RICE UNIVERSITY

Water Drop Tribology of Graphene and Polymer Nanocomposites

by

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ABSTRACT

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Basic physics teaches us that the frictional force (lateral force) needed to move objects on surfaces are proportional to load (normal force) – Amonton’s Laws. In tribology, this force is proportional to contact area, whereas Amonton is just a special case for contact area scaling with load. Such established laws do not seem to apply to small drops on flat, smooth surfaces in which frictional forces have an inverse relation to contact area and have time component prior to movement. Such phenomena can be explained by Shanahan-deGennes were intermolecular forces are considered for a deformed surface. Graphene is a special case where no time component is observed and frictional forces are attributed to its chemical homogeneity and stability. In the second part of this thesis, graphene is considered as nanofiller to build up polymer nanocomposites via Layer by Layer (LbL). Graphene Nanoribbons derived from multi-walled carbon nanotubes (MWCNT) offers a special case for thermoplastic polyurethane nanocomposites in that of thermally activated twisting morphology influences nanocomposite properties. Finally an electric field driven transdermal hydrogel drug delivery device has been demonstrated by just using CNTs, polyvinyl-borax gel and a CNT membrane.
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Chapter 1

Introduction

1.1. Carbon Nanomaterials

Carbon is a fascinating and versatile material. Without it, living systems could not exist (except for outlandish alternative biochemistry theories). We use carbon every day in our lives from the strands of fabrics we wear to the liquids we cook and keep warm. All ecosystems depend on this four valence electron element to convert matter into energy and vice versa. As the 15\textsuperscript{th} most abundant element on earth, it has three well known solid allotropes: amorphous carbon, diamond, and graphite and harnessed these allotropes into heat generation, jewelry, and pencil writing. There are even specialized branches of science such as organic chemistry which studies the reactions of carbon-based molecules. Another is metallurgy, which found by adding small amounts of carbon results in steel – the staple of modern structures. Though used since prehistory, it was not until the seventeenth
century carbon was given serious investigation. The last century, carbon fibers were introduced and employed as loading bearing materials. The applications of polymer chemistry (a natural extension of organic chemistry) make use of many chains of carbon atoms bonded to one another. The last three decades have seen new carbon allotropes (figure 1:1) in fullerenes\textsuperscript{1}, carbon nanotubes (CNTs)\textsuperscript{2}, and graphene\textsuperscript{3} have attracted vast amount of research into their physical and chemical properties for future technological applications. This thesis focuses on two of the three allotropes, CNTs and graphene, for possible technological applications.

\textbf{Figure 1:1 Carbon fullerenes, nanotubes, and graphene\textsuperscript{4}.}
1.1.1. Carbon Nanotubes

The typical way carbon nanotubes (CNTs) are introduced in literature (even in theses) is to cite Iijima’s paper in 1991 and extol upon the overly hyped properties CNTs have. I see no reason to break tradition here. CNTs are sp² hybrid bonded carbon atoms arranged in hallow, cylindrical structure with the ends capped in half sphere shapes also made of the same element and bond type. Diameters range from sub-nano to nanometers and nano to centimeter lengths with aspect ratios ranging from 45:1 to over 100,000,000:1. CNTs mostly come in two different flavors (figure 1:2a): Single Walled CNTs (SWNTs) and Multi-Walled CNTs (MWNTs). Depending on their chirality, CNTs can be either semiconducting or metallic in electrical nature. This is distinguished structurally by indexing (figure 1:2b) the pair of indices (n, m) where n and m are whole integers of the unit vectors along two directions in the honeycomb crystal lattice of CNTs. If m = 0, then CNTs are called zigzag and if n = m then armchair; otherwise they are chiral (figure
1:2c). Armchairs are usually metallic and zigzag are semiconducting.

Figure 1:2 Schematic of (a) graphite with structural relation to SWNT, and MWNT; (b) crystalgraphic basis of CNTs; and (c) three different structures of CNTs.

In the absence of structural defects, CNTs have a Young's Modulus estimated from 270 to 950 GPa and tensile strength 11 to 63 GPa. These numbers originate from the strong sp² bonds among the carbon atoms, 2D symmetry, and absence of slip planes and directions. These figures have been the impetus of applications in next generation composite materials and the fabled “space elevator”. Strong,
conductive CNTs spun fibers has been demonstrated but with the use of toxic super acids and expensive machinery\textsuperscript{11}. Armchair or metallic CNTs have an electrical conductivity 1,000 times higher than copper, suggesting CNTs could find applications in electrical wiring and power cables\textsuperscript{12}. Zigzag or semiconductor CNTs have been fabricated in electrical devices such as transistors\textsuperscript{13}, solar cells\textsuperscript{14}, and other energy harvesting devices\textsuperscript{15}. The electrons along the CNT axis exhibit ballistic conduction, meaning that electrons hardly lose any energy due to low or any scattering events. CNTs have a thermal conductivity (across axis) of 3500 Wm\textsuperscript{-1} K\textsuperscript{-1} and 1.52 Wm\textsuperscript{-1} K\textsuperscript{-1} (radial)\textsuperscript{16}. Compared to copper which only have 385 Wm\textsuperscript{-1} K\textsuperscript{-1} makes CNTs attractive in heat sink applications\textsuperscript{17}. All these properties are highly dependent on CNTs being clean of any structural defects or impurities\textsuperscript{18}. 
Figure 1: General schematic of (a) CNT CVD growth reactor, (b)-(c) two proposed growth mechanisms, and (c) microscopy images of CNTs. 

Arc discharge and laser ablation have been used to make CNTs in the past with mediocre to moderate yields and quality. But the most economical and
therefore practical CNT fabrication is Chemical Vapor Deposition (CVD) using hydrocarbon gas and metal catalysts (figure 1:3a). In brief, metal nanoparticles (NP) of iron or some other transition metal are immobilized in a flat substrate (100-200 µm oxide on Si wafer) and heated to several hundred degrees. Two types of gases are then bled into the CVD chamber in a controlled manner: a carrier gas (hydrogen or argon) and a carbon rich gas (methane, ethylene). The two gases mix and react at the surface of the metal nanoparticles, forming CNTs. Much of CNT quality and type (zigzag, armchair) depend on the metal NP surface such as crystal plane, size, and morphology. Defects or impurities on the metal NPs could carry into CNTs during growth (figure 1:3b). Though not fully understood, advances have been done into CVD growth systems that can discriminate between semiconducting or metallic CNTs (figure 1:3c). CNT sponges, graphene-CNT hybrids, and fullerene-CNT hybrids have been created via CVD.

