THE EFFECT OF GRAPHENE NANOFLAKE REINFORCEMENT ON THE
MECHANICAL AND ELECTRICAL PROPERTIES OF POLYVINYLIDENE
FLUORIDE

By

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Jennifer Lynch

And approved by

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New Brunswick, New Jersey

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ABSTRACT OF THE THESIS

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Thesis Director:
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Polyvinylidene fluoride (PVDF) is a semicrystalline thermoplastic polymer that is unique because it is electrically active, a property not common in polymers. PVDF is used in many industries due to its good mechanical properties, resistance to chemicals, and most importantly, piezoelectric properties. PVDF has been used as the matrix for many composites with both inorganic and organic fillers. This study involves uniform, high-shear melt-mixing graphite within PVDF to exfoliate graphite into graphene nanoflakes (GNFs) within the PVDF matrix in the concentrations of 0, 5, 10, 20, and 30 wt. %. These GNF-PVDF composite samples were characterized using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), mechanical testing (tensile and nanoindentation), and electrical conductivity testing. Results indicate enhancements in both mechanical and electrical properties due to the addition and subsequent exfoliation of graphite into GNFs directly within PVDF.
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Chapter 1 Introduction

Polymers are composed of molecules of high molecular weight with many repeating subunits (monomers). Due to their low density, low cost, and ease of molding, polymers are one of the most popular materials today. However, common downsides include low stiffness, temperature limitations, and static electricity accumulation. As a result, carbon-reinforced polymer matrix composites (C-PMC) are very popular and offer enhanced mechanical, thermal, and electrical properties as compared to polymers alone. These composites have a variety of uses and are being used in traditionally wood, metal, ceramic, and glass applications.

Common carbon fillers include carbon fiber, carbon nanotubes, graphite, and graphene. This study focuses on graphene as an enhancer and such composites can be categorized as a graphene reinforced polymer matrix composite (G-PMC). Graphene, a single-atomic layer of graphite, has exceptional mechanical properties (1 TPa Young’s modulus)\(^1\) and electrical properties (order of \(10^8\) S/m)\(^2,3\). While graphene has highly desirable characteristics, it is both expensive and difficult to produce, making G-PMCs impractical for commercial applications.

Polyvinylidene fluoride (PVDF), is a semi-crystalline thermoplastic polymer with favorable characteristics such as low cost, good mechanical properties, resistance to chemicals, thermal stability, and unique pyroelectric and piezoelectric properties\(^4,5\). With enhanced properties, a G-PVDF composite has promising applications as a sensor.

In this study, PVDF is processed with mined graphite flakes using a uniform, high-shear melt-mixing machine. During shear mixing, the graphite is exfoliated into graphene nanoflakes (GNFs) directly within molten PVDF. These GNFs are broadly termed as such
due to the distribution in the number of resulting layers. Graphite is added to PVDF in the following weight percentages, 0, 5, 10, 20, and 30 wt. % and all five concentrations were post processed to fabricate ASTM standard specimens and thin films. The objective of this work is to create a low-cost G-PMC and characterize its mechanical, thermal, and electrical properties. Scanning electron microscopy (SEM) is used to observe the dispersion and distribution of GNFs, as well as the particle-matrix interaction. Tensile testing and nanoindentation are used to determine the young’s modulus and the reduced modulus, respectively. Differential scanning calorimetry (DSC) is used to determine the melt temperature, heat of fusion, crystallization temperature, heat of crystallization, and the resultant crystallization for each concentration. Volume conductivity and sensor capabilities were both characterized using a source measure unit (SMU). This study summarizes the detailed effects in situ shear exfoliation of graphite into GNFs directly within PVDF during uniform shear melt-mixing.
Chapter 2 Background

2.1 Polyvinylidene fluoride

PVDF is a semi-crystalline thermoplastic that is popular due to its low cost, good mechanical properties, resistance to chemicals, high dielectric permittivity, pyroelectric properties and piezoelectric properties\(^4,6\). The most unique properties are its high dielectric permittivity, pyroelectric, and piezoelectric properties, which makes PVDF a widely investigated polymer. These properties are particularly useful and interesting because typically polymers are insulators and can store static electricity. Both the dielectric and pyroelectric properties involve changing the material’s polarization; one is changed via an applied electric field and the other is changed via a change in temperature. The piezoelectric properties represent the relationship between mechanical stress and electrical charge\(^7\), which makes PVDF composite a strong contender for strain gauge applications. Both the piezoelectric and pyroelectric responses rival that of ceramics, however, PVDF offers additional benefits such as its lower cost, flexibility, low acoustic impedance and high-frequency operation\(^8\). PVDF is utilized in several industries, including chemical processing, construction, healthcare, biomedical and nuclear waste handling.

The chemical structure of PVDF is displayed in Figure 1. PVDF is a long chain of the repeating unit (CH\(_2\)CF\(_2\))\(_n\) with approximately 55% crystallinity\(^8\). PVDF exhibits at least four crystalline phases, known as \(\alpha\), \(\beta\), \(\gamma\), and \(\delta\)\(^8,9,10\). Others acknowledge a fifth crystalline phase, \(\varepsilon\)\(^4,5,11\). The most common phases are \(\alpha\), \(\beta\), and \(\gamma\)\(^5,8\). The \(\alpha\)-phase is the most common and occurs naturally during cooling from a melted state, however, the \(\beta\)-phase is the most desirable. In the \(\beta\)-phase, spontaneous polarization can occur and has the highest ferro- and piezoelectric properties which is why it is a common research focus
If the $\beta$-phase is optimized, the dipoles can be more parallel with each other, therefore optimizing the degree of piezoelectricity. Traditionally, the $\beta$-phase was obtained via stretching and subjecting it to high pressures. New methods have used doped nanoparticles as a reinforcement to obtain the $\beta$-phase\(^\text{11}\).

