and dispersion (i.e., distribution of PAN and SWNT) improve, the PAN molecular conformation and its interaction with the SWNT increased from case 1 to case 4. For this reason, by combining the experimental evidence (i.e., increase in mechanical properties, fiber orientation, and effective SWNT mechanical contribution as the nanotube dispersion quality improved), the difference in the mechanical performance from F-1 to F-3 fibers may be explained by the various compositions of different PAN-SWNT interaction levels within composite fibers. This study provides critical and complementary experimental and computational evidence indicating how molecular conformation and confinement evolve and vary with nanotube dispersion and translate into structural features within the material.
Figure 5.5 (a through d) Molecular dynamics simulation snapshots of PAN/SWNT free interactions under 300 K with initial configurations of: (a1) three PAN chains located on one side of a SWNT, (b1) three PAN chains located on one side of a SWNT bundle, (c1) three PAN chains located inside and outside of the dispersed SWNT bundles with different bundle sizes, and (d1) three PAN chains located within space the dispersed individual SWNT. The final configurations of each case after 2 ns were shown in (a2), (b2), (c2) and (d2), respectively. The PAN-SWNT and fitted PAN-PAN interaction energies for all cases were plotted and summarized in (e1) and (e2), respectively.

5.4. CONCLUSIONS

To conclude, the CNT dispersion qualities associated with bundle size during the spinning dope preparations are experimentally studied. It is found that the dispersion quality of the CNT (i.e., CNT bundle size) depends on the sonication time as well as the types of nanotubes. The optimum sonication time found in this work is 48 hours, and the most effective CNT type
in terms of dispersion is the C-tubes (i.e., SWNT/DWNT) with 99 wt% purity purchased from Cheaptubes Inc.. It is also found that the polymer chains are able to prevent dispersed CNT from rebundling and to improve the CNT dispersion quality. In addition, the optimized polymer-assisted dispersion parameters are used to fabricate polymer/CNT composite fibers. It is found that the composite fibers spun from spinning dopes using same dispersion procedure possessed significant differences in both CNT morphological distribution and mechanical performances. This is mainly due to fiber spinning factors (i.e., good and bad solvent exchange for fiber gelation, laminar-flow effects, and solution temperature difference from spinning dope to the cold methanol bath) that lead to the inconsistency in polymer-CNT interactions and the resultant variations in nanotube bundle size.

MD simulations reveal the fundamental relationship between the SWNT dispersion levels (i.e., PAN-SWNT interactions under various SWNT dispersion conditions) and resultant composite fiber properties. As the dispersion level is increased from large SWNT bundles to full exfoliation of the SWNT tubes, the highest PAN-SWNT bonding energy and the lowest PAN-PAN interaction energy of all cases are observed. It is also observed that the PAN chains conformation is more extended due to the confinement effect from the SWNT. As the SWNT dispersion becomes more uniform, this conformational confinement effect is more pronounced. The PAN exhibits fully extended-chain morphology on the SWNT surface for the most dispersed case.

All results present in this chapter (both experimental and computational) provide insight towards understanding the effect of CNT dispersion quality on the polymer/CNT composite fiber processing with high CNT loading. In the next chapter, the laminar-flow effect on the polymer interphase formation as well as the fundamental polymer-SWNT interaction is studied in detail.
Chapter 6 LAMINAR-FLOW RATE EFFECTS ON THE POLYMER-CNT INTERACTIONS

6.1. INTRODUCTION

As mentioned in Chapter 1 that a laminar-flow gel-spinning approach can be used to introduce the initial drawing of fibers during processing. This drawing process not only significantly affects the initial alignment of the polymer chains and CNT in the fiber, but it may also trigger specific polymer-CNT interactions (e.g., promotions of extended-chain polymer-CNT interphase formation). For this reason, the control of the laminar-flow rates which determine the initial draw ratio (i.e., the initial stretching caused by the flow speed difference) of the fibers before it is subjected to post-spinning treatment (i.e., hot-drawing process) should be carefully studied. In this chapter, both experimentation and computation methods are utilized to explore various polymer-CNT interactions under different laminar-flow rates; in order to understand the conditions required to promote an extended-chain interphase morphology.

For the experimental portion of the study, two different polymers (i.e., PVA and PAN) are used to produce polymer/SWNT composite fibers with high SWNT loadings (> 5 wt%) using the laminar-flow gel-spinning apparatus. By adjusting the spinning dope injection speed while keeping the coagulation flow speed constant, variations of initial drawing rates could be accurately controlled. The mechanical properties as well as the crystallization behavior of the final materials are also characterized, in order to associate the fiber performances with the changes in the initial drawing rates.

For the computational aspects of this study, full-atomistic MD simulations on the polymer/SWNT/solvent system corresponding to different fiber processing conditions are also performed to investigate the interaction energy between polymer chains and SWNT surface. The influence of controlling polymer-SWNT interactions during fiber processing on the experimental formation of the polymer interphase structure is also discussed.
6.2. METHODS

6.2.1 Materials
Two types of polymers were used in this work to produce polymer/SWNT composite fibers. PVA (molecular weight 325,000 g mol\(^{-1}\), Mowiol 235) was obtained from Kuraray America Incorporation. PAN-co-MAA (molecular weight 513,000 g·mol\(^{-1}\)) was obtained from Japan Exlan Company. SWNT (purity > 99 wt%, MWNT content < 2%) was obtained from Cheaptubes Inc.. Dimethyl sulfoxide (DMSO) and N,N-Dimethylacetamide (DMAc) were purchased from Sigma-Aldrich and used as-received.

6.2.2 Solution Preparation
The spinning dopes for the PAN/SWNT and PVA/SWNT composite fibers are prepared using a similar polymer-assisted approach presented in Chapter 5. SWNT for both systems is dispersed in pre-dissolved polymer/solvent solutions (1:1 weight ratio of SWNT and polymer) sonicated for 48 hours. After sonication, additional polymer powder and solvents are added into the dispersion to achieve final spinning dope with PAN 7wt% and PVA 10 wt% with respect to the solvents content, respectively. A final SWNT concentration of 5 wt% with respect to the solid content of the polymer is used for both cases. In addition, as discussed in Chapter 4, the undercooling process performed during the spinning dope preparation is tend to be beneficial for promoting polymer-SWNT interactions. For this reason, all spinning dopes prepared in this work are also homogenized under a constant solution temperature of 90 °C for the first two hours, and subsequently cooled down to 60 °C for another 22 h of mixing to achieve an optically homogeneous dope for spinning.

6.2.3 Laminar-flow Apparatus and Fiber Preparation
A laminar-flow gel-spinning apparatus is developed to produce the fibers in this work. As shown in Figure 6.1, this setup contains a reservoir where the coagulation bath is pumped into the glass tube to form the laminar-flow by a step-wise fluid pump. The spinning dope is injected into the coagulation bath by a syringe pump at the beginning of the glass tube where the elongational flow initially forms. Since the flow speed of the coagulation bath is kept constant throughout fiber spinning process, a lower the dope injection speed leads to a higher
initial draw ratio on the gel fibers. In other words, the initial draw ratio of the fiber can be accurately controlled by changing the dope injection speed using the digital syringe pump. The choice of the dope injection speed range should also take into account the different behaviors of the polymers (i.e., PVA and PAN). In general, the highest and lowest dope injection rates are defined by the minimum and maximum drawing rate applied to provide minimum draw ratio (i.e., draw ratio of 1) or to cause fiber breakage (i.e., maximum draw ratio), respectively. The intermediate laminar-flow rate is defined as the median values within the range determined. As the laminar-flow progresses, the gelation process occurs and the fibers will form and travel with the flow to the end of the glass tube where fiber collection is performed.

**Figure 6.1** Schematic of the laminar-flow gel-spinning apparatus used in this work to fabricate polymer/SWNT control and composite fibers. By adjusting the injection speed of the spinning dope while keeping the coagulation laminar-flow speed constant, the initial drawing rates (i.e., the speed difference at the tip of the needle) can be accurately controlled.

Upon collection at the end of the glass tube, as-spun fibers are further soaked in a quiescent coagulation bath for additional time (i.e., 0.5 to 1 hours) to ensure complete gelation. Subsequently, the hot-drawing process is performed on the fibers to achieve the final samples.
For both the control and composite fibers of each polymer type with different initial draw ratio, the hot-drawing ratio of each temperature stage is kept similar on purpose. By doing this, the effect of the hot-drawing process on the fiber morphologies and performances would be comparable. In this case, the influence of the initial laminar-flow rates could be assessed. Detailed spinning parameters for both PVA and PAN fibers are listed in Table 6.1.

Table 6.1 Spinning parameters for PVA and PAN fibers using laminar-flow gel-spinning setup

<table>
<thead>
<tr>
<th>Polymer Types</th>
<th>Dope Injection Speed (mL/min)</th>
<th>Initial Draw Ratio</th>
<th>Hot-drawing Draw Ratio</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>90 °C</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>PAN Control (7 wt%)</td>
<td>0.45</td>
<td>1</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>1.3</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>1.8</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>3.1</td>
<td>7.9</td>
</tr>
<tr>
<td>PAN Composite (SWNT 5wt%)</td>
<td>0.45</td>
<td>1</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>1.3</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>1.8</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>3.1</td>
<td>8.5</td>
</tr>
<tr>
<td>PVA Control (10 wt%)</td>
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<td>1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>1.2</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.5</td>
<td>7.0</td>
</tr>
<tr>
<td>PVA Composite (SWNT 5wt%)</td>
<td>0.6</td>
<td>1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>1.2</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>
6.2.4 Sample Characterization

Tensile tests were performed using a dynamic mechanical analyzer G2-RSA model (manufactured by TA Instruments) with gauge length of 15 mm and strain rate of 0.05 mm·s⁻¹. Wide-angle X-ray diffraction (WAXD) patterns were obtained on multi-filament bundles using Rigaku RAPID II (operating voltage at 40 kV, current at 30 mA, CuKα, \(\lambda = 0.1541 \text{ nm}\)) manufactured by Rigaku Americas Corporation.

6.2.5 Modeling Procedure

In order to capture the fundamental polymer-SWNT interaction behavior under various laminar-flow rates, polymer/SWNT/solvent systems are constructed in the computational domain. For baseline polymer-SWNT interaction studies, each system contains polymer chains with 200 monomers and atactic configurational arrangement, as well as SWNT (armchair (8, 8)) with diameter of 1 nm and a tube length of 49.2 nm. All simulations are performed using the constant volume and constant temperature canonical ensemble (NVT) under vacuum. The equations of motions are integrated using velocity verlet algorithm with integration time step of 1 fs, and the temperature was controlled by Nose-Hoover thermostat. All systems are equilibrated at 300 K (damping constant of 2.0) for 2 ns (approximately two million iteration steps) to stabilize the interactions. The polymer-SWNT interaction energies are extracted directly from the simulation data and CVFF potentials. All simulations are conducted using Dell Precision Tower 7910 workstation.