Among the issues holding back CNT applications are CNT toxicity to humans, though studies are ongoing to understand how it affects cellular mechanisms. Another major drawback are separating and dispersing CNTs at the molecular level. Depending on application, current methods for separating CNTs by size and chiral type can be laborious and even damage CNTs. CNTs tend to aggregate due to strong Vander Waals interactions and small sizes. This makes composite processing quite challenging since any property enhancement hinges on excellent dispersion. Few protocols exist such as acid treatment, sonication, or surfactant wrapping. Acid treatment attacks the alkene groups on CNTs imparts oxygen-bearing functional groups along the side walls and strained bonds but also induces
defects and partial loss of sp² bonding to sp³, resulting in decreased electrical and mechanical property. In fact any type of functionalization will reduce the physical properties of CNTs. However, interesting functional chemistry has been done exploiting this feature and most of the bond strain energy is at the end caps which lends itself to chemical attack first²⁹. Super acids have been demonstrated to disperse CNTs making this the first true solvent for CNT-composite processing, but super acids are extremely reactive and toxic³⁰. Sonication can breakup individual CNTs but the effect is not permanent³¹. Surfactant can disperse CNTs Hydrogels can disperse CNTs because of the complex 3D polymer structure entrapping individual tubes.³²

1.1.2. Graphene

Same deal as with CNTs in section 1.1.1; state the hyped up properties of graphene and fantasize on applications that will most likely not happen. Only this time literature usually cites Geim and Novoselov’s 2004 work; got a 2010 Nobel Prize³³ and everyone is spending lots of money on empty promises. Graphene is a single layer of two dimensional sp² hybridized bonding aromatic allotrope of carbon arranged in a hexagonal pattern (figure 1:4a). This can be visualized as a one atom thick chicken wire with carbon-carbon bond lengths at 0.142 nm, interlayer bond energy of 2.5 eV/nm², and interplanar spacing of 0.335 nm³⁴. This high interlayer bond energy is due to the stack-layered nature of graphite (figure 1:4b), high surface area of individual graphene sheets, and weak Vander Waals forces between them. Just as with CNTs, these properties make graphene to isolate into individual sheets
challenging. To mechanically separate individual sheets a large amount of mechanical force of \( \sim 300 \text{ nN/\mu m}^2 \) is required\(^3\). Graphene is the basic constituent of graphite, where sheets of graphene are stacked together and held in place by Vander Waals forces. Graphene's primitive unit cell (figure 1:4c) of is composed of two non-equivalent atoms, which span two sub lattices that are translated from each other by lattice constant of 0.14 nm\(^3\). This is due to graphene's carbon–carbon bonds which are hybridized orbitals generated by the superposition of its 2s with 2p\(x\) and 2p\(y\) orbitals. These planar orbitals form the thermodynamically stable and covalent localized \( \sigma \)-bonds with its three nearest-neighbor atoms in the hexagonal lattice, and are responsible for most of the binding energy and for the mechanical properties of the graphene layer. The orbital left over, 2p\(z\), are unhybridized and span a \( \pi \) symmetry configuration and overlap of these orbital states between near neighboring atoms plays a major role in graphene's electronic properties (figure 1:4d).
A simple molecule, however, graphene hosts a plethora of exotic properties such as charge carriers with Fermi velocities close to the speed of light with the implication of a table top model to study quantum electrodynamics phenomena, an
area of science formerly restricted to high energy particle physics\textsuperscript{38}. A single isolated sheet of graphene has electron mobility at room temperature to be over 10,000 cm\textsuperscript{2}V\textsuperscript{−1}s\textsuperscript{−1} with holes nearly that same value\textsuperscript{39}. Graphene has a lower room temperature resistivity than that of silver\textsuperscript{40}. This value only seems to be limited by basal plane defects, phonon scattering at the edges, and the substrate graphene is on\textsuperscript{41}. Graphene is a semi-metal or zero bandgap semiconductors with Dirac-like fermion electrons\textsuperscript{42}. This places graphene as a possible material for future solar cells\textsuperscript{43}, transistors\textsuperscript{44}, electrodes\textsuperscript{45}, and displays\textsuperscript{46}. At room temperature, the thermal conductivity of single-layer graphene is estimated at $\sim 5.30 \times 10^3$ Wm\textsuperscript{−1}K\textsuperscript{−1} which is higher than that of carbon nanotubes. According to the Wiedemann–Franz law, graphene’s thermal conductivity is acoustic phonon mode dominated. Just like in carbon nanotubes, the absence of surface defects, the Umklapp Process suppression is attributed to graphene’s high thermal conductivity value and scales as the number of layers is reduced\textsuperscript{48}. Unlike CNTs, the ballistic thermal conductivity of graphene is isotropic; meaning that transport is the same no matter the direction. Unfortunately, supported substrates also effects thermal conductivity where phonons seep out across the interface and all phonon (optical, acoustic) modes scatter strongly.

Thermal conductivity of graphene on SiO\textsubscript{2} substrate has been reported at 600 Wm\textsuperscript{−1}K\textsuperscript{−1} at room temperature\textsuperscript{39}, but it is still higher than copper. With these exceptional thermal management properties, graphene is seriously considered for CPU heat sinks.

Graphene is considered one of the strongest known materials. The following mechanical properties of graphene are: breaking strength of 42 N/m, intrinsic
mechanical strain of ~ 25%, and in-plane Young’s modulus estimated over at E ~ 1.0 TPa\textsuperscript{49}. These experimental numbers have been confirmed by several theoretical simulations. These mechanical properties of graphene make them light, stiff, and flexible materials – suitable candidates for nanoelectromechanical systems (NEMS). In a similar vein to strained silicon for bandgap engineering, graphene’s electrical properties can be altered by small strains from external forces. This brings up the application of using graphene-based MEMS and NEMS for resonator and pressure sensor devices. Graphene Nanoribbons (high aspect ratio graphene strips) show a similar pattern when strained along the ribbon direction. GNRs experience metal–semiconductor transitions as mechanical at ~ 0.1% strain\textsuperscript{50}, and for zigzag show a more pronounced response. Interestingly, defect engineering (intentionally inducing defects) of graphene has been shown to alter both mechanical and electronic properties just like silicon and other electronic materials.