![Figure 1. Chemical structure of PVDF](image)

2.2 Graphite exfoliation

Graphite is a naturally occurring crystalline form of carbon with high thermal stability, electrical conductivity, thermal conductivity, chemical stability, and lubricious properties. Bulk graphite is a layered material with stacked parallel layers separated by 3.41 Å and bonded with van der Waals interactions, which allows for sliding but are strong enough to make single layer exfoliation difficult and costly\(^\text{12}\). A single, one atom thick layer of graphite is known as graphene. Graphene has covalently bonded carbon atoms forming a hexagonal shape within the layer, while the interlayer van der Waals forces acting between the layers are not as strong. Graphene has strong chemical bonding, resulting in excellent mechanical properties, intrinsic electrical conductivity and thermal conductivity, and impermeability to gases\(^2\). The electrical properties of graphene are further benefited by the high aspect ratio, high mobility of charge carriers, and unique transport performance\(^\text{13}\). While graphene has many positive characteristics, the high cost and difficulty in production limits the usability.
Graphene was first isolated using Scotch tape in 2004. After this breakthrough, other exfoliation techniques to produce graphene from bulk graphite were investigated, including chemical, physical and thermal exfoliation. Chemical exfoliation became a popular technique to isolate graphene by inserting large alkali ions between graphite layers. While successful at a small scale and low yield, chemical exfoliation methods tend to produce non-uniform graphene with smaller area diameter due to chemical etching of the graphene edges. Other disadvantages of chemical exfoliation include the multi-step process, acidic environment, and damaged particle edges. Both physical exfoliation and thermal exfoliation can be used to preserve particle edges. Physical exfoliation, also referred as mechanical exfoliation, includes the stirring, shaking and ultrasonication of bulk graphite. These techniques often rely on exfoliation in water, which increases the spacing of the material (i.e., intercalation) for easier exfoliation. The resultant nanosheets are typically between 6-7 atomic layers and there is no confirmation that monolayers can be produced from these mechanical techniques. Thermal exfoliation reaches single and few layers graphene sheets via high temperatures and high pressures. This method is seen to be more effective than mechanical exfoliation, but sometimes produces defective and wrinkled graphene. Recently, new exfoliating techniques have been introduced such as electrochemical exfoliation, thermal quenching, and supercritical fluid exfoliation. While these techniques are the newest and least studied, they have resulted in a range of number of layers from monolayers to 10 layers. In these newer methods, the yield is low and the potential for re-stacking is high.

Graphene can be synthesized using chemical vapor deposition (CVD) and epitaxial growth. Using CVD to grow graphene has become popular after the grown graphene
exhibited 90% of the theoretical strength of pristine graphene\textsuperscript{22}. Both CVD and epitaxial growth make good graphene sheets with limited deformations and are ideal for electronic applications, but these methods do not scale up well for applications needing larger amounts of graphene and are costly.

Regardless of how the graphene is produced, another challenge faced is adding the graphene to a polymer matrix to create a polymer matrix nanocomposite enhanced with graphene. In-situ graphite exfoliation directly within a polymer is the focus of this study because it produces graphene from bulk graphite directly into the matrix to create a graphene enhanced polymer matrix nanocomposite with advantageous properties.\textsuperscript{23}

2.3 In-situ graphite exfoliation

Previous work performed at Rutgers University showed graphite was exfoliated into GNFs directly within polymers during uniform shear melt-mixing. Theoretically, when applied shear stresses surpass the interlayer shear strength (ISS) of graphite\textsuperscript{23}, which is approximately 0.14 GPa\textsuperscript{24}, graphite can be exfoliated. Few-layer graphene and multi-layer graphene, referred to as graphene nanoflakes (GNFs) were obtained by in situ, uniform-shear exfoliation within molten polymer\textsuperscript{23}. The degree of graphite exfoliation directly correlated to number of processing cycles or number of shear events\textsuperscript{23}. The in-situ exfoliation method aided strong particle-matrix interaction, as well as GNF dispersion and distribution within the polymer matrix, providing a significant enhancement in modulus. The modulus enhancement achieved ranged from 300 – 500 %, depending on the matrix polymer\textsuperscript{25}. 
Chapter 3 Experimental Method

3.1 Materials

A polymer matrix composite (PMC) was created by uniform shear melt-mixing of PVDF (Kynar 720 pellets manufactured by Arkema) and graphite flakes (Asbury Park Graphite). The PVDF is a semi-crystalline thermoplastic suitable for several applications due to its physical and chemical properties. This grade of PVDF is reported to have a specific gravity of 1.77-1.79, melting temperature of 165-172°C, and tensile strength of 34-55 MPa by the manufacturer. Both materials were conditioned prior to use to remove volatiles. The PVDF was held under vacuum for at least 4 hours prior to processing. The graphite flakes were dried in a convection oven overnight (approximately 12 hours) at 185°C.