For laminar-flow rates and nanotube size studies, solvent molecules are added to both systems. The solvent box is constructed using a molecular dynamics software package. A laminar-flow field is generated by imposing an additional acceleration force on each of the solvent molecules along the SWNT axial direction. In addition, the magnitude of the acceleration force applied on the solvent molecules could be altered in order to adjust the laminar-flow rate. The drawing of the polymer chains caused by different laminar-flow rates in simulation corresponds well to the initial draw ratio of the fiber introduced by different dope injection speed from experimentation. To explore the effect of nanotube size, the number of nanotubes is changed from a single tube to a 7-tube hexagonal bundle. This also enabled exploration of different nanotube surface effects on the polymer-SWNT interactions under laminar-flow.
The selected laminar-flow rates are also monitored in order to should take different behaviors of polymer chains into consideration. In general, the high and low laminar-flow rates are defined as the maximum and minimum shear rates applicable to the as-spun fibers without causing breakage (high) or to provide minimum positive draw ratio (low), respectively. The intermediate laminar-flow rate is defined as the median value between the high and low laminar-flow rates. This also corresponds to the experimental parameters used.

6.3. RESULTS AND DISCUSSIONS

6.3.1 Mechanical Properties

The mechanical performances of the control and composite fibers for both PAN and PVA are evaluated through tensile testing. Due to the different natures of the chains as well as the different polymer-SWNT interaction that each polymer possesses, the range for the initial dope injection rates by the syringe pump were determined to be 1.2–3.5 m/min (equivalent initial draw ratio of 1–3.1) and 2.3–3.5 m/min (equivalent initial draw ratio of 1–1.5) for PAN and PVA, respectively. Figure 6.2 compares the control and composite fibers properties for both PAN (Figure 6.2a) and PVA (Figure 6.2b) as a function of their own dope injection rates (bottom x axis) or initial draw ratios (top x axis).

![Figure 6.2](image)

*Figure 6.2 Tensile strength (curves with ▼ symbol) and Young’s modulus (curves with ■ symbol) of the control (dotted lines) and composite fibers (solid lines) for both PAN (a) and PVA (b) as a function of initial dope injection rates. Compared to the control fibers for both polymers, the composite fibers generally possess higher mechanical properties at the minimum dope injection rate (i.e., maximum initial draw ratio).*
It is found that, for both PAN and PVA control fibers (dotted curves in Figure 6.2), plateauing behaviors for both fiber tensile strength and the Young’s modulus occurred after the initial draw ratio of the fibers increased from a lower value to a higher value (i.e., 1.8 to 3.1 for PAN, and 1.2 to 1.5 for PVA). This indicates that higher laminar-flow rates can result in disruptions of polymer control fiber morphologies and subsequently lower their mechanical performance as the result. In the contrast, the composite fibers for both cases did not show the same property decrease trend in the same draw ratio region where the control fiber properties were decreasing (i.e., 1.8 to 3.1 for PAN, and 1.2 to 1.5 for PVA). Instead, the strongest fiber performances in both cases were observed at the highest draw ratio point. This indicates that the organized chain morphologies that were previously disrupted by the high laminar-flow in the control cases can now be maintained by the introduction of SWNT. Since the Young’s modulus is generally associated with the fiber orientation and the tensile strength is generally associated with the fiber defects, the addition of SWNT and the introduction of the polymer-SWNT interaction is believed to contribute to the improvement of both properties. Representative stress-strain curves for each case are plotted in Appendix B (Figure B.2).

6.3.2 WAXD Analysis and Orientation

In order to investigate the changes in the fiber orientation under various laminar-flow rates with and without the presence of SWNT, WAXD analysis was used to obtain orientation factors for both cases. Representative WAXD profiles for each case are given in Appendix B (Figure B.1). The d-spacing and the crystal size of the predominant crystallization planes for both polymers are listed in Table 6.2.

The representative WAXD patterns of the control and composite fibers for each polymer are shown in Figures 6.3a1 and 6.3a2, the fiber orientation factor can be calculated using Wilchinsky’s equation:

\[
f_b = \frac{3 \cos^2 \theta_{\text{fiber-axis}} - 1}{2}
\]

(6.1)

\[
\cos^2 \theta_{\text{fiber-axis}} = 1 - \frac{(1 - 2 \sin^2 \rho_1)(\cos^2 \phi)}{\sin^2 \rho_1 - \sin^2 \rho_2}
\]

(6.2)
\[
\frac{1}{\cos^2 \phi_0} = \frac{\int_0^{\pi/2} I(\phi) \sin \phi \cos^2 \phi \ d\phi}{\int_0^{\pi/2} I(\phi) \sin \phi \ d\phi}
\]  
(6.3)

\(f_b\) is the orientation factor of the fiber. The subscripts 1 and 2 refer to the two respective crystallization planes used in the orientation calculation. For instance, \(\{110\}\) and \(\{020\}\) were used for PAN fibers, and \(\{101\}\) and \(\{200\}\) were used for PVA fibers. The azimuthal intensity profile of each plane chosen is needed for calculating \(\overline{\cos^2 \phi_0}\) using equation (6.3), and substitute into equation (6.2) to calculate \(\overline{\cos^2 \theta_{fiber-axis}}\). The azimuthal patterns used in this work are shown in Figures 6.3b1 and 6.3b2. \(\rho\) is the angle between the given plane normal and the two non-chain-axis directions (i.e., \(a\) and \(b\) axis for PAN, \(a\) and \(c\) axis for PVA in the crystal unit cell). The calculated \(\rho\) values for both polymers are listed in Table 6.2. The final orientation factors \(f\) for all fibers are shown in Figures 6.3c1 and 6.3c2.

As shown in Figure 6.3c, the orientation factor analysis results are in good agreement with the trend of mechanical properties for the fibers. It is observed that the control fibers for both cases (dotted curves with ▼) had similar decreases in fiber orientation as compared to the mechanical properties. However, the orientation of the composite fibers, only exhibit an upward trend from low to high draw ratio. This confirmed that the introduction of the SWNT aided the orientation of the polymer chains in both fibers. This increase trend may have been maintained due to the polymer-SWNT interactions. In contrast, the polymer chains in the control fibers could only withstand the laminar flow up to a certain speed. Beyond this critical speed (i.e., 1.9 m/min for PAN and 3.1 m/min for PVA), fiber orientations were significantly interrupted. This contributes to the decrease in the control fiber properties as discussed in Section 6.4.1.
Table 6.2. WAXD Determination of d-spacing and the crystal size for the predominant planes in PAN and PVA control and composite fibers

<table>
<thead>
<tr>
<th>Polymer Type</th>
<th>PAN</th>
<th>PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dope Injection Rate (m/min)</td>
<td>3.5 2.7 1.9 1.2</td>
<td>3.5 3.2 3.1 2.3</td>
</tr>
<tr>
<td>Crystal Size on Major Plane (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>(110) for PAN</em></td>
<td>Control</td>
<td>15.6 17.3 17.6 18.5</td>
</tr>
<tr>
<td><em>(101) for PVA</em></td>
<td>Composite</td>
<td>9.8 10.5 11.0 11.7</td>
</tr>
<tr>
<td>Crystallinity (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>52 54 60 59</td>
<td>46 56 52 59</td>
</tr>
<tr>
<td>Composite</td>
<td>50 55 54 54</td>
<td>43 50 67 74</td>
</tr>
<tr>
<td>$\rho$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2\theta$ (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$-spacing (nm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.3 WAXD patterns of control and composites fibers for PAN (a₁) and PVA (a₂). The lowest dope injection rate cases (i.e., 1.2 m/min case for PAN and 2.3 m/min case for PVA) are selected for all fiber patterns. Representative azimuthal scans of the two crystallization planes used to calculate the Herman’s orientation factors (f) for PAN and PVA are shown in (b₁) and (b₂), respectively. Comparisons of the f’s between the control and composite fibers for PAN (c₁) and PVA (c₂) as a function of the dope injection rates are also illustrated.

6.3.3 Polymer/SWNT/Solvent Simulations under Different Flow Rates
As discussed in Section 6.4.2 of this chapter, the introduction of SWNT under the influence of the laminar-flow can be beneficial to the overall fiber mechanical properties as a result of chain orientation. This is most likely due to the presence of polymer-SWNT interactions during shearing. To further investigate this interaction and resultant chain morphologies under various laminar-flow conditions, full-atomistic MD simulations on the polymer/SWNT/solvent system were performed.
Baseline Polymer-SWNT Interaction Simulations

Before applying laminar-flow to the systems, baseline polymer-SWNT interaction studies for the two polymer types (i.e., PVA and PAN) were performed. In these control simulation cases, solvent molecules were removed to eliminate their effects. One polymer chain with 200 monomers was near the top of the SWNT with a close distance to induce polymer-SWNT interaction. The baseline polymer-SWNT interaction energies and the snapshots of their initial and final configurations are shown in Figure 6.4.

As shown in Figures 6.4a and 6.4b, it is found that PAN chain exhibit a physical wrapping behavior in the vicinity of the SWNT after 2 ns of free interaction at 300 K. However, the PVA chains formed semi-crystalline regions at the SWNT surface. This indicates that the nature of interaction between PVA and SWNT is very different as compared to PAN and SWNT, and may be related to chain configuration (Figures 6.4a₁ and 6.4a₂). A quantitative comparison for both systems is provided by plotting the polymer-SWNT (Figure 6.4c₁) and polymer-polymer interaction energy (Figure 6.4c₂). Due to the limited size of these simulation, all interaction energies were normalized by the number of monomers (i.e., 200 in both cases) in order to achieve more generalized results. It was found that the interaction energy per monomer between PVA and SWNT is ~7.5 Kcal/mol, whereas for PAN-SWNT it is ~1.2 Kcal/mol. This shows that PVA is able to form a stronger interfacial bonding with SWNT as compared to PAN.
Figure 6.4 Baseline polymer-SWNT interaction simulation study for PAN (a₁ through a₃) and PVA (b₁ through b₃) at 300 K under a vacuum environment using a NVT ensemble. Initial configurations (a₂ and b₂) for both systems contain 200 monomers of each polymer, where the chemical structure of the monomer for PAN and PVA are given in (a₁) and (b₁), respectively. Final configuration snapshots for both systems are shown in (a₃) and (b₃). The polymer-SWNT and polymer-polymer interaction energies (normalized by number of monomers) are given in (c₁) and (c₂). Compared to PAN, PVA was found to have stronger interaction with SWNT and other PVA monomers and formed semi-crystalline regions at the SWNT surface.

The stronger monomer-monomer bonding exhibited by PVA as compared to PAN can be contributed to the OH groups for the PVA, which results in the inter-chain hydrogen bonding. This is exhibited by the PVA with folded-chain crystals formed. By forming an ordered structure in the vicinity of the SWNT, stronger interactions between the PVA and the nanotubes are possible. Furthermore, this baseline study also confirms that PVA has the ability to crystallize at the SWNT surface. This is directly related to the formation of
subsequent interphase regions within the PVA/SWNT composite fibers discussed in Chapter 3. The PVA-PVA interactions also suggest crystallization may be more facilitated as compared to PAN. This is expected to play a role in the polymer-SWNT interactions and the resultant chain morphologies that occur under various laminar-flow conditions. These results will also provide insight regarding stabilization and computational time needed to form specific interfacial structures. As discussed, the ideal structure for improving the mechanical properties in the fiber is to promote extended-chain crystalline interphase regions. For this reason, the PVA/SWNT system is chosen for the subsequent laminar-flow rates analysis in this work.