Graphene has an estimated specific surface area of over 2600 m\textsuperscript{2}g\textsuperscript{-1} making it a great candidate to immobilize catalyst particles, composites, and drug delivery systems\textsuperscript{51}. The optical transmittance is measured at ~98% (for a single sheet) making it very attractive for transparent electronic devices\textsuperscript{52}. Since graphene is an atomically smooth surface its tribology had proven very interesting in friction studies and the origin of heat dissipation when sliding across a surface behaves. Investigating how Graphene’s surface responds to dynamic conditions (such as liquid drops sliding across its surface) that have implications for nanofluidics\textsuperscript{53} and Lab on Chip (LoC) devices. The edges of graphene have mixed sp\textsuperscript{2}/sp\textsuperscript{3} bonding features which in itself has interesting chemistry and tribology\textsuperscript{54}.
Despite the exotic properties of graphene, manipulation of their physical features for technological applications is lacking. The deficiency of an electronic band gap greatly restricts its role in logic devices. Strategies have been developed to induce a band gap in graphene which include chemical doping, interaction on different substrates, and application of mechanical forces or external electromagnetic fields. Stacking of graphene layers to form bi-layers, tri-layers or even stacked graphite structures seems like a strategy for band gap opening. Semiconductor lithography has been employed to fabricate large graphene sheets into smaller, nano-scale ones that can induce lateral confinement of charge carriers, resulting in strips of graphene - graphene nano-ribbons (GNR). Cutting graphene this way leads to the energy band-gap scaling inversely with the width. These GNRs can also be synthesized by unzipping of carbon nanotubes by liquid chemical acid or gas-plasma combination treatment. Just like CNTs, defects and impurities also compromise graphene’s physical properties; developing fabrication techniques that limit or eliminate these defects while achieving high yield is needed for applications. Top-down and bottom-up techniques have been established for graphene synthesis with varying degrees of graphene quality and yield. Among them are: mechanical cleaving exfoliation, chemical exfoliation, chemical synthesis, and chemical vapor deposition. A flow chart diagram of all graphene synthesis is shown in figure 1.
Figure 1:5 Different processes used to make GO from graphite\textsuperscript{58}.

The first demonstration of single and few layer graphene property from graphite was in 2004 by Novoselov and Geim, where adhesive tape was used to exfoliate graphite into graphene layers on silicon wafer substrates known as the Scotch Tape Method\textsuperscript{59}. Why they got the Nobel on this is beyond me since graphene’s properties have been known since the 1960s. In brief, the experiment entailed plasma etching highly ordered pyrolytic graphite (HOPG) down to 1 mm and pressed it against polymer photoresist followed by baking. Then with Scotch Tape, by hand, gently applied the tape to the exposed HOPG surface and slowly
peeled away. Individual flakes of graphite were stuck to the tape and were put into an acetone solution; dissolving the tape and releasing the flakes floating on the surface. From the acetone solution, the graphene sheets were transferred to n-type silicon on insulator (SOI) wafer and followed by water-alcohol workup. This was the first time graphene was made into logic devices and electrically characterized. Though mechanical exfoliation method does a great job at exfoliating single layers of graphene, the process is laborious and results are not always reproducible. Wafer-sized graphene is limited due to the size of the precursor materials used.

Chemical intercalination of graphite is process where graphite is solution dispersed and exfoliated by inserting large ionic species between the graphite layers. Like mechanical exfoliation, chemical intercalating is another mechanical way to convert graphite into graphene. Unlike mechanical exfoliation, chemical intercalating uses ionic forces and atomic sizes to infiltrate and force open graphite’s stack layers into single sheets. The only class of materials that can go in-between this interlayer distance are alkali metals and their alloys which form ionic species in solution and have a small enough ionic radius and ionization potentials. Once in, the number and ionic forces are strong enough to overcome the Vander Waals forces; expanding the stack-layers to a point where a few-layer graphene can disperse in solution. This intercalated compound experiences an exothermic reaction when it reacts with the solution, leading hydrogen generation, which separates the graphitic layers. Finally, the resultant single and few-layer exfoliated graphene are filtered and followed by aqueous workup. Other alkali systems have been demonstrated to operate at room temperature and pressure – making this type
of processing very attractive. One major drawback is the use of such small alkali metal ions which are detrimental to electronic devices unless measures are taken to remove them\textsuperscript{63}. Yield still remains low and the reaction requires inert, moisture-free atmospheres.

One popular way to make graphene from graphite powder is mixing it in a heated solution of oxidants and acids and stirring it for a few hours\textsuperscript{64}. The graphite in this protocol undergoes a chemical exfoliation process similar to the aforementioned process. Unlike aforementioned process, it dramatically alters the chemical and physical properties of graphite in such a way that popular opinion has named this form graphite as graphene oxide or graphite oxide (GO). This process attacks the alkene character of graphite and imparts functional groups upon graphite such as epoxy, carbonyl, carboxyl, ketones, lactones, hydroxyl, and phenol groups at sheet edges and basal planes as well as structural defects from the acid-oxidant cocktail\textsuperscript{65}. In a way, this process is similar to acidic treatment of CNTs. These functional groups and defects disrupt the aromatic character of graphite by partial rehybridizing sp\textsuperscript{2} bonding to sp\textsuperscript{3}. With 3-D bonding instead of 2-D, these results in graphene adopting a non-planar morphology. Because of this breaking up of the π carbon conjugation system and structural defects, GO sheets are insulators with high oxygen-carbon ratios (O: C). The highly polar functional groups render the material hydrophilic and attract water molecules, which further intercalation of the interlayer spacing. The exact chemical structure of GO has remained ambiguous at present due to non-stoichiometric composition, protocol type, and starting graphite material quality. Though still debatable, the Lerf-Klinowski model\textsuperscript{66} (from
spectroscopy and microscopy of GO) is the popular visual schematic of the structure of GO (figure 1:6a, b). Because GO is hydrophilic, it can be readily dispersed in a wide variety of polar aprotic organic solvents and form stable suspensions for weeks (figure 1:6c). This makes GO very attractive in a variety of solution-based fabrication methods. GO’s functional groups offer many reactive sites for intelligent covalent or non-covalent functionalization resulting versatile strategy for composite fabrication.
There are several protocols for GO synthesis have been used: Brodie, Staudenmaier, and Hummers. All three protocols involve oxidation of flake graphite using strong acids and oxidants but vary in acid type, amount, and yield. The Brodie protocol involved mixing oxidizing agent potassium chlorate (KClO₃) to slurry of flake graphite in fuming nitric acid. Nitric acid reacts strongly with aromatic carbon materials including CNTs which result in oxygen-containing
functionalities (carbonyls, ketones, etc.). This reaction is dangerous since KClO₃ is a commonly used for blasting caps for dynamite and there have been fatalities using this method. Studenmaier improved on Brodie’s work by adding KClO₃ in controlled aliquots over the course of the reaction and adding concentrated sulfuric acid (H₂SO₄) to reduce the amount of damage to graphite. Though similar degrees of oxidation (C: O~2:1) as Brodie, the Studenmaier can be just as dangerous as the reaction produces ClO₂ toxic gas and can decompose explosively⁷⁰. Hummers developed a much safer and shorter protocol for fabricating GO by mixing flake graphite with potassium permanganate (KMnO₄) and sulfuric acid (H₂SO₄). Though there are variations to the Hummers protocol, the active species bimetallic dimanganeseheptoxide (Mn₂O₇)⁷¹ oxidizes the alkene bonds over aromatic double bonds in graphite. In addition to being safer, Hummers protocol has the largest interlayer distance and less graphite damage (i.e. holes).