3.2 Material preparation

PVDF and graphite flakes were added to a Randcastle microbatch mixer that imparts elongational flow, folding, and uniform shear to exfoliate graphite into GNFs within PVDF. Starve-feeding was utilized to load PVDF followed by the proper graphite concentration, and the components were mixed under a nitrogen environment. PVDF was added first and mixed for 5-10 minutes before the graphite was added in 3-5 batches with a 4-minute wait between batches. Once the graphite was loaded, the materials were mixed for a mixing time of 90 minutes. Five compositions were made using 0, 5, 10, 20, and 30 weight percent (wt. %) graphite within PVDF. The compositions are labeled as (wt. % graphite) G-PVDF, where the G refers to the GNF-reinforcement (Table 1). The processing conditions are shown in Table 2. The processing temperature was approximately 204 °C but varied slightly with concentration. The revolutions per minute (RPM) varied with
concentration due to the increase in amps with increasing graphite concentration. The RPMs were set lower with increasing graphite concentration in order to maintain the proper amps to avoid power shut down.

Table 1. Compositions of wt. % GNF reinforcement in PVDF and corresponding label

<table>
<thead>
<tr>
<th>wt. % GNF</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>PVDF</td>
</tr>
<tr>
<td>5</td>
<td>5G-PVDF</td>
</tr>
<tr>
<td>10</td>
<td>10G-PVDF</td>
</tr>
<tr>
<td>20</td>
<td>20G-PVDF</td>
</tr>
<tr>
<td>30</td>
<td>30G-PVDF</td>
</tr>
</tbody>
</table>

Table 2. Processing conditions used for melt-mixing using the Randcastle batch mixer

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>Mix time (min)</th>
<th>RPM</th>
<th>Volume PVDF (cc)</th>
<th>Volume G (cc)</th>
<th>Total Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>199</td>
<td>90</td>
<td>150</td>
<td>61.80</td>
<td>0</td>
<td>61.80</td>
</tr>
<tr>
<td>5G-PVDF</td>
<td>204</td>
<td>90</td>
<td>120</td>
<td>58.71</td>
<td>2.43</td>
<td>61.14</td>
</tr>
<tr>
<td>10G-PVDF</td>
<td>204</td>
<td>90</td>
<td>120</td>
<td>55.62</td>
<td>4.87</td>
<td>60.49</td>
</tr>
<tr>
<td>20G-PVDF</td>
<td>213</td>
<td>90</td>
<td>200</td>
<td>62.92</td>
<td>12.39</td>
<td>75.31</td>
</tr>
<tr>
<td>30G-PVDF</td>
<td>204</td>
<td>90</td>
<td>15</td>
<td>60.96</td>
<td>20.58</td>
<td>81.53</td>
</tr>
</tbody>
</table>

The material was collected from the mixer as extrudate through an approximately 4 mm diameter port, and the remaining material inside the rotor itself was collected by removing the rotor from the mixer. The extrudate and bulk pieces from the batch mixer were cut into pieces that were fed into a tabletop mini-injection molding machine. All extrudate was held under vacuum prior to mini molding. Type 5 tensile specimens and impact specimens were molded in accordance with ASTM D638 and ASTM D256, respectively. Table 3 lists the temperature and pressure parameters used to produce each type of specimen.
Table 3. Processing parameters for mini-molding impact and tensile specimens of G-PVDF

<table>
<thead>
<tr>
<th>Composition</th>
<th>Impact Temperature (°C)</th>
<th>Impact Pressure (kPa)</th>
<th>Tensile Temperature (°C)</th>
<th>Tensile Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>210</td>
<td>~414-552</td>
<td>210</td>
<td>~414-552</td>
</tr>
<tr>
<td>5G-PVDF</td>
<td>220</td>
<td>483</td>
<td>220</td>
<td>483</td>
</tr>
<tr>
<td>10G-PVDF</td>
<td>227</td>
<td>~414-552</td>
<td>227</td>
<td>~414-552</td>
</tr>
<tr>
<td>20G-PVDF</td>
<td>230</td>
<td>483</td>
<td>230</td>
<td>621</td>
</tr>
<tr>
<td>30G-PVDF</td>
<td>240</td>
<td>621</td>
<td>240</td>
<td>621</td>
</tr>
</tbody>
</table>

G-PVDF films were compression molded for each concentration. The extrudate and bulk pieces were cut into smaller pieces and fed into a 250 W coffee grinder to create a powder. This powder was compression molded using a heated Carver press, according to the conditions in Table 4 and films were fabricated ranging in thickness between 150-200 microns. The films were pressed and held for 30 seconds 3 times to obtain desired thickness, rotating the pressing blocks 90 degrees each time.

Table 4. Conditions used during compression molding of G-PVDF films

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature (°C)</th>
<th>Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>210</td>
<td>4137</td>
</tr>
<tr>
<td>5G-PVDF</td>
<td>200</td>
<td>3447</td>
</tr>
<tr>
<td>10G-PVDF</td>
<td>200</td>
<td>3447</td>
</tr>
<tr>
<td>20G-PVDF</td>
<td>200</td>
<td>3447</td>
</tr>
<tr>
<td>30G-PVDF</td>
<td>200</td>
<td>3447</td>
</tr>
</tbody>
</table>

3.3 Material Characterization

3.3.1 Morphology

Images depicting the morphology of each sample were taken using field emission scanning electron microscopy (FESEM/SEM, Zeiss Sigma Field Emission SEM). The Secondary Electron (SE2) detector with an electron high tension (EHT) of 5 kV settings
were used during imaging. The SEM samples were prepared by cryogenic fracture of mini molded specimens and mounted onto aluminum studs via carbon tape. All specimens were gold coated with an Electron Microscopy Sciences 150 T ES Coater system with a 10 nm layer of gold. The surface observed was parallel to the direction of flow. SEM micrographs will be used to observe dispersion and distribution of the GNFs and the adhesion between the PVDF matrix and GNF particles.