Effect of SWNT on the Polymer Morphology under Laminar-Flow

For the laminar-flow rate studies, a region in the as-spun fiber during the flow-spinning process is first visualized and illustrated in Figure 6.5a. As shown in the schematic, at the injection starting point where the polymer spinning dope initially comes out, only the outer shell of the gel-fiber is experiencing the drawing forces (i.e., indicated by green arrows) from the coagulation bath (i.e. methanol); whereas the center of the fiber still contained mostly DMSO solvent due to the slow solvent exchange process. In other words, even though the fiber elongation (i.e., shown by red arrows in the scheme) is caused by the drawing force provided by the outer flowing methanol solvent particles, the actual initial stretching experienced by the polymer chains and SWNT are still solvated by DMSO (i.e., initial stretching is at the onset of solvent exchange). For this reason, DMSO molecules were selected and added into the simulation box with a density of 0.5 g/cc to act as the solvent media. Different magnitudes of gravitational acceleration were imposed on the DMSO molecules along the nanotube direction to create different laminar-flow rates. Since a NVT ensemble (i.e., 0 °C for solvent temperature in experiments) is applied on top of the gravitational acceleration of the atoms, particles can only accelerate for short amounts of time before reaching the desired system temperature due to the velocity increase. The acceleration effect of the particles was then suppressed by the temperature regulator of the NVT ensemble. Therefore, all solvent particles moved at a constant velocity under desired temperature. The system temperature for the first 1 ns of simulation is plotted in Appendix B (Figure B.3b).
Different initial magnitudes of acceleration result in different final constant moving velocities for the solvent particles. Figures 6.5b and 6.5c shows a comparison between PVA chain behavior in quiescent DMSO and in flowing DMSO.

**Figure 6.5** (a) Schematics of the fiber gelation process during spinning in the laminar-flow. The region of interest is highlighted in rectangle. (b) MD representation for the region of interest in a quiescent state with one PVA chain (200 monomers each chain), one SWNT (diameter: 1 nm, length: 49.19 nm, chirality: armchair (8, 8)), and DMSO molecules filling the whole simulation box with density of 0.5 g/cc. (c) MD snapshot of the polymer chain morphology for the system under laminar-flowing.
Prior to investigating the effects of various laminar-flow rates on the polymer/SWNT system, another baseline simulations for understanding the influence of SWNT on the polymer morphology under flow conditions were conducted. Two scenarios were considered in this study. Systems with two PVA chains (i) with and (ii) without an individual SWNT (Figures 6.6a and 6.6b) were subjected to the same laminar-flow rate conditions (i.e., acceleration: $1 \times 10^{-7}$ Kcal/gram-Å, final flow speed: 5–20 m/min). The snapshots of the final PVA chain morphologies with and without the presence of SWNT were also given in Figures 6.6c and 6.6d.

![Figure 6.6 Initial MD configurations of 2 PVA chains (a) with and (b) without the presence of SWNT in DMSO solvent. The DMSO molecules are hidden for viewing purpose. After applying low flow rate (acceleration: $1 \times 10^{-7}$ Kcal/gram-Å, final flow speed: 5–20 m/min) onto the DMSO particles, the final morphologies of the PVA chains for both cases are given in (c) and (d), respectively. It is observed that the polymer chains without the presence of SWNT tend to coil after applying flow due to the polymer-polymer interactions and entropic coiling, whereas the chains form a more extended-chain with SWNT present in the laminar-flow.]

As shown in Figure 6.6, a distinct morphological difference in the polymer chains with and without the presence of SWNT after laminar-flow is observed. With the presence of SWNT,
the PVA chains closely interact with the nanotube surface and gradually formed extended-chain morphology under the effect of laminar-flow (Figure 6.6c). This morphology is very different from the case without laminar-flow in Figure 6.4b, where PVA formed folded-chain crystalline region around the nanotubes. This is most likely due to the combined effects of the strong polymer-SWNT interaction as well as the laminar-flow that elongated the chains in the tube direction. By having this morphology, the alignment of the PVA along the fiber axis as well as the order of the polymer region is significantly improved. This phenomenon is also confirmed in the experimental domain where composite fibers orientation and mechanical performance kept the increase trend as the laminar-flow rate increased (Section 6.4.1).

While starting with the same polymer chain configuration, the case without SWNT showed a major coiling behavior of the polymer after laminar-flow (Figure 6.6d). Although the final morphology did not show any folded-chain crystallization behavior due to good polymer-solvent interaction, the inter-chain interactions and the folding preference of the chains still resulted in the coiling of the chain. This indicates that without the confinement of the SWNT present in the system, polymer chains cannot withstand the laminar-flow and instead form coiled conformations at the local regions. Such disordered polymer regions not only disrupt the alignment of the polymer chains along the laminar-flow direction (i.e., fiber direction), but can also create defective regions during fiber spinning/processing and subsequently lower the mechanical performance of the fibers. This was also confirmed experimentally in Section 6.4.1. Polymer chain confinement scenario (i.e., number of PVA chains change from one to two chains) was also investigated in simulation. The resultant PVA-SWNT interaction energies for both cases are given in Appendix B (Figure B.3a)

Simulations with Different Laminar-flow Rates

By confirming that SWNT can assist the PVA chains to form extended morphology under laminar flow, variations in laminar-flow rates on the polymer-SWNT interaction as well as on the formation of the extended-chain polymer interphase near SWNT surface are explored. Three laminar-flow conditions are generated: (i) low laminar-flow (acceleration: $1 \times 10^{-7}$ kcal/gram-Å, final flow speed: 5–20 m/min), (ii) intermediate flow (acceleration: $1 \times 10^{-5}$
kcal/gram-Å, final flow speed: 100–150 m/min), and (iii) high laminar-flow (acceleration: \(1\times10^3\) kcal/gram-Å, final flow speed: > 10,000 m/min). The selection of each flow for computation is reflective of processing possibilities. In particular, Condition-I is within the flow rate range used for fibers spinning in the current experiments; Condition-II is close to the upper speed limits capable for the gel-spinning laminar-flow apparatus; and Condition-III is a flow speed that exceeds the current experimental capacity but may be possible for a properly designed system. The speed range of each flow stage in the simulation domain was determined by averaging velocities of all solvent atoms upon reaching steady-state of the systems (i.e., system temperature and free energy stabilized, polymer chains moved at constant speeds) as well as by measuring the moving distance with respect to the timeframe that each snapshot was taken from the systems. Final configuration snapshots of the systems as well as the corresponding PVA-SWNT interaction energies are summarized and plotted in Figure 6.7.

**Figure 6.7** Final configurations of PVA/SWNT/DMSO systems subjected to (a) low flow rate (acceleration: \(1\times10^7\) Kcal/gram-Å, final flow speed: 5 – 20 m/min), (b) intermediate flow rate (acceleration: \(1\times10^5\) Kcal/gram-Å, final flow speed: 100 – 150 m/min), and (c) high flow rate (acceleration: \(1\times10^3\) Kcal/gram-Å, final flow speed: > 10,000 m/min). Solvent molecules were hidden for viewing purpose. (d) The interaction energies between PVA chains and SWNT were also summarized.
As shown in Figure 6.7, the final PVA chain morphologies differ under the effect of each laminar-flow condition. The highest laminar-flow rate (Figure 6.7c) resulted in morphological disruptions for the polymer chains near SWNT as compared to the lower conditions used. Gaps between the chains and SWNT caused by the disrupted polymer chains at the polymer/SWNT interface are observed. This is also confirmed by comparing the polymer-SWNT interaction energy with all cases (Figure 6.7d). The high flow rate case exhibits the highest PVA-SWNT interaction energy (i.e., weakest interaction between the two components). In addition, since the boundary conditions of the simulation box are set to be periodic, the polymer chains in the high flow rate case actually travel with the laminar-flow and periodically sliding along the SWNT surface. This is indicated by the zig-zag shape of the interaction energy curve. This is mainly due to the impact of strong flow on the polymer chains, which surpass the PVA-SWNT energy threshold and caused the interaction to become unstable.

Condition-I and Condition-II (i.e., closer to the real experimental conditions) both exhibit much lower and smoother PVA-SWNT interaction energy curves as compared to Condition-III. This shows the necessity of controlling flow rates within a range such that the PVA-SWNT interaction will not be disrupted in order to produce and preserve the desired extended chain morphologies at the interphase. However, when comparing the low and intermediate flow rate cases, morphological and energetic differences are also noticed. While both cases show extended morphology of the polymer, for Condition-I a small amount of dangling chains as well as some randomly folded chains are observed. For Condition-II, the chains show a completely extended morphology along the SWNT surface. This observation is also reflected by the interaction energy curves, where the intermediate case shows the lowest interaction energy (i.e., strongest PVA-SWNT interaction) among all three cases. This suggests that, in order to achieve desired extended-chain interfacial morphology, a good control of laminar-flow rate with the combined effect of polymer-SWNT interaction is necessary.

Another factor that is considered is the bundle size of the SWNT. Since this work focuses on producing composite fibers with high SWNT loadings, SWNT are more likely to stay in the
bundle form during and after the fiber processing. This was shown using the dispersion studies outlined in Chapter 4. For this reason, the interactions between the polymer chains and the SWNT bundles under the effect of various laminar-flow rates are also studied. Similar to the previous studies, a 7-hexagonal SWNT bundle was used to replace the individual nanotube in the aforementioned cases. Final configuration snapshots of the systems as well as their corresponding PVA-SWNT bundle interaction energies were summarized and plotted in Figure 6.8.

![Figure 6.8](image)

**Figure 6.8** Final configurations of PVA/SWNT bundle/DMSO systems subjected to (a) low flow rate (acceleration: $1 \times 10^{-7}$ kcal/gram-Å, final flow speed: 5–20 m/min), (b) intermediate flow rate (acceleration: $1 \times 10^{-5}$ kcal/gram-Å, final flow speed: 100–150 m/min), and (c) high flow rate (acceleration: $1 \times 10^{-3}$ kcal/gram-Å, final flow speed: > 10,000 m/min). Solvent molecules were hidden for viewing purpose. (d) The interaction energies between PVA chains and SWNT bundle were also summarized.

As shown in Figure 6.8, different morphological and energetic trends are observed for the SWNT bundle cases as compared to the exfoliated individual tubes (Figure 6.7). From the polymer chain morphology point of view (Figures 6.8a to 6.8c), as the laminar-flow rate increases, the extended-chain structure became more disrupted. In addition, as compared to the individual nanotube cases, polymer chains morphologies on the SWNT bundle surface are
less ordered and less extended for all cases. Interfacial defects caused by the polymer chains folding and twisting are also found to be more significant. This is mainly due to the local pinning of the chains on the bundle surface caused by the additional nanotubes interacting with the polymer; as well as the different surface structure (i.e., grooves) of the bundles as compared to the individual tubes. This observation was also confirmed by the PVA-SWNT bundle interaction energy plots (Figure 6.8d). For the SWNT bundles, Condition-I shows the lowest PVA-SWNT bundle energy (i.e., strongest interaction) among all cases. For this reason, the low flow rate that corresponds to the real experimental speed range was determined to be the optimum value for SWNT bundle. As indicated in the individual tube simulations, it would be ideal to have well-dispersed individual nanotubes within the composite fibers in order to withstand higher flow rates and to form less interrupted extended chain polymer structure. However, the bundle simulations with low flow rate are more in agreement with the experimental observations for producing continuous composite fibers due to the existence of nanotube bundles in high concentration cases.