Like CNTs, GO can be functionalized with a variety of different chemical groups using well-established organic chemistry reactions. Covalent functionalization has been demonstrated in all four methods: nucleophile substitution⁷², electrophilic addition⁷³, condensation, and elimination⁷⁴. Epoxy groups on the basal planes can be modified by ring opening reactions under various conditions such as amines attacking alpha carbons. The carboxylic acid group of GO can be used in coupling reactions to amides and esters on GO⁷⁵. The hydroxyl group reaction of GO with diisocyanates results in isocyanate-modified GO that can be used in polymerization reactions. Interestingly, polymerization reactions such as grafting approaches have been used to graphene with polymer chains tethered to
them\textsuperscript{76}. Non-covalent functionalizations that operate electrostatic or hydrogen bonding physical adsorption of molecules on GO sheets such as polymer wrapping\textsuperscript{77}, diazonium salts\textsuperscript{78}, surfactants\textsuperscript{79}, small chain aromatics\textsuperscript{80}, and even biomolecules\textsuperscript{81}. In other words, almost all the work done with respect to CNT functionalization has been applied to graphene oxide functionalization.

![Figure 1:7 Chemical reduction of (a) GO to RGO and (b) proposed mechanism\textsuperscript{82}.](image)

GO can be reduced to a graphene-like state similar to the properties of pristine graphene by removing the hydrophilic functional groups by reducing agents; turning GO back to hydrophobic graphene-like compounds. Just as the properties of GO are different from pristine graphene, so is the reduction of GO which is why it is called reduced graphene oxide (RGO) in literature. Reduction by chemical means include three main reducing agents: hydrazine monohydrate ($\text{N}_2\text{H}_4$), lithium aluminum hydride (LAH), and sodium borohydride (NaBH$_4$) in aqueous suspensions of GO shown in figure 1:7a. All three are known to remove most of GO’s oxygen functionalities with variance in selectivity and restore the graphitic $\pi$-network back to its planar morphology\textsuperscript{83}. LAH reacts too strongly with
water and therefore is not commonly used. \( \text{N}_2\text{H}_4 \) is the most studied reducing agent for GO and proposed scheme is illustrated in figure 1:7b for epoxide to alkene reduction\(^8^4\). Nitrogen can be covalently bound to carbon which can alter the electronic properties of RGO; functioning as an n-type dopant. Whether this is a help or hindrance depends on application. \( \text{NaBH}_4 \) is a slower reaction, reacts slower to water and is selective to carbonyls but does not dope RGO\(^8^5\). Thermal reduction is another method to make RGO by rapidly heating GO in heating furnaces, microwaves, or laser sources\(^8^6\). Though this process avoids dangerous chemicals, gas pressures evolved from oxygen functional group degradation damage RGO and significant loss of mass limits the scalability. Though few functional groups are present in hydrophobic RGO, functionalization is still possible via \( \pi - \pi \) or Vander Waals interactions and physical adsorption of polymers or other diazonium salts\(^4^9\).

Because RGO is similar to pristine graphene, it will collapse out of solution and aggregate when it can unless surfactants are used to re-disperse RGO. In low concentrations of \((0.5 \text{ mg ml}^{-1})\), RGO sheets under basic conditions (pH>8) can be electrostatically stabilized due to the few remaining functional groups\(^8^7\). One experiment made use of negative surface charges in GO sheets from carboxylic acid and phenolic hydroxyl groups form a stable suspension when reduced by hydrazine in the presence of ammonia. A drawback in using oxidizing acidic solutions is the physical breaking up flake graphite into smaller sheets and the introduction of defects (i.e. holes)\(^8^8\). Therefore, products of GO and RGO sheet sizes will always be smaller than the precursor flake graphite. Since holes are introduced, no amount of reducing protocols can repair this defect; and RGO will never attain the same
properties as pristine graphene\textsuperscript{37}.

The most practical graphene synthesis for pristine, electronic grade devices is chemical vapor deposition (CVD). CVD is a bottom-up chemical process by which a substrate is exposed to thermally decomposed liquid or gas precursors and deposited onto the substrate surface at high temperatures in low or ambient pressures. A generic schematic is shown in figure 1:8a. Earliest CVD experiments date back to 1975 on the deposition of graphitic materials on platinum (Pt) by CVD from the decomposition of ethylene (C\textsubscript{2}H\textsubscript{4})\textsuperscript{89}. Since then, other transition metals have been investigated with Ni and Cu having the advantage of cost and ability to wet chemical etch away substrates leaving graphene intact\textsuperscript{90}.

Figure 1:8 Schematic of (a) CVD graphene and (b) growth mechanics\textsuperscript{91}.