3.3.2 Thermal Properties

Differential scanning calorimetry (DSC) was performed using a TA Instruments Q1000 on all of the compositions. A heat cool heat (HCH) cycle was used from -70 °C to 205 °C at a rate of 10 °C/minute in a nitrogen environment. Small specimens, approximately 10 mg in weight, were cut from the mini molded specimens and crimped within an aluminum standard pan and lid. Two specimens were tested for each composition and results averaged. The melting temperature (Tm), the heat of fusion (ΔHf), the crystallization temperature (Tc), the heat of crystallization (ΔHc), and their respective calculated percent crystallinity are reported. The percent crystallinity was calculated using equation [1], for which ΔHf is the heat of fusion measured from the melting peak in the first and second heat and from the crystallization peak in the cooling curve, ΔHcc is the heat of cold crystallization, and ΔH°f is the heat of fusion of 100 % crystalline PVDF determined to be 105 J/g.26 Cold crystallization does not occur in these PVDF samples and is thus equal to zero in equation [1]. The glass transition is not visible in the curves and is thus not reported.

\[
X_c = \frac{\Delta H_f - \Delta H_{cc}}{\Delta H°_f}
\]  

[1]
3.3.3 Mechanical Properties

Tensile mechanical property characterization was conducted in accordance with ASTM D638 for type 5 specimens using an MTS QTest/25 Elite Controller. During testing, an extensometer was mounted to the specimen and a 5kN load cell was utilized. Specimens were pre-loaded and then immediately loaded with a cross head rate of 1 mm/min. At least 5 specimens were tested until failure for each composition, and the average of five specimens reported for the sample. The strain at break, stress at break, and elastic modulus (E) is reported.

Nanoindentation was performed using a NanoTest Vantage system with a diamond Berkovich tip. The G-PVDF samples were approximately 12.5 mm by 12.5 mm by 3 mm cut from the mid-section of the gauge length of the injection molded impact specimens (section 2 in Figure 2). The test area was a 14 indent by 14 indent grid (1950 µm by 1950 µm) with 196 total indentations spaced 150 µm apart. The load increased gradually from 0.5 mN to 200 mN over the 196 indentations. The reduced modulus and hardness are reported.

3.3.4 Electrical Properties

Electrical conductivity was measured in accordance with ASTM D4496 for the 10G-PVDF, 20G-PVDF, and 30G-PVDF. Three specimens were cut from the injection molded impact specimens. Specimens were segmented along the length (1, 2, and 3), as shown in Figure 2. The direction of flow is from 1 to 3. The specimens were approximately 12.5 mm by 12.5 mm by 3 mm and the conductivity was taken both parallel and orthogonal to the flow. Two opposing faces were coated with conductive silver paint according to Figure 3. Voltage was provided using a Keithley 2450 Source Measure Unit (SMU) in a
voltage sweep from 0 to 200 V and adjusted to a lower voltage to manage the circuit running through the segment. The volume resistivity and conductivity are calculated using equations [2] and [3] where $\rho_v$ is the volume resistivity, $R_v$ is the resistance from the source unit, $A$ is the cross sectional area of the diode surface, $t$ is the distance between diode surfaces, and $\sigma_v$ is the volume conductivity. The volume conductivity of each concentration is reported.

$$\rho_v = R_v \frac{A}{t} \quad [2]$$

$$\sigma_v = \frac{1}{\rho_v} \quad [3]$$

Figure 2. Depiction of electrical conductivity sample

Figure 3. (a) Orthogonal to flow (b) Parallel to flow
3.3.5 Sensor Performance

Sensor capability was tested on the 20G-PVDF films. The film was cut and affixed to a 35G-PEEK flexural specimen using a two-part silver epoxy. The prepared samples are shown in Figure 4. The specimen was loaded in a 3-point bend set up using an Instron 5982 universal testing system with a 1 kN load cell, simultaneously attached to a Keithley 2450 SMU. The SMU was set to voltage bias at 10 V and a current limit of 1 A, and the sample was cyclically loaded and unloaded to 20 N. The cycle involved loading to 20 N, a wait period, unloading to 0 N, and another wait period. This entire cycle took approximately 1 minute 30 seconds, approximately 30 seconds to reach the 20 N load, 30 second hold once the load is reached, instant de-load and manual force zero, and 30 second hold before the load is re-initiated. These samples were loaded over 35 cycles. This experiment is used to confirm the piezoelectric properties of our material.

Figure 4. (a) Top view of sensor testing specimen (b) Side view of sensor testing specimen
Chapter 4 Results and Discussion

4.1 Uniform shear mixing

During uniform shear melt-mixing, the degree of exfoliation is dependent on a few factors, such as the mixing time, RPM (and the resulting shear rate), the total volume (cc) of material added to the batch mixer, and the volume of each component (concentration). The RPM and volume capacity (cc) for each GNF concentration are graphed in Figure 5. The volume (measured in cc) added to the mixer for PVDF and graphite are labeled as V_PVDF and V_Graphite, respectively. In this study, the mixing time was constant at 90 min for 0, 5, 10, 20, and 30 wt. % GNFs in PVDF.