These simulation results indicate that the presence of CNT in the composite fibers can help templating the polymer chains to form more extended morphologies during laminar-flow gel-spinning process. In addition, proper selection of the laminar-flow rate can result in the initial formation of the interphase region with extended chain conformation. By combining experimental observations, the increase in the composite fiber mechanical performances caused by the increase in the initial fiber draw ratio created by the laminar-flow can be explained at the atomic level. This joint experimental and computational study provides guidance for optimizing laminar-flow rate during fiber spinning process for the formation of polymer interphase.

6.4. CONCLUSION

By using both experimental and computational methods, this chapter studies the effects of laminar-flow rate during the fiber spinning process on the composite fiber properties as well as on the fundamental polymer-CNT interactions. From experimental studies, PVA and PAN were used to produce polymer/SWNT composite fibers with high nanotube loadings using the laminar-flow gel-spinning apparatus. Fiber orientation and mechanical properties were
analyzed using WAXD and tensile testing methods, respectively. It was found that the fiber orientation and mechanical properties generally increases as the fiber initial draw ratio caused by the laminar-flow improves. For control fiber cases, this positive relationship was only valid within a specific drawing range. A significant decrease in the chain alignment and the mechanical properties of the control fibers were observed once the draw ratio exceeded this range. However, for the composite cases, the introduction of the CNT improved the stability of the composite fibers to allow for higher initial drawing without sacrificing chain alignment. The polymer-CNT interactions also provided extra confinement to the polymer chains and prevented them from recoiling during high drawing conditions. As a result, the alignment and mechanical performance of the composite fibers produced from high initial drawing condition were significantly improved as compared to the control fibers with the same initial drawing conditions.

Full-atomistic MD simulation was also used to explore the change in polymer chain morphology as well as in the fundamental polymer-CNT interaction energy under various laminar flow conditions. Three flow rates (i.e., high, intermediate, and low) were selected by taking consideration of the experimental conditions, and subsequently applied on the solvent molecules to create laminar flows. Polymer chain interactions with individual CNT as well as the CNT bundle under the effect of various laminar-flow rates were also studied. It was found that the introduction of CNT improved the stability of the polymer chains in terms of forming more extended-chain interfacial morphology. And the successful formation of the polymer interphase region was dependent on combined effects of polymer types, laminar-flow rate, and quality of the nanotube dispersion.

In the next chapter, the mechanical contribution of the polymer interphase region within the composite fiber is studied in detailed. The fiber strengthening mechanism with and without the interphase is also investigated. Lastly, the effective mechanical contribution from the nanotubes is explored.
Chapter 7 MECHANICAL CONTRIBUTION OF THE POLYMER INTERPHASE IN COMPOSITE FIBERS

7.1. INTRODUCTION

Considering that the presence of the polymer interphase region in the composite fibers improves the mechanical properties of the fibers by enhancing stress transfer between the polymer matrix and the CNT. The previous chapters have outlined studies that investigate the necessity of controlling the degree of undercooling and CNT dispersion quality during spinning dope preparation, as well as optimizing the laminar-flow rates during fiber spinning in order to promote the formation of such interphase structures. The local mechanical contribution of the interphase region in the fiber, however, has not yet been explored. For this reason, this chapter outlines a quantitative study of the properties of the interphase and the effective CNT contribution in the composite fibers with high CNT concentration.

In this chapter, the PVA/SWNT composite fibers with the presence of polymer interphase produced from Chapter 4 are used for mechanical characterization. The effective contributions from the SWNT within the composite fibers are calculated using theoretical analysis. Based on the WAXD simulation results obtained from Chapter 4, the enhancement mechanism with and without the interphase regions present are also analyzed at the atomic level. SMD simulation is used to explore the interfacial strength of between the nanotube and the interphase region.

7.2. METHODS

7.2.1 Fiber Preparation and Characterization

Detailed description of the PVA/SWNT composite fiber spinning procedure was given in Chapter 4. The nanotube dispersions were studied by electron microscopy in order to determine the length distribution of the SWNT after sonication. Diluted droplets of the dispersions were dried on silicon and imaged by SEM. Images were analyzed using the software package Image J (version 1.44o). It was found that after 48 h of bath sonication the SWNT length varied considerably. The average SWNT length distribution based on more than 100 measurements of distinct tubes was $1.5 \pm 1.1 \mu m$. This experimental length value is
used in conjunction with the theoretical analysis of the mechanical properties for the PVA/SWNT composite fibers produced in this work. Tensile tests were performed on a dynamic mechanical analyzer G2-RSA model (manufactured by TA Instruments) using gauge length of 10 mm and strain rate of 0.05 mm·s⁻¹.

### 7.2.2 Interphase Modeling Procedure

**Steered Molecular Dynamics (SMD)**

Non-equilibrium SMD simulation, a tool that has been widely implemented to investigate complex morphological changes of macromolecules, was used in this work to quantify the adhesion strength and the associated energy barriers within nanotubes bundles as well as between CNT and polymer interphase. SMD is the most widely used force measurement tool for simulation studies, and is similar to AFM tip, optical tweezer, and force probe experimental techniques used to study molecular binding energy. By applying a moving spring force towards a target tether point that combines the effects of force and displacement loadings, molecular conformational change in the system along the moving direction can be measured while allowing conformations unable to be achieved via independent force or displacement controlled loading. A driving force applied to selected atoms and this is described by Equation 7.1.

\[
F_{SMD} = K_{spring} (R - R_o)
\]

\(K_{spring}\) is a harmonic spring constant, and \(R_o\) is the distance from spring end to a target tether point. It has been reported that \(K_{spring}\) selections (and thus loading rate) with orders of magnitude difference can affect the total energy landscape of the physical system. In this work, it was found that the \(K_{spring}\) values between 0.2 to 200 Kcal/mol·Å² have little influence on the force/energy output values and was kept constant at 1 Kcal/mol·Å² for all cases. In addition, it was found from the previous study that the pulling rate (i.e., 5 m/s – 100 m/s) dependency of the hexagonal sheets inter-layer interactions was very minor. For this reason, all pulling cases were performed using pulling speed of 100 m/s for the purpose of computational efficiency purpose.
The theoretical foundation providing validity for the SMD methods is given by Jarzynski’s equality, a relationship between equilibrium free energy differences and work done through non-equilibrium processes. The second law of thermodynamics states that the average work done on the system cannot be smaller than the free energy differences of the system between its initial and final states (Equation 7.2).

\[ \Delta F = F_{\text{initial}} - F_{\text{final}} \leq \langle W \rangle \] (7.2)

\( F_{\text{initial}} \) and \( F_{\text{final}} \) are the free energy of the system at the initial and final states, respectively. \( \langle W \rangle \) is the work done on the system caused by any non-equilibrium process. The equality only holds in the case of a quasistatic process (i.e., system changed from initial state to final state infinitely slowly). In Jarzynski’s equality, however, this equivalence holds regardless of the speed of the process (Equation 7.3).

\[ e^{-\Delta F/kT} = \left\langle e^{-W/kT} \right\rangle \] (7.3)

\( k \) is the Boltzmann constant and \( T \) is the temperature of the system. This equality ensures that various non-equilibrium processes can be used for free energy calculation; and the speed of the process (i.e., pulling speed in SMD) will not affect the overall result. The rate independency results of the SMD pulling method used in this dissertation are given in Appendix C.

**Modeling Procedure**

For a baseline CNT bundle inter-tube adhesion study, two SWNT bundles with different bundle sizes (i.e., one 7-hexagonal nanotubes bundle with length of 6.9 nm and diameter of 3.9 nm, and one 19-hexagonal nanotubes bundle with length of 6.9 nm and diameter of 6.4 nm) were created and stabilized at 5 K using NVT ensemble, in order to reach an equilibrium state prior to pulling. For the 7-hexagonal bundle case, one end of the 6 outer circle nanotubes was fixed to provide a reference point, and at the opposite end the center nanotube surrounded as used to apply a SMD force (Figures 7.1a and 7.1a). For 19-hexagonal bundle case, one end of the 12 outmost circle nanotubes was fixed to provide a reference point, and at the
opposite end the 7 center nanotubes were used to apply a SMD force (Figures \textit{7.1b}_1 and \textit{7.1b}_2). The numbers of nanotubes for both cases were selected such that the pulled nanotube/bundle was fully surrounded by the outer nanotubes to simplify interactive area calculations. The force exerted on the spring was monitored and recorded as the pulling simulation proceeded. All forces were normalized based on the contact area between the nanotubes (i.e., interfacial area between the pulled nanotubes and fixed nanotubes). All simulations are conducted using Dell Precision Tower 7910 workstation.

In order to investigate the adhesion strength between the polymer interphase and the SWNT surface, three interphase arrangement scenarios were designed. For scenario-1, the initial configuration of the system was adopted from the laminar-flow study of the individual SWNT with intermediate flow rate case (i.e., the most extended PVA chain morphology with the lowest PVA-SWNT interaction energy) (Figure \textit{7.1c}). This scenario was aimed at understanding the interphase adhesion strength to the surface of individual SWNT. To achieve initial conformations for Scenario-1, solvent molecules (i.e., DMSO) were removed from the original after-flow configuration file, and the PVA/SWNT system was subsequently stabilized/equilibrated using a NVT ensemble at 5 K for 10 ps prior to SMD. The bottom layer of the nanotubes was fixed while the free ends of the chains were pulled in the z-direction to peel the interphase off from the SWNT surface.

The adhesion strength between the polymer interphase and the SWNT bundle was also studied in scenario-2. The initial configuration of scenario-2 was adopted from the interphase growth study presented in \textbf{Chapter 4 (Figure 7.1d)}. To achieve initial conformation prior to SMD, the surrounding amorphous PVA chains were first removed from the original configuration file and the PVA/SWNT system was subsequently stabilized/equilibrated using a NVT ensemble at 5 K for 10 ps until the PVA-SWNT interaction energy reached minimum value. One end of the nanotubes was fixed while the opposite end of the polymer chains were pulled in the y-direction until full delamination.
Figure 7.1 Initial configurations of baseline adhesion studies with top view and side view of 7-hexagonal SWNT bundle ($a_1$ and $a_2$) and 19-hexagonal SWNT bundle ($b_1$ and $b_2$). (c) Interphase pulling study where the initial configuration was obtained from the laminar-flow rate MD study presented in Chapter 6 (i.e., individual SWNT case with intermediate flow rate). And (d) the interphase pulling study where the initial configuration was obtained from the interphase growth study presented in Chapter 4 without the surrounding amorphous polymer chains. (e) The stress transfer within the thick interphase region to the SWNT bundle surface was also studied by creating initial configuration based on the experimental observation. The thickness of the interphase was ~8.2 nm to match the coating thickness of the nanotube bundle from SEM images in Chapter 4. Red and green regions indicate the pulling and fixing areas in the simulations, respectively.

A more realistic scenario was as built to attempt to take into account relate to the experimental evidence for interphase thickness. It was observed from the SEM images in Chapter 4 that the polymer coating thickness was ~ 8.2 nm. For this reason, an initial configuration of scenario-3 was created such that multiple extended-chain interphase layers were lying on top of a 7-hexagonal SWNT bundle surface (Figure 7.1e). The thickness of the interphase layer was measured to be around 8.2 nm as well. The system was subjected to NVT ensemble at 5 K for 10 ps prior to SMD. To simulate the stress transfer mechanism in...
the composite fiber upon tensile testing, the top two layers of the interphase region (i.e., highlighted in red in Figure 7.1e) were pulled using SMD in the y-direction while fixing the opposite end of the SWNT bundle.