Large, single layer graphene has been grown using a mixture of methane and hydrogen gas on Cu foils at 1000°C (figure 1:8b). One technique used solid poly-
methyl methacrylate (PMMA) as a carbon source with ethanol vapor and argon plasma was successful in making graphene\textsuperscript{91}. Another CVD technique made possible roll-to-roll production by a combination of dry transfer printing and wet-chemical etching of mostly single layer, 30-in. graphene films on flexible copper substrates\textsuperscript{74}. Interestingly, cookies, chocolate, grass, plastics, roaches, and even dog feces have been used as carbon sources to make high quality CVD grown graphene. As with CNTs, the catalyst directs graphene yield and quality. Also, just like all transition metal catalysts, the catalytic power is a strong function of d-orbitals and crystalline feature\textsuperscript{92}. For Ni, graphene forms by surface segregation and precipitation on (111) orientated Ni. For Cu, surface adsorption on (111) orientated Cu. This is due in part to the closed and open d-band orbitals at the Fermi Level for Cu and Ni respectively. From metallurgical phase diagrams, it is known that carbon solubility in transition metals is a function of temperature and formation of metastable phases such as Ni$_3$C which promotes carbon precipitation. Ni has higher carbon solubility than Cu resulting in C, Ni atom exchange near the surface\textsuperscript{93}. Upon cooling, the carbon diffuses out, segregates, and precipitates at the Ni surface forming graphene. Since diffusion is faster at grain boundaries, more graphene layers at the grain boundary as compared to intra-crystalline domain regions\textsuperscript{59}. In addition to grain boundaries, edges and steps of the substrates can act as nucleation sites for graphene growth. Graphene has been determined it forms monolayer and bilayer sheets on the single crystal Ni surface due to its atomically smooth surface and the absence of grain boundaries. However, polycrystalline Ni can lead to the formation of few-layer graphene (> 2 layers)\textsuperscript{36}. Another experiment used dislocations and grain boundaries
in Cu thin films to direct C atoms to the Cu-dielectric interface and form graphene. In contrast to Ni, Cu does not form any metastable phases as the C-Cu solubility is too low; therefore, all carbon atoms are adsorbed, nucleated and graphene growth propagation steps are all at the surface. Longer reaction times allow for full coverage and once the surface is fully covered with graphene, the growth process terminates\textsuperscript{94}. Transfer of graphene sheets from metal catalysts to other substrates is a project on of its own. This transfer invariably damages the film in the form of cracks, ripples, and kinks resulting in lower surface area and roughness; and therefore lower electrical property via scattering events\textsuperscript{95}. In one typical method, polymethylmethacrylate (PMMA) is spin cast onto graphene, and then wet etched to remove the Cu substrate. Some transfer-free methods have been developed with graphene grown directly onto insulators. In one process, deposition of Cu 100 nm thin film on dielectric substrates was done by e-beam evaporation with subsequent CVD-grown graphene onto the Cu film. Then, the Cu film is de-wetted and evaporated from the surface by sublimation. Therefore, direct synthesis of graphene on dielectric substrates bypasses the post synthesis graphene transfer process, hence avoiding the inclusion of defects and contamination in graphene\textsuperscript{86}.

### 1.2. Polymer Nanocomposites

Polymers are chemically and physically distinct from the other classes of materials. The word polymer is derived from the Greek words, “poly” and “meros” meaning many parts, first coined by Jonas Berzelius in 1833\textsuperscript{96}. Though basic understanding of polymers was not realized until a century later; humans have been
using polymers in the form of silk, cotton, and rubber. Most scientists thought polymers were large aggregates of small molecules similar to colloids held together by some type of secondary attractive force. This misconception was laid to rest when in 1920 Hermann Staudinger put forth the idea that polymers were long chains of repeating chemical structural units held together by covalent bonds and weak forces (Vander Waals) between these chains. This idea, along with advances in organic chemistry, led to rapid development of polymer science to where designing at the molecular level is commonplace. Polymers can linear – long chains with high degrees of polymerization or branched – where polymer chains attached to main, longer chains or cross-linked where individual chains bonded to one another, creating a rigid, three-dimensional network such as epoxies and gels. Polymers can be made from two or more different monomers reacted together and can be distributed randomly (random copolymers) or in structured sequences (block copolymers) with distinct physical properties.

One of the most important and unique properties of polymers are glass transition temperature (T_g). A glass is an amorphous solid, meaning it has no long-range order or symmetry in its packing of molecules or atoms. Glasses resemble liquids at standard temperature and pressure in this regard as liquids have no long-range order. However, a glass is not a solid but does not flow over observable human timescales. All polymers are amorphous due to their large chain-like structure. Very few can crystallize but not fully and are called semi-crystalline. As a solid polymer is cooled, the molecular relaxation times of the chains decrease and density increases; the space between chains or free volume decreases. As this
happens, chain movement will be so sluggish that thermodynamic equilibrium packing of the chains cannot be attained and has now undergone what is called a glass transition; from soft, rubbery state to a hard, glassy state (figure 1:9). Knowing this value is critical as the reason for the 1986 Space Shuttle Challenger Incident was due to rubber O-rings used below its $T_g$.

Figure 1:9 $T_g$ as a function of temperature and morphology.

Polymer nanocomposites are an active research field for exotic properties not achieved by any type monomer manipulation or polymerization. A composite material is a material composed of two or more constituent materials having physically or chemically different properties yet remain in separate, discrete parts distinguishable at small scales. One part of the composite is called the matrix
material is the larger material by mass or volume. Within this matrix lies the other constituent material called the filler. Usually the filler is in the shape of a particulate, fibrous, or laminate at smaller length scales and concentrations than the matrix. Both size and shape of the filler influence at least one of the matrix materials properties. A nanocomposite is a composite with at least one constituent material in the 1 to 100 nm length scale called nanofillers. What makes nanocomposites attractive is their high surface area, which enhances filler-matrix interactions, therefore, lower filler loading compared to traditional composites. A successful nanocomposite will have synergetic properties derived from its constituent materials only if the nanofiller is uniformly dispersed within the matrix and a strong, stable interface forms between the nanofiller and matrix exists.
When nanofiller particles approach the radius of gyration, $R_g$, of the polymer, the local conformation is changed. This influence is manifested in modified tensile strength$^{104}$, $T_g$ $^{105}$, solvent resistance$^{106}$, barrier$^{107}$, electrical-thermal conductivity$^{108}$, and flame retardant properties$^{109}$. The phase is composed of matrix material, but physically modified by the close proximity to the nanofiller behaves so differently that it is considered a separate phase – the interphase phase$^{110}$. This is the main reason why predicting nanocomposite properties often fail$^{111}$. Another unusual property of polymer nanocomposites (figure 1:11) is when the concentration of...
nanofillers approaches a critical threshold called the Percolation Threshold\textsuperscript{112} (PT). At PT, nanofillers are near or at physical contact within the nanocomposite and a network are formed. Depending on the electronic state of the nanofiller, very high conductivities (thermal, electrical, gas barrier)\textsuperscript{113} can be observed in an otherwise poor conductor matrix material. \textsuperscript{114}

\textbf{Figure 1:12 (a) conventional, (b) intercalciated, (c) completely exfoilated polymer nanocomposite\textsuperscript{115}}.