The volume of the polymer stayed fairly consistent throughout all of the concentrations, and the volume of the graphite slowly increased in accordance with the weight percent increase. Except for the 30G-PVDF sample, all compositions were mixed higher than 100 RPM. For 30G-PVDF, the RPMs were maintained much lower since the mixing machine power was at its maximum at only 15 RPM. Melt-mixing this high-volume concentration of graphite within PVDF and shear exfoliating graphite into GNFs increases the viscosity of the material and would require modifying the mixing machine to increase the power capability to avoid machine shutdown. The RPM produce a shear rate that is calculated from equation [4], where Δr is the gap between the rotor and barrel wall, and r is the radius of the rotor. The shear rates and RPM are listed in Table 5.

\[
shear \ rate = \left( \frac{RPM}{60} \right) \left( \frac{2\pi r}{\Delta r} \right)
\]

[4]
Figure 5. Processing parameters for 0, 5, 10, 20, and 30 wt. % GNFs in PVDF

Table 5. Calculated shear rates and RPM for all G-PVDF concentrations

<table>
<thead>
<tr>
<th>Composition</th>
<th>RPM</th>
<th>Shear Rate (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>150</td>
<td>1202</td>
</tr>
<tr>
<td>5G-PVDF</td>
<td>120</td>
<td>962</td>
</tr>
<tr>
<td>10G-PVDF</td>
<td>120</td>
<td>962</td>
</tr>
<tr>
<td>20G-PVDF</td>
<td>200</td>
<td>1603</td>
</tr>
<tr>
<td>30G-PVDF</td>
<td>15</td>
<td>120</td>
</tr>
</tbody>
</table>

Figure 6 shows a picture of injection molded specimens for 0, 5, 10, 20, and 30 wt. % GNFs in PVDF. Visually, the surface looks uniformly black for 5, 10, and 20 wt. % GNFs in PVDF, indicating good mixing and exfoliation of GNFs within PVDF. However, 30G-PVDF exhibits a speckled surface, indicating the presence of particulates large
enough to see with the eye. The lower RPMs achieved during batch mixing 30G-PVDF were too low to provide efficient graphite exfoliation into GNFs, and thus the degree of exfoliation is lower in 30G-PVDF (i.e., more layers within some GNFs). The 20G-PVDF showed just a few speckles on the surface, as well, which may be due to not enough polymer being added to the mixer and may also require a longer mixing time to provide a higher degree of exfoliation of graphite into consistent GNFs (i.e., a consistent number of layers within the GNFs).

Figure 6. Injection molded impact specimens: PVDF, 5G-PVDF, 10G-PVDF, 20G-PVDF, and 30G-PVDF (left to right)

4.2 Morphology of GNF Enhanced PVDF

The morphology of 5, 10, 20, and 30 wt. % GNFs in PVDF are shown in the SEM micrographs at low, medium, and high magnification in Figure 7, Figure 8, and Figure 9, respectively. At low magnification (1000x, 20 µm scale), images show that GNFs are well distributed within 5, 10, 20, and 30 wt. % GNFs in PVDF in Figure 7 (a, b, c, d), respectively. However, in the 30G-PVDF, various sized particles are visible with some larger diameter GNFs. This wider distribution in GNF size is due to the lower RPM used during processing, which induced lower shear strain rate and lower shear stresses. Thus,
graphite exfoliation into GNFs was less efficient in the 30G-PVDF sample. With increasing GNF concentration, the composite viscosity rises, requiring more power to mix. Modification of the batch mixer is needed to increase the power to allow for efficient exfoliation of high graphite concentrations.

At medium magnification (5000x, 10 μm scale), the GNFs appear oriented within the PVDF matrix for 5, 10, and 20 wt. % GNFs in PVDF, as seen in Figure 8 (a, b, c), respectively. The GNFs are aligned parallel to the flow direction. However, in the 30G-PVDF, the GNFs show some orientation and some random orientation, as well as some larger diameter GNFs. During shear exfoliation, graphite is exfoliated (i.e., graphene layers are sheared off from graphite) and these graphene layers fracture across the AB basal plane. For 30G-PVDF, fracture across the basal plane occurred less often than in lower GNF concentrations, as evidenced by some larger diameter GNF particles in Figure 8d.

At high magnification (20,000x, 20 μm scale), the particle-matrix interaction between GNFs and PVDF is visible in Figure 9. For all concentration, there is very good adhesion between GNF planar surfaces and PVDF matrix, as well as between visible GNF edges and PVDF matrix. There is some gap spacing between GNFs and PVDF, which is due to pull out during cold fracture used to prepare SEM specimens and not indicative of the morphology.
Figure 7. SEM micrographs of (a) 5G-PVDF, (b) 10G-PVDF, (c) 20G-PVDF, (d) 30G-PVDF at low magnification (20 μm scale)
Figure 8. SEM micrographs of (a) 5G-PVDF, (b) 10G-PVDF, (c) 20G-PVDF, (d) 30G-PVDF at medium magnification (10 μm scale)
4.3 Thermal Property Results

The first heating, cooling, and second heating curves for the G-PVDF compositions are shown in the Figure 10, Figure 11, and Figure 12, respectively. Table 6 lists the results for $T_m$, $\Delta H_f$, $X_c$, $T_c$, and $\Delta H_c$ based on the first heat, second heat, and cooling curves.