7.3. RESULTS AND DISCUSSIONS

7.3.1 Mechanical Properties of PVA/SWNT Fibers with Polymer Interphase

The mechanical performances of the control and composite PVA/SWNT fibers produced in Chapter 4 with (F-B) and without (F-A) interphase structure were evaluated by tensile testing. Properties of control, F-A and F-B fibers are listed in Table 7.1. Compared to the control fibers, the Young’s modulus of F-A and F-B fibers shows an increase of 67% and 446%, respectively. Comparatively, the tensile strength of the F-A and F-B fibers also increases by 125% and 308%, respectively. The toughness of the F-A and F-B fibers also increases by 82% and 208%, respectively. The highest tensile strength for the F-B fiber (4.9 GPa) is greater than some commercially available polymer high-performance fibers, such as the PVA fibers produced for concrete reinforcement (0.88 GPa) and Kevlar (3.6 GPa). The highest toughness from F-B fibers (202 J g⁻¹) is greater than that of Kevlar (33 J g⁻¹) and spider dragline silk (165 J g⁻¹).²⁵⁹

Figure 7.2a shows the typical strain-stress curves for the control and composite fibers (F-A and F-B). The stress-strain curves show that at the same value of elongation at break (~11%), the F-A fibers show intermediate improvement of mechanical performance as compared to the control fiber. The F-B fibers exhibiting interfacial crystal structure of PVA show even greater improvement in Young’s modulus and tensile strength as compared to the F-A fibers. Figure 7.2b shows a comparison of the Young’s modulus and tensile strength distribution of the control, F-A and F-B fibers versus some of the commercially available fibers as well as various other PVA/SWNT fibers.²⁸⁹,²⁹⁵,²⁶⁰ It can be clearly seen that the F-B fibers produced in this work combines both high modulus and high tensile strength, and this is most likely due to the presence of interphase PVA structure which contribute to better stress-transfer between the SWNT and the matrix.
<table>
<thead>
<tr>
<th></th>
<th>Control Fibers</th>
<th>F-A Fibers</th>
<th>F-B Fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective fiber diameter ( )^{\text{(*)}} ) [( \mu \text{m} )]</td>
<td>22</td>
<td>9.2</td>
<td>9.9</td>
</tr>
<tr>
<td>Tensile modulus [GPa]</td>
<td>21.8 ± 3.0</td>
<td>36.3 ± 1.3</td>
<td>119.1 ± 8.6</td>
</tr>
<tr>
<td>Elongation-to-break [%]</td>
<td>11.4 ± 1.7</td>
<td>10.7 ± 0.7</td>
<td>9.7 ± 1.1</td>
</tr>
<tr>
<td>Tensile Strength [GPa]</td>
<td>1.2 ± 0.3</td>
<td>2.5 ± 0.1</td>
<td>4.4 ± 0.5</td>
</tr>
<tr>
<td>Toughness [J g(^{-1})]</td>
<td>55.8 ± 12.3</td>
<td>101.4 ± 11.4</td>
<td>171.6 ± 30.4</td>
</tr>
<tr>
<td>Effective modulus of SWNT [GPa]</td>
<td>---</td>
<td>201.5(^{\text{a})}) – 1042.1(^{\text{b})})</td>
<td>1539.8(^{\text{a})}) – 8574.4(^{\text{b})})</td>
</tr>
<tr>
<td>Effective modulus of SWNT with polymer interphase contribution</td>
<td>---</td>
<td>---</td>
<td>577.1(^{\text{a})}) – 2967.6(^{\text{b})})</td>
</tr>
<tr>
<td>Effective tensile strength of SWNT [GPa]</td>
<td>---</td>
<td>16.9(^{\text{a})}) – 88.1(^{\text{b})})</td>
<td>47.1(^{\text{a})}) – 253.0(^{\text{b})})</td>
</tr>
</tbody>
</table>

\(^{*})\) Effective fiber diameter \( D \) was calculated using the weight method, which is given by 
\[
D = 2\sqrt{\frac{w_c l_c}{\rho_c (1 - \eta_o)}},
\]
where \( \rho_c \) is the density of the composite fiber, \( \rho_p \) is the density of the composite fiber, \( \rho_p \) is the density of fully crystallized PVA, \( \rho_{SWNT} \) is the density of PVA provided by manufacture and \( w \) is the weight concentration of the SWNT in the composite fibers. The weight \( w \) and length \( l_c \) of the composite fibers.

\(^{\text{a})}\) Calculated value under SWNT aligned \( (\eta_o = 1) \) condition

\(^{\text{b})}\) Calculated value under SWNT randomly oriented \( (\eta_o = 1/5) \) condition
Figure 7.2 (a) Stress-strain curve for PVA/SWNT control and composite fibers. Compared to the control fiber, F-A fiber (no interphase) shows intermediate improvement on both modulus and tensile strength. F-B (interphase present) shows the most mechanical improvement with tensile strength of 4.9 GPa. (b) Comparison of Young’s modulus and tensile strength distributions of the control, F-A and F-B fibers in this work versus the same properties of other commercially available high-performance fibers and various PVA/SWNT composite fibers ((1) Vigolo et al., > 60 wt% of SWNT; (2) Xu et al., 0.3 wt% of SWNT (3) Young et al., V_{SWNT}: 2 – 31 vol%).

7.3.2 Hydrogen Bonding in Polymer Interphase Region

From Chapter 4, WAXD analysis is used to study the crystallization behavior difference between fibers with and without the interphase formation. Two correspondent polymer unit cells were also built to generate the simulated X-ray patterns that matched the experimental results. Not only can these unit cells provide information about the chain packing locations, but also reveal inter-chain interactions which are directly related to the strengthening mechanism of the interphase. It is widely accepted that hydrogen bonding exists between PVA chains due to the presence of hydroxyl groups. This interaction strongly influences the overall PVA properties as well as the stress transfer between chains. For this reason, the O-H···O hydrogen bonding between the two PVA chains in different unit cells with respect to their predominant crystallization planes were examined. As illustrated in Figure 7.3, the O-O distance is composed of the length of the hydroxyl bond (OH group) and the length of the H···O non-bounded potential. It has been shown that the van der Waals radius for O is around...
0.14 nm, which means any oxygen atoms that are closer to around 0.28 nm can experience repulsion. More precisely, the strongest O-H···O bonding can be found at O-O distance of 0.273 nm by bond valence calculation. From the distance measurement shown in Figures 4.4b and 4.4c, the hydrogen bond length for F-A (i.e., (101) crystallization plane) and F-B (i.e., (001) crystallization plane) were 0.3252 nm and 0.2785 nm, respectively. This suggested that as the crystallization plane changed from (101) to (001), the polymer chains become more adjacent to each other and as a result experience stronger inter-chain hydrogen bonding. This strong interaction between polymer chains introduces more chain resistance upon stretching and may also result in the greater mechanical improvement as observed for the F-B fibers.

**Figure 7.3.** Schematic of O-H···O hydrogen bond formation between two polymer molecules. The total hydrogen bond distance is composed of length of the hydroxyl bond and the H···O interaction distance determined by the non-bounded potential.
### 7.3.3 Mechanical Contributions from SWNT and Interphase

The SWNT enhancement efficiency was studied by calculating the effective Young’s modulus and tensile stress of the SWNT based on the mechanical properties of control, F-A, and F-B fibers. The composite Young’s modulus and tensile stress are given by Equations 7.4 and 7.5, respectively:\[\text{\textsuperscript{33}}\]

\[Y_c = (\eta_o \eta_1 Y_{SWNT} - Y_{PVA})V_{SWNT} + Y_{PVA} \tag{7.4}\]

\[\sigma_c = (\eta_o \eta_1 \sigma_{SWNT} - \sigma_{PVA})V_{SWNT} + \sigma_{PVA} \tag{7.5}\]

\(V_{SWNT}\) is the volume fraction of SWNT in the composite fiber. \(Y_{SWNT}, Y_{PVA}\) and \(Y_c\) are the effective Young’s modulus of the SWNT, control PVA and composite fiber, respectively. \(\sigma_{SWNT}, \sigma_{PVA}\) and \(\sigma_c\) are the tensile stress of SWNT, control PVA and composite fibers, respectively. \(\eta_o\) is the orientation factor which has values of \(\eta_o=1\) for perfectly aligned fibers and \(\eta_o=1/5\) for randomly oriented fibers. \(\eta_1\) is the length efficiency factor described by Equation 7.6.\[\text{\textsuperscript{265}}\]

\[\eta_1 = 1 - \frac{\text{Tanh}(a \cdot l_{SWNT} / D_{SWNT})}{a \cdot l_{SWNT} / D_{SWNT}} \tag{7.6}\]

\(a\) is given by Equations 7.7 and 7.8, respectively:

For Young’s modulus calculation:

\[a = \sqrt{- \frac{3 Y_{PVA}}{2 Y_{SWNT} \ln V_{SWNT}}} \tag{7.7}\]

For tensile stress calculation:

\[a = \sqrt{- \frac{3 \sigma_{PVA}}{2 \sigma_{SWNT} \ln V_{SWNT}}} \tag{7.8}\]

\(D_{SWNT}\) is taken as the bundle diameter of the SWNT measured from SEM analysis of the fractured composite (10.3 ± 4.4 nm) and \(l_{SWNT}\) is the average length of the SWNT after 48 h of sonication and determined to be 1.5 ± 1.1 μm. The average (~1.5 μm) as well as the upper (~2.6 μm) and lower (~0.4 μm) nanotube length distributions are taken into account when determining the effective modulus and strength of the CNT in the composites. The calculated curves for effective \(Y_{SWNT-eff}\) and \(\sigma_{SWNT-eff}\) as a function of \(\eta_o\) are shown in Figure 7.4. The theoretical curves are given by calculating \(Y_c\) and \(\sigma_c\) values using \(\eta_o=1\), \(Y_{SWNT (\text{Experimental})} = 1470\) GPa, and \(\sigma_{SWNT (\text{Experimental})} = 52\) GPa\[\text{\textsuperscript{30}}\] (experimental values of SWNT bundles) conditions first,
and subsequently using $Y_c$ and $\sigma_c$ values as constants in Equations 7.4 and 7.5 to compute the relationship between $\eta_o$ and $Y_{SWNT-eff}$ or $\sigma_{SWNT-eff}$.

According to the calculation, the effective $Y_{SWNT-eff}$ for the F-B fibers ranges from 1539.8 GPa ($\eta_o = 1$) to 8574.4 GPa ($\eta_o = 1/5$) and the effective $\sigma_{SWNT-eff}$ for the F-B fibers range from 47.1 GPa ($\eta_o = 1$) to 253.0 GPa ($\eta_o = 1/5$). These results suggest that as the orientation factor changes from 1/5 to 1, the calculated values approach the real properties of SWNT (as mentioned), which have been experimentally and theoretically determined.\(^{42, 50, 266-268}\)

Since the fibers are spun under laminar-flow and subsequently drawn, the SWNT in the fiber systems will tend to be more aligned than randomly distributed. Therefore, recognizing that a certain degree of disorientation of SWNT will remain in the composite fiber, the minimum effective Young’s modulus and tensile strength of the SWNT for F-B fibers are 1539.8 GPa and 47.1 GPa, respectively. By comparing these values with the same analysis for the F-A fibers, the effective $Y_{SWNT}$ and $\sigma_{SWNT}$ values of F-B fibers are 664% higher and 179% higher, respectively. This result confirms that by inducing interfacial crystallization of PVA during fiber processing, a stronger PVA/SWNT interphase has been created, and subsequently better load transfer from the PVA matrix to SWNT has been achieved.