Unfortunately, all types of polymer nanocomposites suffer any practical application as nanofillers have the tendency to self-aggregate (during or post-processing) due to their high surface area and Vander Waals forces between them\textsuperscript{116}. This has not been the problem with conventional polymer composites (figure 1:12a) since fillers are at the macroscale and property enhancement was simple – just add enough filler. For nanocomposites, usually intercalated configuration is the best attainable (figure 1:12b) by sonication and functionalization. However, as mentioned before, functionalization can damage nanofillers and in some instances, even sonication\textsuperscript{117}. The most ideal configuration is figure 1:12c where the nanofiller are dispersed uniformly throughout the polymer
nanocomposite. Though this configuration is usually difficult and expensive to attain, polymer nanocomposites have been made into gels\textsuperscript{118}, thin films\textsuperscript{119}, foams\textsuperscript{120}, and fibers\textsuperscript{121}.

### 1.2.1. Graphene-based Nanocomposites

Graphene-based polymer nanocomposites offer unique property reinforcement that other fillers do not have. Often considered the carbon cousins of exfoliated clays\textsuperscript{122} based on their size and morphology, graphene-based nanofillers have reactive handles not available in exfoliated clays or pristine CNTs. This makes it relatively easy to functionalize them with a number of well-established chemistries and descent dispersion. Compared to either CNTs or exfoliated clay, graphene has a higher surface area and tensile strength. The barrier properties are expected to be better; sheet vs. rod morphology\textsuperscript{123}, as a sheet would have a higher torturous path for gas molecules to travel through. In addition, the electrical conductivity is higher than CNTs. When reaching the percolation threshold, this could lead to conductive, strong, gas barrier thin film polymer nanocomposites.

Graphene-based nanofillers, just like any nanofiller, suffer from the same problems: dispersion and lack of wetting the matrix polymer. The large surface area to volume ratio of and Vander Waals forces make it relatively easy for graphene-based nanofillers to aggregate into clusters during nanocomposite fabrication. Surfactants (ionic or non-ionic) can wrap around nanofillers to disperse them by physical adsorption but hard to remove after polymer mixing. Ultrasonication is commonly used but sometimes the high frequency sound waves breaks up the nanofillers and
can even lead to damage\textsuperscript{124}. Polymer melt extrusion can destroy agglomerate density by high shear intensity but high shear rates could damage nanofillers and even polymer matrix. Surface functionalization has been largely successful at dispersing and forming stable interfaces between nanofillers and matrix. Such strategies include covalent attachment of chemical moieties onto the nanofiller and subsequent bonding (ionic\textsuperscript{125}, covalent\textsuperscript{126}, or hydrogen\textsuperscript{127}) with the local polymer chain. Others are grafting from or grafting to\textsuperscript{128} of pre-polymers to the nanofiller surface. Unfortunately, any type functionalization modifies the sp\textsuperscript{2} graphene network and diminishes at least one physical property (mechanical, electrical, or thermal). However, some defects could be beneficial to reinforcement by furthering polymer entanglement with the nanofiller. \textit{In situ} polymerization\textsuperscript{129} has been done, though lower degrees of polymerization have been observed mostly likely due to graphene nanofillers acting as a steric hinders to the reaction. Solution processing where polymer and nanofiller are dissolved in the same reaction vessel, mixed, and solvent evaporated has been the common and cheap method of making nanocomposites\textsuperscript{130}. Because of this, graphene-based polymer nanocomposites have been made by this method for this thesis.

\textbf{1.2.2. CNT-based Hydrogels}

Hydrogels are three-dimensional crosslinked hydrophilic polymer chains via ionic, hydrogen, covalent, or physical entanglements with the ability to absorb high water content\textsuperscript{131}. By definition, hydrogels are classified as at least 70\% solvent (in this case water, hence ‘hydro’ gels) by volume and the rest as polymer material\textsuperscript{132}. 
As a composite of solid and liquid components, hydrogels differ greatly from both parents chemically and physically. They can undergo large volume changes by exuding or absorbing water and can be designed to respond to a host of external stimuli. Because of these properties, hydrogels are often employed as super absorbents (as in diapers, medical bandages), contact lenses, and tissue scaffolds for tissue regeneration. Their network of hydrophilic polymer chains has been exploited to uptake, store, and release drugs or proteins at predetermined times and amounts. Because of their biocompatibility, hydrogels are used as an artificial extracellular matrix to grow tissues for tissue engineering applications. Hydrogels have been made mechanically strong, capable of being compressed and recovering over many cycles. With balancing hydrogen bonding and electrostatics, hydrogels can self-heal when damaged.
Figure 1:10 Hydrogel-stimuli release mechanism\textsuperscript{139}.

The unique response to external stimuli makes hydrogels very interesting for actuation devices by using pH\textsuperscript{140}, temperature\textsuperscript{141}, or electromagnetic stimuli\textsuperscript{142} (figure 1:13). The crosslinked density, depending on chemical bond, can be broken and reformed. This allows a method of controlled release of solvent or some other chemical loaded in the hydrogel. Recently, hydrogels have been made into nanocomposites with a variety of nanoparticles including CNTs\textsuperscript{143}, clay\textsuperscript{144}, and graphene oxide\textsuperscript{145} with the same impetus as composites - when editing hydrogel polymer network can no longer achieve the desired properties. Designing such
hydrogel composites presents additional challenges; not only the nanofillers must disperse in the solvent but also be compatible with the polymer. This has led to the realization of hydrogel soft machines\textsuperscript{132}, sensors and actuators\textsuperscript{146}. In this thesis work, a biomedical device based hydrogel for drug release. Of the different types of external stimuli\textsuperscript{147}, electric fields are the basis of this study for ease of use. Imparting hydrogels with nanofillers is an active research field and is motivated by the same impetus as composites.
2.1. CNT Hydrogel Fabrication

As mentioned before, hydrogel devices have been made to release chemical molecules by an external stimulus. However, most stimuli like temperature or pH does not lend to precise control to drug release\textsuperscript{142}. For tighter control, low power electric fields and CNT hydrogel composites are thought to achieve this type of control. Hydrogel precursor materials, polyvinyl alcohol (PVA) and Borax were purchased from Sigma Aldrich and $M_w$ of 61,000 and 140,000 were used in this study. PVA is a linear polymer with OH groups decorating the main chain and is a nontoxic, biocompatible polymer\textsuperscript{148}. Borax\textsuperscript{149} is just a mineral used simple household cleaner and bug repellant. Single walled CNTs were made by the purified HipCo\textsuperscript{28} (High Pressure Carbon Monoxide) process here at Rice University. This
process, shown in figure 2:1 is a CVD technique using iron pentacarbonyl (Fe (CO)₅) in a gas flow of carbon monoxide. The CNT growth mechanism is shown in figure 1:3b and discussed. Thermal decomposition of Fe (CO)₅ occurs when bled into the chamber and reacted with Fe nanoparticles immobilized on a 200 µm silicon oxide on silicon wafer substrate around 1000 °C for 1 hour. After growth, the CNTs were purified by first baking it in an Ar atmosphere to rid of any reactant gases. Next the CNTs were washed in hydrochloric acid (HCl) to remove Fe nanoparticles and amorphous carbons. Finally, CNTs were baked again under the same inert atmosphere and temperature. CNTs were bought in a 100 mL glass container from Rice and appeared fluffy.