The melting temperature of PVDF is 170 °C, and ranges between 166 – 169 °C for 5, 10, 20, and 30 wt. % GNFs in PVDF. The lowest $T_m$ appears for 20G-PVDF at 166 °C and is 4 °C lower than PVDF alone, which may be due to an increased occurrence of surface crystallization of PVDF on newly created GNF surfaces (surface crystals are typically smaller than crystals formed in the bulk). Once the thermal history is erased, the second heat shows a nearly constant $T_m$ for all samples between 168 – 169 °C.
The crystallization temperature for PVDF is 142 °C and 150 °C for 5, 10, 30 and 30 wt. % GNFs in PVDF. Thus, the addition of GNFs to PVDF resulted in a crystallization temperature 8 °C higher compared with the PVDF alone but remains constant with all GNF concentrations. The GNFs likely acted as a nucleation site for crystal growth, which aided surface crystallization and resulted in a higher crystallization temperature26.

The heat of fusion is fairly constant for all concentrations and between the first and second heat, ranging between 30-33 J/g in the first heat and 31-33 J/g in the second heat. The heat of crystallization is also similar across all concentrations, ranging between 28-30 J/g. The calculated degree of crystallization is fairly constant for all concentrations for the first heat, second heat and cooling curve, ranging between 28.9-31.1%, 29.8-31%, and 26.8-30.1%, respectively. Nanoparticles within a crystallizing thermoplastic often act as a nucleation site for crystallization and provide the opportunity for surface crystallization of the polymer on the nanoparticle surface26. In the GNF-enhanced PVDF samples, the addition of GNFs do not appear to have a significant effect on the overall crystallization when heated and cooled at a rate of 10 °C/min. Further DSC experiments are required at various heating rates to potentially separate surface crystallization of PVDF occurring on the GNF surfaces from bulk crystallization of PVDF. Typically, surface crystallization results in smaller crystal size than those forming in the bulk, which causes surface crystals to melt at a lower temperature than larger bulk crystals.
Figure 10. First heating curve

Figure 11. Cooling curve
Figure 12. Second heating curve

Table 6. Thermal Properties measured from DSC

<table>
<thead>
<tr>
<th>% GNFs in PVDF</th>
<th>First Heat</th>
<th>Cooling</th>
<th>Second Heat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m^1$ (°C)</td>
<td>$\Delta H_f^1$ (J/g)</td>
<td>$X_c^a$ (%)</td>
</tr>
<tr>
<td>0</td>
<td>170</td>
<td>31</td>
<td>29.6</td>
</tr>
<tr>
<td>5</td>
<td>169</td>
<td>31</td>
<td>29.1</td>
</tr>
<tr>
<td>10</td>
<td>168</td>
<td>30</td>
<td>28.9</td>
</tr>
<tr>
<td>20</td>
<td>166</td>
<td>32</td>
<td>30.9</td>
</tr>
<tr>
<td>30</td>
<td>168</td>
<td>33</td>
<td>31.1</td>
</tr>
</tbody>
</table>

4.4 Mechanical Testing Results

4.4.1 Tensile Testing Results

The tensile mechanical property results for the G-PVDF composites are shown graphically in Figure 13 (a-b) and listed in Table 7. Stress-strain graphs are shown in Figure
13b and Figure 14, where Figure 13b is truncated to better compare the PVDF to the other composites, while Figure 14 goes until failure. As shown in Figure 13a, the tensile modulus increases linearly with GNF concentration up to 20G-PVDF, reaching a maximum of 8.60 GPa (556.5 % higher than PVDF alone). This significant increase in modulus is attributed to efficient graphite exfoliation into GNFs that are well-dispersed and uniformly distributed within PVDF with efficient stress transfer between GNFs and the matrix, as shown in the morphology images (Figure 7c, Figure 8c, Figure 9c). For 30G-PVDF, the modulus value is 7.91 GPa, which is below the linear trend. The red line shows the linear increase in average modulus from PVDF to 20G-PVDF and the theoretical value calculated for 30G-PVDF of 12.3 GPa. The experimentally determined modulus of 7.91 GPa is lower than the theoretical value likely due to the lower RPM used during processing (Table 5). Since the shear rate depends on RPM, the shear rate was lower for the 30G-PVDF sample, which resulted in less efficient graphite exfoliation (i.e., less efficient size reduction). The resulting GNF particles have a larger distribution in size, including thickness (number of graphene layers) and diameter, and thus the morphology is not optimal for the 30G-PVDF sample, as shown in Figure 7d and Figure 8d.

The stress-strain curves shown in Figure 13b show the stress at break increases with GNF concentration, but not as significantly as the increase in modulus. The stress at break for the 20G-PVDF is 60.5 MPa compared to the 37.0 MPa in the PVDF alone. A similar decrease is seen in the stress at break as in the modulus for the 30G-PVDF compared to the 20G-PVDF (53.7 MPa and 60.5 MPa). As shown in Figure 14, the elongation at break decreases with increasing GNF concentration, which is a similar result as fiber reinforced
polymer matrix composites\textsuperscript{27}. Intuitively, as the composite becomes more and more stiff, ductility tends to decrease.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figures.png}
\caption{(a) Tensile modulus of all G-PVDF concentrations (b) Stress-strain curve of all concentrations at region of interest}
\end{figure}

\begin{table}[h]
\centering
\caption{Mechanical properties of G-PVDF concentrations found from tensile testing}
\begin{tabular}{llll}
\% GNFs in PVDF & Strain at Break & Stress at Break & Modulus (GPa) \\
\hline
0 & 68.8 & 37.0 & 1.31 \\
5 & 17.6 & 10.4 & 3.24 \\
10 & 8.5 & 7.3 & 5.12 \\
20 & 3.5 & 60.5 & 8.60 \\
30 & 2.4 & 53.7 & 7.91 \\
\end{tabular}
\end{table}
4.4.2 Nanoindentation Results

The reduced modulus and hardness of 0, 5, 10, 20, and 30 wt. % GNFs in PVDF are shown in Figure 15 and Figure 16, respectively, and results summarized in Table 8.