**Figure 7.4.** (a) Effective Young’s modulus and (b) tensile strength of SWNT for both F-A and F-B fibers as a function of the orientation factor ($\eta_o$). Both effective Young’s modulus and tensile strength of SWNT gradually approach real values of SWNT as ($\eta_o$) increases from 1/5 (randomly distributed) to 1 (perfectly aligned). The SWNT length ($L$) variation has been taken into account when generating the theoretical curves.
Based on this theoretical analysis using Equations 7.4 to 7.8, the predicted effective modulus value at $\eta_o = 1$ for the SWNT in the F-B was rather high. Typically, both experimental and theoretical SWNT modulus values of 1 TPa or greater are associated with individual single-wall nanotubes as opposed to bundles/ropes. In this work the PVA/SWNT fibers contained SWNT bundles with sizes in the order of 10 nm in diameter, and the predicted and measured modulus values reported for SWNT bundles are usually only a few hundred gigapascals. For the F-A fibers where there was no interphase present, the bulk-PVA matrix was solely reinforced by the SWNT bundles. The resultant predicted effective modulus for fully aligned SWNT was ~201 GPa, and this value was within the ranges experimentally and theoretically obtained for nanotube bundles.\textsuperscript{269, 270} However, for the F-B fibers consisted of interphase- and bulk-PVA, it is important to take the influence of this interphase structure into account for the mechanical performance.

**Modified Analysis with Interphase Contribution**

Based on the WAXD and SEM evidence, it was clear that the interphase region was predominant throughout the F-B fiber. To determine the effect of this templated polymer structure on the mechanical properties in the composite, additional theoretical analysis for the modulus of the F-B PVA/SWNT fiber was performed. This was done by first modifying Equation 7.4 without considering the mechanical contribution from the SWNT (Figure 7.5a). The Young’s modulus of the fiber that received contributions from both the matrix and the interphase can then be determined using Equation 7.9.

$$Y_c = V_{PVA} Y_{PVA} + V_{interphase} Y_{interphase}$$  \hspace{1cm} (7.9)

$V_{PVA}$ and $V_{interphase}$ are the volume fraction of the PVA bulk and interphase in the vicinity of the SWNT, respectively. $Y_{PVA}$ and $Y_{interphase}$ are the Young’s modulus of the PVA control fibers (i.e. bulk-PVA) and fully crystalline (i.e. interphase-PVA), respectively. The volume fraction of the interphase region was calculated using the crystal size obtained from WAXD and SEM data assuming the each SWNT bundle was uniformly coated by interphase-PVA. $V_{interphase}$ was determined to be ~38.32%. $Y_{interphase}$ was taken to be 255 GPa, and this value was based on experimental X-ray analysis for fully crystalline PVA along the axial direction.\textsuperscript{271} Therefore, using Equation 7.9, the overall modulus of the fiber without SWNT contribution
(i.e., $Y_c$) was estimated to be ~109.7 GPa. This was below the real composite average modulus of ~119 GPa, which indicated that the mechanical contributions from both the matrix and the interphase were not sufficient of attaining the overall fiber properties. In other words, the additional SWNT also played a role in reinforcing the PVA in the composite.

**Figure 7.5** (a) Schematic showing the SWNT bundle as a void, where this structure is used to determine the effective modulus contribution for the interphase-PVA in the F-B fibers. (b) Curves showing the effective modulus of SWNT as a function of orientation factor ($\eta_o$) taking into account the interphase-PVA in the F-B fiber. A two-fold increase of stress transfer from the PVA matrix to the SWNT is observed in the F-B fibers. (c) A bar chart showing the effective modulus contributions from each component present in the control PVA, and F-A and F-B PVA/SWNT fibers.
By confirming the mechanical properties of the F-B fibers were a combination of the three components (i.e., matrix, interphase, and SWNT), Equation 7.4 was then further modified to now take into account the potential effect of the interphase (see Equation 7.10). In this way, a more accurate prediction of the effective modulus reinforcement of the SWNT bundle in the F-B composite was found. Equation 7.10 is given by:

\[
Y_c = (\eta_o \eta_0 Y_{\text{SWNT-eff}}^2 - Y_{PVA} - Y_{\text{interphase}})V_{\text{SWNT}} + V_{PVA} Y_{PVA} + V_{\text{interphase}} Y_{\text{interphase}}
\]

where, \( Y_{\text{SWNT-eff}} \) is the new effective Young’s modulus of the SWNT after taking the interphase-PVA contribution into account. Based on this analysis, the effective modulus for the SWNT ranges from 2293.1 GPa to 434.1 GPa for randomly \( (\eta_o = 1/5) \) to fully aligned \( (\eta_o = 1) \) tubes, respectively (Figure 7.5b). It should be noted that by including the interphase contribution the approximation for the modulus of the SWNT was more in line with other measured values for SWNT bundles. It should also be noted that the effective modulus of the SWNT in the F-B fiber was still significantly higher than what was observed for the F-A fibers (no interphase) (i.e. 434.1 GPa as compared to 201.5 GPa at \( \eta_o = 1 \)).

Figure 7.5c shows the effective modulus contributions from each component present in the control, F-A, and F-B fibers. It is clear that the presence of the SWNT templated interphase-PVA significantly affects the fiber properties, and results in an increase of stress transfer from the matrix to the filler.

7.3.4 Interfacial Strength between Interphase and SWNT

From all the analysis presented above, it has been confirmed that the formation of a polymer interphase in the vicinity of SWNT plays a very important role in the improvement of the composite fiber mechanical properties. However, the interfacial strength between the interphase and the nanotubes has not been explored quantitatively. For this reason, this section aims to utilize SMD simulation methods to investigate the adhesion strength between the polymer interphase and SWNT.

Baseline Nanotubes Adhesion Simulation

Before conducting pulling tests on the interphase-SWNT models, baseline studies of the inter-tube adhesion within SWNT bundles themselves were studied. A detailed modeling
procedure was given in Section 7.2.2. Two SWNT bundle pulling cases were considered in this work and the detected pulling force values normalized by the interactive area between the pulled and fixed bundle/tube are plotted in Figure 7.6. The persistence length of SWNT was reported to be 271 nm, meaning that the elastic behavior of the nanotubes would remain upon pulling if its length is shorter than this value.\textsuperscript{272} For both baseline cases, the nanotube length was 6.9 nm, indicating that the whole tube length should be taken into account when calculating the interactive area. When comparing the pulling force values, it was found that the tube-tube adhesion strength due to the vdW forces was very similar for both cases with strength ranging from 110 MPa to 130 MPa. This confirmed a stable interaction between nanotubes themselves for the model and set the baseline strength values for the interphase-SWNT adhesion comparison.

![Figure 7.6 SWNT bundle interfacial strengths measured using SMD method. Two cases were considered: (1) one nanotube pulled out of a 7-hexagonal tube bundle (black curve) and (2) 7 nanotubes pulled out of a 19-hexagonal tube bundle (red dash curve).](image)

\textbf{Figure 7.6} SWNT bundle interfacial strengths measured using SMD method. Two cases were considered: (1) one nanotube pulled out of a 7-hexagonal tube bundle (black curve) and (2) 7 nanotubes pulled out of a 19-hexagonal tube bundle (red dash curve).
Interphase-SWNT Adhesion Simulations

After obtaining the baseline adhesion strength between nanotubes within bundles, the interfacial strength between the interphase region and the SWNT was studied by using SMD methods. As mentioned in the modeling procedure in Section 7.2.2, three different interphase conformations obtained from previous studies were used. Figure 7.7 summarizes the detected pulling force values normalized by the interactive area between the pulled interphase and the fixed SWNT. Since the polymer chains exhibit stick-slip behavior upon peeling in Scenario-1, the persistence length of the PVA chains (i.e., 0.16 nm \(^2\)) is used to calculate the effective interactive area. For both Scenario-2 and Scenario-3, the interphase region is pulled as a whole off the bundle surface without showing any elastic deformation. Therefore, the whole interactive area between the nanotubes bundle and the polymer is calculated and used to normalize the forces.

**Figure 7.7** Interphase-SWNT interfacial strengths measured using SMD method. Three different scenarios were considered. (a) Scenario-1: interphase chain peeling from the individual nanotube (black solid curve), the initial configuration was adopted from the intermediate flow rate case in Chapter 6. (b) Scenario-2: interphase coating pulling from the 7-SWNT bundle (blue dotted curve), the initial configuration was adopted from the interphase growth studies in Chapter 4. Scenario-3: Thick interphase region (~8.2 nm thickness) pulled from the top surface of the SWNT bundle (red dash curves). For comparison purpose, the baseline SWNT bundle interfacial strengths from Figure 7.6 are also shown.
As shown in Figure 7.7, depending on the initial configuration of the systems, a significant deviation in the interphase strength was noticed. Although the stick-slip behavior of the polymer chains in Scenario-1 (Figure 7.7a) cause the force measured to periodically vibrate, the tensile strength and Young’s modulus range of the interphase are found to be 1.1–6.1 GPa and 153.4–205.2 GPa, respectively. These values are one order higher than the baseline SWNT inter-bundle strength. However, for both Scenario-2 and Scenario-3, the interfacial properties obtained are much lower than Scenario-1 and are comparable with the baseline bundle adhesion properties. The tensile strength of the interphase for Scenario-2 and Scenario-3 are found to be 0.10 and 0.034 GPa, respectively; and the Young’s modulus of the interphase for Scenario-2 and Scenario-3 are determined to be 0.84 and 0.72 GPa, respectively. These properties are lower than the SWNT bundle separation force threshold.

As described in Section 7.3.2, the inter-chain hydrogen bonding may also contribute to the strengthening of the material. In order to understand the contribution of hydrogen bonding to the overall properties, the changes in the number of hydrogen bonds within the PVA interphase for Scenario-1, -2, and -3 during pulling are recorded and plotted in Figure 7.8.

![Figure 7.8](image)

**Figure 7.8** Change in the number of hydrogen bonds at the polymer interphase as a function of pulling time for (a) Scenario-1, as well as (b) Scenario-2 and Scenario-3.

When comparing Figure 7.8a with the interphase-CNT interfacial strength curve in Figure 7.7a, the number of hydrogen bonds decreases significantly after the initial two maximum
interphase strength peaks occur (i.e., pulling time after 0.05 ns in both figures). The hydrogen bond number becomes somewhat stable after this initial decrease, and the interfacial strength measured from the interphase also corresponds and varies within the range that is slightly lower than the maximum strength values. This indicates that the initial hydrogen bonds between the polymer chains may provide additional force to prevent interfacial failure.

On the other hand, Figure 7.8b shows the change in hydrogen bond numbers during pulling for Scenario-2 and Scenario-3. These values differ from Scenario-1, since for these two cases the interphase region is pulled out as a whole and did not take into account the persistence length for the PVA chain. Therefore, the number of hydrogen bonds slightly increases as a result. The absolute number of hydrogen bonds also differs for each scenario considering the amount of chains present in each simulation box.