![Diagram of CVD process](image)

2CO(g) $\xrightarrow{\text{Fe(CO)}_5}$ C(s) + CO₂(g)
$T = 1050^\circ\text{C}$
$P = 10 \text{ atm}$

**Figure 2:1 HipCo process for CNTs used in hydrogel device[^89].**
To prepare the gel solutions, 4 grams of PVA powder was added to a 100 ml DI water solution in a 150 mL Pyrex beaker, magnetically stirred and heated to 90°C for 40-45 minutes until the solution became clear to make a 4% PVA solution. Other concentrations with 4%, 6% and 8% of both the low and high M_w were prepared in the same manner. In a separate 150 ml beaker 4 grams of Borax was added 100 ml DI water, stirred and heated also in the same manner. 25 ml of each PVA solution (4 to 8%) was mixed with .02 grams of CNT, stirred for 30 minutes followed by 1 hour of sonication to make a black colored solution. Then .025 ml of Borax solution was added to the mix and stirred until gelation starts. All of the steps were followed with the exception of adding CNT to prepare the control hydrogels.
2.2. Experimental Setup

There were two sets of experiments that were carried out. The initial one was created to measure the effectiveness of drug release from CNT infused gel system, while second part utilized the actual device to measure its release. 2.0 ml of
PVA solution with 0.3 ml of Rhodamine B was combined with 1.0 ml Borax to compose a gel matrix held together by hydrogen bonds between the two components. Two different types of gels were made; one with the PVA/CNT/Rhodamine B and Borax and one without any CNT (figure 2:2a, b). Tests were conducted with PVA/Borax/Rhodamine B gels against PVA/Borax/CNT gels with Rhodamine B to measure the difference in the release rate. To conduct the experiment, placement of a gel on one of the gold wires while leaving the second wire empty, attached both wires to a Styrofoam bar before submerging them in 40 ml deionized water for 30 minutes. Electrodes were attached to a power supply and release rate of the drug was measured by giving the gel a forward as well as a reverse bias of 0.1 V and 0.05 Amps (figure 2:3). A control experiment was performed in addition to measure the release rate without any bias. UV-Vis was conducted after the time period passed to measure the release of the dye for each concentration.

Figure 2:3 Schematic of hydrogel-drug release testing.
In the other part of the experiment, a device was made out of the hydrogel system. A gold plated PET sheet by supper coating was used as the back substrate to the device. The PET substrate was attached to a flat copper strip and placed the prepared gel into a PDMS component with a hole of 5.55 mm radius and 2.44 mm depth. A CNT (also from HipCo) membrane with another copper strip attached to it was placed on top of the gel membrane system. The same CNT membrane was used for all of the experiments. This was done to keep this as a control so all the data were comparable. The device was covered with a Millipore filter, a washer and quartz diffuser and the whole structure was clamped for a tight seal. The diffuser was filled completely with deionized water so that the drug can be released into it. The device was then attached to a stand for easy access. The copper electrodes were connected to a power supply and release rates were measured with a forward, reverse and no voltaic bias. Release rates were taken every 30 minutes for 2 hours. The measurements were determined with the UV-Vis spectrophotometer in every 30 minutes.

Each concentration of HPVA, and MPVA of 4%, 6% and 8% were tested with constant 4% Borax concentration, 0.3 ml of Rhodamine B and .02 grams of CNT for the gels where CNT was used. For analysis of the data, a Shimadzu UV-3600 was used to detect the amount of drug released \textit{in situ}. The highest drug release was from 6% MPVA. UV-Vis was used to measure the height of the peak of Rhodamine B at the wavelength of 553 nm, which was determined by seeing the highest peak Rhodamine B produced when mixed with deionized water only. Then the
absorbance of the Rhodamine B dye and multiplied it with the volume. Then divided that with the slope of Rhodamine B calibration curve times the grams of gel. This data showed the amount of moles of drug released per grams per hour.

Figure 2:4 $G'$ and $G''$ of hydrogels with (a)-(b) drug and (c)-(b) drug and CNT.

Before CNT hydrogel devices were tested, the hydrogels themselves were subject to dynamic testing to determine if their mechanical stability is sufficient for future human trials as drug release devices. Using a TA Instrument Q800 Rheometer in compression mode, the hydrogels were sheared at physiological temperatures.
(96°C) from .05 to 100 Hz frequency at 5 % strain. For epidermal drug patch on the arm, these values are considered to be relevant. From figure 2:2, 2 and 4% hydrogels performed lower compared to the 6 and 8 %. Both moduli from 6 and 8 % hydrogels maintained their gel properties on all scanned frequencies. Figure 2:2 (d) both moduli of 4 % cut max out at around ~50 Pa, while 2% is a little higher and was too low to show in (d). Even with CNT and drug loading 6 and 8 & had well over 100 and 1000 Pa respectively.

A membrane was used as both electrode and control mechanic for drug release amount. CNTs mats grown using chemical vapor deposition were coated with a layer of polyether sulphone (PES) by phase inversion process to form the membrane. Polyethersulfone was supplied by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120°C; N-methylpyrrolidinone (NMP) from Merck was used as the solvent. The CNTs mats were produced by CVD Flat sheet membrane as shown in figure 2:5 was prepared according to the dry/wet phase inversion technique. The solution was poured onto a clear, flat and smooth glass plate. Stainless steel support casting knife was used to spread the solution to a uniform thickness by pneumatic force.