The reduced modulus for PVDF is 3.3 GPa and increases with increasing GNF concentration up to 10 wt. % GNFs in PVDF with a maximum value of 4.5 GPa (36 % increase). However, the reduced modulus decreases for 20G-PVDF and 30G-PVDF below that of 10G-PVDF to 3.8 GPa and 4.1 GPa, respectively. As seen in the morphology images (Figure 7-Figure 9), the GNF distribution and dispersion is less uniform in the 20G-PVDF and 30G-PVDF samples, which may inhibit an increase in reduced modulus with increasing GNF concentration above 10 wt. % GNFs. Furthermore, the standard deviation increases as GNF concentration increases. Since nanoindentation is a surface test, any surface defects or inconsistencies can significantly affect results, and the composite samples may have a less uniform surface than PVDF alone due to the presence of the GNFs.
The enhancement with increasing GNF concentration in PVDF is much greater in the tensile modulus. For 10G-PVDF, there is a 291% and 36% increase in tensile modulus and reduced modulus, respectively. This suggests that the bulk stiffness measured during the tensile test is highly dependent on the adhesion and edge-covalent bonding between the GNFs and PVDF while the “surface” stiffness measured as the reduced modulus in nanoindentation is not as dependent on the particle-matrix interaction.

![Graph showing reduced modulus of G-PVDF concentrations](image)

**Figure 15. Reduced modulus found from nanoindentation of all G-PVDF concentrations**

The hardness results are displayed in Figure 16. There is a slight increase in hardness from PVDF to 5G-PVDF, and a decrease after that as GNF concentration increases. The hardness ranges from 140-215 MPa, with the 5G-PVDF having the highest hardness and the 30G-PVDF having the lowest hardness. The degree of exfoliation in the 20G-PVDF and especially in 30G-PVDF is lower (i.e., GNFs with a larger distribution in
the number of layers) than in 5G-PVDF and 10G-PVDF, as shown in the morphology images. During nanoindentation of the higher concentrations, the indenter may impact GNFs with a higher number of layers that are potentially sliding across each other during testing, resulting in lower hardness values and higher standard deviation. Hardness is also a surface measurement, which seems to obscure the reinforcing effect of the GNFs in the PVDF. A more effective test may be to use a larger diameter indenter to provide more consistent results.

**Figure 16.** Hardness found from nanoindentation of all G-PVDF concentrations
Table 8. Reduced modulus and hardness of G-PVDF samples found from nanoindentation

<table>
<thead>
<tr>
<th>% GNFs in PVDF</th>
<th>Reduced Modulus (GPa)</th>
<th>Hardness (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.3</td>
<td>194</td>
</tr>
<tr>
<td>5</td>
<td>3.8</td>
<td>215</td>
</tr>
<tr>
<td>10</td>
<td>4.5</td>
<td>212</td>
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<tr>
<td>20</td>
<td>3.8</td>
<td>170</td>
</tr>
<tr>
<td>30</td>
<td>4.1</td>
<td>140</td>
</tr>
</tbody>
</table>

4.5 Electrical Testing Results

4.5.1 Electrical Conductivity Results

Electrical conductivity was determined in two directions (parallel and orthogonal to flow) on the 10G-PVDF, 20G-PVDF, and 30G-PVDF samples. The electrical conductivity was not measured for samples with less than 10 wt. % GNFs, since 10G-PVDF displayed low conductivity. The electrical conductivity in the parallel and orthogonal directions are presented in Figure 17 and Figure 18, respectively, for which the electrical conductivity for all 3 segments is averaged for each GNF concentration and each direction.

In Figure 17a-b, the electrical conductivity in the parallel direction is shown. The 30G-PVDF has the highest conductivity on the order of $10^{-3}$ S/mm, which is comparable to the conductivity of other semiconductors (between silicon and germanium)\(^{28}\). The 10G-PVDF and 20G-PVDF have similar conductivities on the order of $10^{-7}$ S/mm, which is within the range of other semiconductors. These electrical conductivity values show that the G-PVDF composites have the capabilities to perform in place of other semiconductors where this order of electrical conductivity is required. The high conductivity in the parallel direction is likely due to GNF orientation, dispersion, and distribution. The GNFs are
aligned in the parallel to flow direction, providing a direct path for electron mobility and the current to travel. In Figure 17a, the 10G-PVDF is more conductive from 160 volts to 190 volts. This suggests that a more conductive path was found at the higher voltage. Future work can be done to optimize pathways for greater electron mobility. GNF with greater than 10 graphene layers seem to have the electronic properties of graphite instead of graphene\textsuperscript{16}, which suggests that in addition to wt. \% affecting the electrical conductivity, the degree of exfoliation will also have an effect.

Figure 17. (a) Electrical conductivity results for parallel test specimens on a logarithmic scale (b) Partial results for parallel test specimens

The electrical conductivity orthogonal to flow is presented in Figure 18. Both the 10G-PVDF and 20G-PVDF samples show a gradual increase in conductivity with the increase of voltage. The highest conductivity is seen in 30G-PVDF, with conductivities on the order of \(10^{-5}\) S/mm. In contrast, the 10G-PVDF and 20G-PVDF have volume
conductivities of $10^{-11}$ and $10^{-9}$ respectively, comparative to the conductivity seen in insulating materials$^{28}$.