In experiments, the interphase failure mechanism in the composite fibers is more complex than the three different scenarios shown above. Many other factors that are non-ideal can affect the interphase contribution significantly. First, the failure mechanism of the interphase upon pulling can be a combination of both horizontal sliding (i.e., similar to Scenario-2 and Scenario-3) and vertical peeling (i.e., similar to Scenario-1) depend on the fiber orientation and the variation in the physical chain entanglements within the interphase. In addition, since the persistence length of the nanotubes and the polymer chains are drastically different, the presence of the nanotube surface can also affect the force response of the polymer chain during tensile testing. Moreover, depending on the dispersion quality of the SWNT within the composite fibers, local confinement of the interphase chains due to the high SWNT concentration can also influence the interphase mechanical behavior by providing additional pre-stress conditions prior to fiber pulling. For all these reasons, the two extreme properties of the interphase obtained from this simulation study (i.e., Scenario-1 for high extreme and Scenario-2 and Scenario-3 for low extreme) provide a range for the interphase mechanical performance.

The rule of mixture analysis presented in Section 7.3.3 assumes that the property of the interphase region was similar to the property of the perfect crystalline region. In the real conditions, however, it is very difficult to achieve complete extension of the polymer chains
even in the vicinity of SWNT due to thermal-dynamics effect as well as molecular vibrations. For this reason, more specific values need to be assigned to the interphase region for more reasonable composite analysis. Mechanical properties of the interphase through different scenarios using SMD in this work were used to re-evaluate the nanotube effective properties in the composite fibers using simple rule of mixture without considering the CNT orientation and length factors (Equations 7.11 and 7.12).

\[
Y_c = V_{\text{matrix}} Y_{\text{matrix}} + V_{\text{interphase}} Y_{\text{interphase}} + V_{\text{SWNT}} Y_{\text{SWNT}}
\]  
(7.11)

\[
\sigma_c = V_{\text{PVA}} \sigma_{\text{PVA}} + V_{\text{interphase}} \sigma_{\text{interphase}} + V_{\text{SWNT}} \sigma_{\text{SWNT}}
\]  
(7.12)

To explore the full potential of the interphase region contributing to the fiber mechanical properties, the high extreme property values measured from Scenario-1 are used in these equations. The calculated effective Young’s modulus and tensile strength ranges for the SWNT bundle were 329.4–547.3 GPa and 16.3–37.4 GPa, respectively. The lower end values were obtained using the highest interphase properties measured in Scenario-1; and the higher end values were obtained using the lowest interphase properties measured in Scenario-1. Based on the calculations these effective values are in good agreement with the experimentally measured CNT bundle properties.\(^{267}\) This potentially suggested an excellent stress transfer from the interphase region to the CNT bundles for better utilizing the nanotube properties. In addition, not only the interphase region provides better polymer-CNT interactions in the composite fibers, but the interphase itself also contribute to the composite mechanical properties by forming more extended chain morphology.

The effective SWNT mechanical contributions in the composite fibers were also calculated using interphase properties from Scenario-2 and Scenario-3. The calculated effective Young’s modulus for SWNT bundle using interphase properties of Scenario-2 and Scenario -3 were 1195 and 1191.4 GPa, respectively. The calculated effect tensile strength for SWNT bundle from Scenario-2 and Scenario-3 were 41.7 and 41.4 GPa. These effective values are higher as compared to the values calculated using Scenario-1 properties. In addition, these effective values overshoot the SWNT bundle properties and even exceed the exfoliated SWNT
properties. This indicates that the interphase properties measured from Scenario-2 and Scenario-3 might be too low as compared to its true contribution in the fibers. For this reason, the true interphase properties might be in the range between the high-end value measured in Scenario-1 and the low-end values measured from Scenario-2 and Scenario-3. More efforts in the future is needed for further investigating the true contribution of the interphase.

7.4. Conclusion

In summary, this chapter explored the roles of the polymer interphase region in the polymer/SWNT composite fibers for enhancing fiber mechanical performances. The mechanical properties of the PVA/SWNT composite fibers with and without the interphase region that produced in Chapter 4 were analyzed using tensile testing. Fibers with the interphase structure showed significant mechanical improvement as compared to the control and composite fibers without the interphase. The interphase strengthening mechanism was analyzed by looking at the inter-chain hydrogen bonding distance based on the simulated polymer unit cells. It was found that the interphase provide a more compact chain packing as compared to the regular polymer crystalline region, which resulted in stronger hydrogen bonding for better stress transfer.

The effective contributions from the nanotubes with and without the presence of the interphase region were also studied by using various forms of rule of mixture equations. It was found that the formation of the interphase helped to better utilize the properties of SWNT as well as to contribute to the composite fiber properties by having more extended-chain morphology. SMD simulation methods were used on various scenarios to measure the interphase strength in the vicinity of SWNT numerically. By adopting various interphase conformations from studies in previous chapters, the range of the interphase Young’s modulus and tensile strength were found to be 36.4–160.0 GPa and 4.5–7.5 GPa, respectively. And the resultant effective properties of CNT after taking consideration of the interphase region properties from the peeling study were found to be 329.4–547.3 GPa in modulus and 16.3–37.4 GPa in strength. These values are in very good agreement with the CNT bundle measurements reported in the literature, indicating an effect utilization of the CNT properties with the presence of interphase polymer.
Chapter 8 SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

8.1. SUMMARIES

The structure of this dissertation is summarized in the above flow chart. This work is dedicated to the understanding of the fundamental polymer-CNT interactions under various key conditions during high CNT loading composite fiber spinning process. Controlling such interactions can lead to the initialization and formation of the polymer interphase region, which is important in terms of its significance in composite fibers. By utilizing both experimental and computational methods, the effects of various fiber spinning factors on the polymer/CNT composite fibers global properties as well as on the polymer chains morphologies due to different polymer-CNT interactions at the atomic-scale have been explored in detailed. This work deepens the fundamental understanding of the polymer-CNT
interactions during fiber spinning process, and also provides several connections related to the process-structure-property relationship in polymer/CNT composite fibers.

8.2. RECOMMENDATIONS

Based on the studies performed in this work and the conclusions drawn from the results, the following recommendations are made for future research efforts that may extend upon the findings outlined in this thesis.

- The fiber spinning apparatus can be used to explore possibilities for other polymer and nano-filler systems. Re-optimization might require for new material combinations.
- The overall laminar-flow conditions can be studied numerically using CFD approaches to better understand the velocity and temperature profile combinations during fiber spinning.
- Coarse-grain simulation method can be used to simulate composite systems at larger scales. More macroscopic simulation of the properties of these materials may help to reveal and enable closer linkages to the experimental domain.
- Laminar-flow simulations can be extended to solvent mixture systems (i.e., solvent/non-solvent or co-solvent conditions) to capture the chain behavior at later stages of the fiber spinning process, or using customized dope preparation and/or spinning conditions.
APPENDIX A: EFFECT OF CNT DISPERSION QUALITY ON POLYMER/CNT COMPOSITE FIBERS WITH HIGH CNT LOADING

Figure A.1. Small-angle X-ray scattering (SAXS) profiles for (a) various DMAc/SWNT dispersion and (b) various DMSO/SWNT dispersion cases.

Table A.1 Summary of the SWNT bundle size for DMAc/SWNT and DMSO/SWNT dispersion studies with various CNT types without polymer assistance

<table>
<thead>
<tr>
<th>Sonication time (hour)</th>
<th>C-Tubes</th>
<th>P-Tubes</th>
<th>SP-Tubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>12.25</td>
<td>9.61</td>
<td>11.85</td>
</tr>
<tr>
<td>48</td>
<td>12.12</td>
<td>8.42</td>
<td>9.61</td>
</tr>
<tr>
<td>60</td>
<td>12.12</td>
<td>11.02</td>
<td>8.46</td>
</tr>
<tr>
<td>DMAc</td>
<td>12.25</td>
<td>12.87</td>
<td>21.88</td>
</tr>
<tr>
<td>aspect ratio 10</td>
<td>26.86</td>
<td>18.26</td>
<td>21.08</td>
</tr>
<tr>
<td>aspect ratio 100</td>
<td>27.18</td>
<td>13.85</td>
<td>26.38</td>
</tr>
<tr>
<td>aspect ratio 1000</td>
<td>27.54</td>
<td>21.16</td>
<td>24.64</td>
</tr>
<tr>
<td>DMSO</td>
<td>26.62</td>
<td>13.62</td>
<td>24.82</td>
</tr>
<tr>
<td>aspect ratio 10</td>
<td>29.6</td>
<td>27.4</td>
<td>27.4</td>
</tr>
<tr>
<td>aspect ratio 100</td>
<td>26.44</td>
<td>8.72</td>
<td>35</td>
</tr>
<tr>
<td>aspect ratio 1000</td>
<td>26.86</td>
<td>27.36</td>
<td>35</td>
</tr>
<tr>
<td>DMSO</td>
<td>25.56</td>
<td>14.22</td>
<td>23.48</td>
</tr>
<tr>
<td>aspect ratio 10</td>
<td>25.56</td>
<td>13.45</td>
<td>23.48</td>
</tr>
<tr>
<td>aspect ratio 100</td>
<td>27.56</td>
<td>14.22</td>
<td>23.48</td>
</tr>
<tr>
<td>aspect ratio 1000</td>
<td>27.56</td>
<td>14.22</td>
<td>23.48</td>
</tr>
</tbody>
</table>
Figure A.2. TGA curve for SWNT, PAN, and PAN/SWNT composite fibers. When comparing these profiles, the weight lost shown in the composite fiber during the thermal charring process is mainly due to the PAN matrix degradation.

Figure A.3. SEM images of the PAN/SWNT composite fiber morphology (a) before and (b) after the thermal charring process.
Figure A.4. Wide-angle X-ray (WAXD) patterns for PAN/SWNT composite (a) F-1, (b) F-2, and (c) F-3 fibers.
APPENDIX B: LAMINAR-FLOW RATE EFFECTS ON THE 
POLYMER-CNT INTERACTIONS

Figure B.1. Wide-angle X-ray diffraction (WAXD) patterns for PVA (a) control and (b) composite fibers, and PAN (c) control and (d) composite fibers under different initial draw ratio.
Figure B.2. Representative stress-strain curves for PVA (a) control and (b) composite fibers, as well as PAN (c) control and (d) composite fibers.

Figure B.3. (a) PVA chain confinement study under the same laminar-flow condition (i.e., intermediate laminar-flow rate), where 1 or 2 PVA chains near CNT surface are subjected in flow for chain confinement investigations. (b) Representative solvent temperature profile during 1 ns of laminar-flow simulation shows the system temperature is controlled accurately by the Nose-hoover thermostat.
Code B.1. LAMMPS code for polymer-CNT baseline interaction studies.

#------------------------
# # Polymer-CNT Baseline Interaction
# # J. Meng
# # Jan 2014
#------------------------
units real
boundary p p p
atom_style full

timestep 1.0

bond_style harmonic
angle_style harmonic
dihedral_style harmonic
improper_style cvff
pair_style lj/cut/coul/cut 8.0 8.0

read_data PAN_SWNT.data

neighbor 0.5 bin
neigh_modify every 1 delay 0 check yes one 5000

group cnt id < 1201

group pan id > 1200
region 1 block INF INF INF INF INF 9.0 units box

group hold_cnt region 1

# Energy calculation

compute peratom all pe/atom
compute pe_tot all reduce sum c_peratom
compute polype pan pe/atom
compute pe_tot_poly pan reduce sum c_polype
compute cntpe cnt pe/atom
compute pe_tot_cnt cnt reduce sum c_cntpe
compute cntpoly cnt group/group pan
compute polypoly pan group/group pan

dump mini1 all xyz 4000 cnt_pan.xyz
dump poly1 pan xyz 4000 poly.xyz
dump cnt1 cnt xyz 4000 cnt.xyz

fix pin1 hold_cnt setforce 0.00 0.00 0.00
velocity hold_cnt set 0.00 0.00 0.00 units box
thermo 500
min_modify dmax 0.01
minimize 0.0 1.0e-8 1000 10000

fix en0 all nve/limit 0.002
run 10000
unfix en0
fix energy_out all ave/time 1 1 1000 c_pe_tot c_pe_tot_poly c_pe_tot_cnt c_cntpoly
c_polypoly file energy.data

velocity all create 300 1245623

fix enl all nvt temp 300. 300. 2

run 2000000
Code B.2. LAMMPS code for Laminar-flow simulation studies.

#------------------------
# Laminar-flow Simulation
# J. Meng
# Jan 2015
#------------------------

units real
boundary p p p
atom_style full

bond_style harmonic
angle_style harmonic
dihedral_style harmonic
improper_style cvff
pair_style lj/cut/coul/cut 8.0 8.0

timestep 1.0
read_restart 2m.restart

neighbor 0.5 bin
neigh_modify every 1 delay 0 check yes one 5000

group dms0 id < 136801
group pva1 id <> 136801 138902
group pva2 id > 143702
group  cnt id <> 138902 143703

group  pva union pva1 pva2

region  1 block INF INF INF INF INF 9.0 units box


group  hold_cnt region 1

group  hold intersect cnt hold_cnt

group  mobile subtract all hold

# Energy calculation

compute  peratom all pe/atom

compute  pe_tot all reduce sum c_peratom

compute  polype pva pe/atom

compute  pe_tot_poly pva reduce sum c_polype

compute  cntpe cnt pe/atom

compute  pe_tot_cnt cnt reduce sum c_cntpe

compute  dmsope dmso pe/atom

compute  pe_tot_dmso dmso reduce sum c_dmsope

compute  cntpoly cnt group/group pva

compute  polypoly pva group/group pva

compute  dmsopoly dmso group/group pva

compute  vxpoly pva property/atom vx

compute  vypoly pva property/atom vy

compute  vzpoly pva property/atom vz
dump mini1 all xyz 12000 cnt_poly2.xyz
dump poly1 pva xyz 4000 poly.xyz
dump cnt1 cnt xyz 4000 cnt.xyz

thermo 500
min_modify dmax 0.01
minimize 0.0 1.0e-8 1000 10000

min_style sd
minimize 0.0 1.0e-8 1000 10000

fix en0 all nve/limit 0.002
run 10000
unfix en0

write_restart before_flow.restart

fix energy_out all ave/time 1 1 1000 c_pe_tot c_pe_tot_poly c_pe_tot_cnt
c_pe_tot_dmso c_cntpoly c_polypoly c_dmsopoly file energy.data

dump vpoly pva custom 20000 vpoly.txt c_vxpoly c_vypoly c_vzpoly

velocity all create 277 1245623
fix en1 all nvt temp 277. 277. 200.
fix pin1 hold setforce 0.00 0.00 0.00
velocity hold set 0.00 0.00 0.00 units box

# Shear Flow
fix flow1 dmos gravity 0.0000001 vector 1 0 0
run 1000000
write_restart 1m.restart
run 1000000
write_restart 2m.restart
run 1000000
write_restart 3m.restart
run 1000000
write_restart 4m.restart
print "all done"
APPENDIX C: POLYETHYLENE ASSISTED EXFOLIATION OF HEXAGONAL BORON NITRIDE IN COMPOSITE FIBERS

Initial configurations of the BN sheet baseline shearing and pulling studies are shown in Figure C.1.

*Figure C.1.* Initial configurations for the h-BN adhesion study showing (a₁) peeling and (a₂) shearing conditions using the Steered Molecular Dynamics (SMD) method; as well as the initial PE chains arrangement for studying the polymer crystallization behavior (b₁) on top or (b₂) on both top and side of the h-BN stacking.
Figure C.2. Steered molecular dynamics (SMD) forces and potential of mean forces (PMF) for both h-BN shearing (a1 and a2) and peeling (b1 and b2) at different pulling rates (from 5 m/s to 100 m/s), respectively.

Table C.1 Non-bonded Lennard-Jones parameters for h-BN/polymer system

<table>
<thead>
<tr>
<th>Type</th>
<th>( \varepsilon ) (Kcal/mole)</th>
<th>( \sigma ) (Å)</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-B</td>
<td>0.094</td>
<td>3.453</td>
<td>-</td>
</tr>
<tr>
<td>N-N</td>
<td>0.144</td>
<td>3.365</td>
<td>-</td>
</tr>
<tr>
<td>B-N</td>
<td>0.114</td>
<td>3.409</td>
<td>( \varepsilon_{B-N} = \frac{2\varepsilon_{B-N}^0}{\varepsilon_{B-B} + \varepsilon_{N-N}} ) [^{48}]</td>
</tr>
<tr>
<td>B-C</td>
<td>0.084</td>
<td>3.390</td>
<td>-</td>
</tr>
<tr>
<td>N-C</td>
<td>0.084</td>
<td>3.390</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure C.3. SMD snapshots of the maximum h-BN sheets separation during polymer matrix pulling for three different cases: (a₁) Case-1: PE matrix on top of the h-BN stacking with one h-BN layer fixed at the bottom; (a₂) Case 2: PE matrix surrounding the h-BN stacking with one h-BN layer fixed at the bottom; and (a₃) Case 3: PE matrix surrounding the h-BN stacking with four h-BN layers fixed at the bottom. The SMD forces and PMF for all cases are summarized in (b₁) and (b₂), respectively.
## Code C.1. LAMMPS code for BN baseline shearing study.

```
#------------------------
# BN double layer, SMD detachment simulation
# J. Meng; S.W. Cranford
# May 2014
#------------------------
units     real
atom_style full
boundary   p p p
timestep   0.5
read_data  BN_double_rev2.data

pair_style   hybrid tersoff lj/cut 20.0
pair_coeff   * * tersoff BN-C-real.tersoff B N B N
pair_coeff   1 3 lj/cut 0.094668 3.453 20.0
pair_coeff   2 4 lj/cut 0.144463 3.365 20.0
pair_coeff   1 4 lj/cut 0.116955 3.409 20.0
pair_coeff   2 3 lj/cut 0.116955 3.409 20.0

neighbor 5 bin
neigh_modify every 10 one 10000
region      1 block INF INF INF INF INF 3.0 units box
group      pin1 id 1 3 5 7 9 11 13 15 17 19
group      pin2 id 210 211 212 213 214 215 216 217 218 219 220
group      pin3 id 21 41 61 81 101 121 141 161 181 201
group      pin4 id 201 202 203 204 205 206 207 208 209
```
group pin union pin1 pin2 pin3 pin4

group pull id > 429

group first_layer region 1

group second_layer subtract all first_layer

compute peratom all pe/atom

compute pe_tot all reduce sum c_peratom

compute firstpe first_layer pe/atom

compute pe_first first_layer reduce sum c_firstpe

compute secondpe second_layer pe/atom

compute pe_second second_layer reduce sum c_secondpe

dump DumpXYZ all xyz 250 BN_rev_100.xyz

minimize 0.0 1.0e-8 1000 100000

fix energy_out all ave/time 1 1 1000 c_pe_tot c_pe_first c_pe_second file
energy_rev_100.data

thermo_style custom step temp pe ke etotal

thermo 1000

fix en00 all nve/limit 0.01

run 5000

unfix en00

fix en1 all nvt temp 5.0 5.0 100

run 10000

compute y_mark all reduce max y

fix anchor first_layer spring tether 5000.0 10.50 -50 0.0 56.5

fix pullf pull smd cvel 0.02 -0.0010 tether 10.50 90.0 0.00 0.0

139

run 6000000

write_restart bn.restart
**Code C.2.** LAMMPS code for BN/PE pulling studies.

```
#------------------------
# BN double layer, SMD detachment simulation
# J. Meng; S.W. Cranford
# May 2014
#------------------------

units real
atom_style full
boundary p p p
bond_style harmonic
angle_style harmonic
dihedral_style harmonic
timestep 0.5

read_restart restart.BNPE
change_box all x scale 1 y scale 2 z scale 1 units box

pair_style hybrid tersoff lj/cut 20.0
pair_coeff * * tersoff BN-C-real.tersoff B N NULL NULL NULL B N

# ref:

pair_coeff 3 4 lj/cut 0.055 3.00 20.0
pair_coeff 3 5 lj/cut 0.055 3.00 20.0
pair_coeff 2 3 lj/cut 0.057 2.75 20.0
pair_coeff 3 3 lj/cut 0.020 2.00 20.0
pair_coeff 3 7 lj/cut 0.057 2.75 20.0
# mixture rule
pair_coeff 1 3 lj/cut 0.04351 2.7265 20.00
```
pair_coeff 3 6 lj/cut 0.04351 2.7265 20.00

# mixture rule for B-C
pair_coeff 1 4 lj/cut 0.0740 3.409 20.0
pair_coeff 1 5 lj/cut 0.0740 3.409 20.0
pair_coeff 4 6 lj/cut 0.0740 3.409 20.0
pair_coeff 5 6 lj/cut 0.0740 3.409 20.0

# mixture rule for N-C
pair_coeff 2 4 lj/cut 0.0857 3.337 20.0
pair_coeff 2 5 lj/cut 0.0857 3.337 20.0
pair_coeff 4 7 lj/cut 0.0857 3.337 20.0
pair_coeff 5 7 lj/cut 0.0857 3.337 20.0

# ref: D. Baowan, Nested boron nitride and carbon-boron nitride nanocones
pair_coeff 4 5 lj/cut 0.06076547 3.369 20.0
pair_coeff 4 4 lj/cut 0.06076547 3.369 20.0
pair_coeff 5 5 lj/cut 0.06076547 3.369 20.0

# interlayer interaction
pair_coeff 1 6 lj/cut 0.094668 3.453 20.0
pair_coeff 2 7 lj/cut 0.144463 3.365 20.0
pair_coeff 1 7 lj/cut 0.116955 3.409 20.0
pair_coeff 2 6 lj/cut 0.116955 3.409 20.0

neighbor 5 bin
neigh_modify every 10 one 10000

group hold id < | 10695 10710

group BN_layer id <= 11706

group PE subtract all BN_layer
compute peratom all pe/atom
compute pe_tot all reduce sum c_peperatom
compute BNpe BN_layer pe/atom
compute pe_BN BN_layer reduce sum c_BNpe
compute PEpe PE pe/atom
compute pe_PE PE reduce sum c_PEpe

dump DumpXYZ all xyz 250 BN_PE_pull.xyz

fix energy_out all ave/time 1 1 1000 c_pe_tot c_pe_BN c_pe_PE file energy.data
thermo_style custom step temp pe ke etotal
thermo 1000

fix hold1 hold setforce 0.0 0.0 0.0
velocity hold set 0.0 0.0 0.0 units box
fix en0 all nvt temp 5.0 5.0 100
run 1000
compute y_mark all reduce max y

fix pullf PE smd cvel 2 -0.0010 tether 0.00 -400.0 -6.00 0.0
run 400000
REFERENCES


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171. Crutchley, R. J. Spin Density Delocalization in Mononuclear and Dinuclear Complexes.


LIST OF PUBLICATIONS