Figure 18. (a) Electrical conductivity results orthogonal to flow for 10, 20, and 30 wt. % GNFs in PVDF (b) Region of interest from (a)

Electrical conductivity is directly correlated to GNF orientation, an isotropic property. The GNFs are oriented in the parallel direction; therefore, it is expected that electrical conductivity will be higher in the parallel to flow direction than in the orthogonal direction. All three of the concentrations had lower conductivity in the orthogonal direction. The 30G-PVDF performs on the order of $10^{-3}$ S/mm in the parallel direction and $10^{-5}$ S/mm in the orthogonal direction. These results confirm the importance of GNF orientation. However, the 30G-PVDF performs better than both other composites, which confirms GNF concentration also plays an important role in the electrical conductivity.

Figure 19a-c shows the electrical conductivity parallel to flow for the three segments tested along the length of the specimen for 10, 20 and 30 wt. % GNFs in PVDF. In all three concentrations, segment 2 was the most conductive, followed by segment 3, and segment 1 being the least conductive (segments are accordioning to Figure 2). This
suggests that the conductivity varies along the length of each specimen. Segment 2, which is the center of the gauge length has the highest conductivity. This suggests electrical mobility was optimized in the center of the specimen. Typically, composite morphology is optimized at the center along the specimen length, and flexural and tensile mechanical property testing is such that the forces are concentrated at the center of the specimen length. As the composite cooled in the mold, the variation in temperature along the specimen length and time in the mold may cause differences in PVDF crystallization. It seems that the morphology is optimized for highest electrical conductivity at the center of the specimen length, and least optimized where the material last entered the mold. These graphs also more clearly show electrical paths stayed consistent, resulting in consistent electrical conductivity readings. Figure 19a, displays the 10G-PVDF, which had a large variation indicating inconsistent consistency, likely due to its low conductivity. Whereas Figure 19b, displays the 20G-PVDF, the highest concentration of GNF with good mixing, resulting in very uniform results. Figure 19c, the 30G-PVDF, was much more conductive which led to more consistency in the reading, however, the large chunks left in the composite may have varied the path taken during testing, resulting in a non-linear trend.
Figure 19. Electrical conductivity parallel to flow for each segment along the length of the specimen (a) 10G-PVDF (b) 20G-PVDF (c) 30G-PVDF

4.5.2 Sensor Testing Results

The 20G-PVDF concentration was used in sensor testing due to the conductivity uniformity seen in Figure 19b and the highest optimized mechanical strength shown in Figure 13a. Two sensors composed of 20G-PVDF were fabricated and tested following the same loading and unloading cycles. Using the equation [5], the sensor data is normalized and graphed in Figure 20.
\[ z_t = \frac{x_t - \min(x)}{\max(x) - \min(x)} \] [5]

Figure 20 shows the sensor performance of 20G-PVDF with a cyclic change in resistance following the 35 loading/unloading cycles. The mechanically loaded specimen is represented by each trough in the resistance, while the unloaded specimen is represented by each crest. There seems to be a change in the sensor response which suggests the sensor can detect mechanical fatigue. The change in resistance is attributed to the distance between GNFs being altered when under tensile strain\(^\text{13}\). In future work, the change in resistance measured by the sensor can be compared to the change in strain measured on the sample being tested during cyclic loading to confirm the quantitative relationship between the two measurements.

![Figure 20. Normalized sensor data for 20G-PVDF](image-url)
Chapter 5 Conclusions

Uniform shear melt-mixing was used to exfoliate graphite into GNFs directly within PVDF to produce GNF reinforced PVDF composites in 0, 5, 10, 20, and 30 wt. % GNFs. During processing, the shear rate determined from the RPM induces sufficient shear stress to exfoliate graphite, create GNFs, and distribute the GNFs uniformly within PVDF. The proper shear rates required for efficient graphite exfoliation were achieved for all concentrations except 30G-PVDF, due to power limitation of the batch mixing machine. With increasing GNF concentration, viscosity of the composite rises and requires more power. The SEM micrographs show good GNF dispersion and exfoliation within PVDF in the lower concentrations and good particle-matrix interaction between GNFs and PVDF in all concentrations. Modification of the batch mixer to increase power would allow for efficient graphite exfoliation in higher GNF concentrations, as well.

The thermal results from the DSC indicate no major shifts in the T_m nor percent crystallinity with the increase of % GNF. The T_c for the PVDF alone is 8°C lower than all other G-PVDF concentrations. An increase in tensile modulus was found with an increase in % GNF. In the 20G-PVDF, the addition of GNF resulted in a modulus over 6 times greater than the PVDF alone. The nanoindentation results also indicate an increase in the reduced modulus with the increase of GNF in the lower concentrations. The electrical conductivity results show an increase in volume conductivity with the addition of GNF and a dependence on GNF orientation. Electrical conductivity is higher in the parallel to flow direction, since the GNFs are oriented along this direction and provide a more direct path for electron mobility (i.e., increasing electrical conductivity). The 30G-PVDF performed like a semiconductor in both the parallel and orthogonal directions. The sensor testing
confirmed the piezoelectric properties of the 20G-PVDF film and indicates a relation between mechanical and electrical interaction.

In future work, the in-situ shear exfoliation process must be optimized for high GNF concentration, thus providing more enhanced electrical conductivity and mechanical properties that are also consistent. Further optimization includes investigation of morphology, structure, and electrical conductivity along the specimen length. With these optimizations, in situ shear exfoliation of graphite into GNFs within PVDF has the potential to produce a commercially viable material with good mechanical properties, electrical conductivity, and piezoelectric properties (sensor performance).
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