### 2.3. Discussion

Polymeric hydrogels have considerable application in controlled drug release devices where the release rate for hydrogels are governed by the size of the solutes, polymer matrix and their interaction with newer approaches beyond simple
diffusion triggered by external stimuli\textsuperscript{150}. Among those, pH stimulation is one of the most utilized choices of controlled release tests which could be fashioned into an implantable biosensor. Other groups have utilized thermally stimulated uptake and release of macromolecules such as vitamin B\textsuperscript{151}, and chymotrypsin from N-isopropylacrylamide\textsuperscript{152} and methylene-bis-acrylamide\textsuperscript{153} based hydrogels release as a function of temperature. UV\textsuperscript{154} or laser\textsuperscript{155} radiation has also demonstrated effective control of release rates in azobenzene functionalized dextran and B-cyclodextrin where intensity of light can either decrease or increase release within short time intervals\textsuperscript{156}. Further developments have shown hydrogel microchip devices can be rapidly fabricated cheaply with drug reservoir release when in contact with skin temperature\textsuperscript{157}. A version of this transdermal hydrogel microchip is demonstrated with good stability and efficiency based on PVA, CNTs, and Borax.
Figure 2:5(a) Hydrogel microdevice with electrodes and (b) schematic drawing of drug delivery system via CNT infused hydrogel. Gel device contains CNT and Rhodamine B that are trapped in a PVA and Borax gel. Quartz fuser is shown in both figures.
A complete CNT-filled hydrogel based transdermal microchip device is illustrated in figure 2:5. The choice of system was based on several factors: design simplicity, common-cheap materials used; release in a pulsatile manner\(^{158}\); reduction of disease transmission\(^{159}\); lower toxicity via control\(^{160}\). Electrical stimulation is thought to cause scission of hydrogel crosslinks\(^{161}\) to release the drug while minimizing toxicity\(^{162}\). In the experiments, the effect of applied bias, CNT, and polymer concentrations were tested on drug release rate as depicted by figure. Rhodamine B dye is used in place model drug due to its fluorescence ability in the UV-Vis spectrometer and no reported side reactions with the hydrogel apart from simple hydrogen bonding which is believed to not hinder release. The Hydrogel concentrations are labeled as 1 denoting 8% HPVA, 2 denoting 6% HPVA, 3 denoting 4% HPVA, 4 denoting 8% MPVA, and 5 denoting 6% MPVA where M stands for medium and H for high molecular weight respectively.
Figure 2:6 Proposed release mechanism of CNT-hydrogel.

When the hydrogel was infused with CNT, the release rate increased with decreasing concentration, but lost the ability to maintain the gel structure when low molecular weight PVA was used and therefore was not included in the studies. An explanation of this is that electric field charges and heats the CNT locally\textsuperscript{163} (figure 2:6) and the energy associated with the local heating disrupts the hydrogen bonding between PVA and trapped borate anions. The effect of the local heating on the drug release may play a role given the confinement of the device design. The hydrogel is charged neutral overall but does have cationic and anionic species as shown in
scheme in figure 2.6. During electrical bias, free ionic species move toward oppositely charged electrodes. This ion mobility depends on size of the ion, charge density, and environment the ion is in. Borate anions are “trapped” in the gel in the form of hydrogen-ion bonding crosslinking polymer chains\textsuperscript{164}. The CNTs are wrapped around by polymer chains, when heated, weakens the local bonding between borate anion and polymer pendant groups, which result in the release of Rhodamine B molecules. However, for the first experiment heating may have fewer roles to play given the significant difference between the forward and reverse bias data\textsuperscript{165}. When the device was placed under a forward bias, the copper strip attached to the CNT membrane acted as the positive lead and the copper strip attached to the gold plated sheet was the negative lead. Under reverse bias, the copper strip attached to the CNT membrane acted as the negative lead and the copper strip attached to the gold plated sheet became the positive lead.
Figure 2.7 Release rates of control (0%) to 8% hydrogel without (a) 2% CNT and (b) with 2% CNT.
From the five hydrogels test, another delivery device was made from 6% MPVA-Borax due to its acceptable combination of stability and release rate as shown by figure 2:7. Base level was determined by electrically stimulating with 0.1 V at 0.05 Amps with forward and reverse bias. It was observed that under reverse bias, there is higher release of the drug than that with a forward bias. While initially there was a high release, it declined every 30 minutes and reached a steady release rate after 90 minutes with a reverse bias. When stimulated with a forward bias there is a slower increase in releases rate that eventually reached a steady state after 90 minutes. This was lower than that was observed with the reverse bias. On the other hand, without any voltage there was a slow increase in release rate over time. This demonstrated that biasing affects the drug release and enables to create a controlled release as well as a regulatory drug delivery system. There was a 50% increase in the release rate with reverse bias compared to that of its positive counterpart under 0.1 V. It was observed the similar trend in the drug release under 0.4 V but the rate is lower than that under 0.1 V. The difference between the hydrogel electrically stimulated with forward bias and no voltage is marginal and after 90 minutes maintained the same release rate. To test the effects of increasing molecular weight, experiments were conducted with 6% HPVA. The results depicted by figure c show that increasing concentration lead to a decrease in release rate of the drug.
Figure 2:8 (a) Drug release with a reverse bias and decreased release rate with forward bias over 120 cycles (b) with bias increased to 0.4V over 5 days.
The membrane part of the device created with the ability to act as a regulator to increase or decrease drug release rate with very low outside stimuli (figure 2:8). The results demonstrate that the addition of CNT can significantly increase the rate of Rhodamine B release from the hydrogels to two and half times more than those released from hydrogels without CNT. Under an electrical field, CNTs lead to localized heating in the gel, causing the disruption of hydrogen bonding between the PVA and Borax molecules; therefore, increasing the release rate of the drug. The hydrogels’ release rate was also affected by the forward and reverse bias, with the drug release rate decreasing and increasing respectively. When placed under a forward bias, the borate anions get attracted to the positive charge of the CNT electrode forming a steric hindrance that retards drug release. However, under reverse bias, borate anions get attracted to the opposite electrode and push the drug down the diffusion gradient to the quartz crystal column. In addition to the forward and reverse bias, the gel device is tunable with increasing and decreasing voltage to create a stepwise release. This enables the control of time, duration and the amount of the drugs’ release rate with a small electrical stimulus.

It was observed that with increasing concentration, the release rate of the drug started from a lower rate of diffusion and yielded lower results after the 2-hour period when compared to the 6% MPVA hydrogel with 0.1 V, but higher results than the 6% MPVA with 0.4 V. This is comparable to the initial testing because it shows that hydrogels of higher concentration take a longer time period to release the drug. The problem lies in that the rate of release of drug when stimulated
electrically at a higher voltage has a much slower response time than desired. One way to overcome this would be to make the hydrogel-CNT complex thinner and form a smaller device\textsuperscript{166}. A compilation of the results can be utilized into making a drug delivery device consisting of 6\% MPVA-Borax-CNT gel and using 0.1 V with the reverse bias to have high release rate and then using the forward bias at 0.4 V to slow down the drug release to a greater degree\textsuperscript{167}. While the hydrogel CNT system proved to be effective in the experimental setting the next step would be to effectively reproduce the result in a clinical environment. One of the challenges is whether the PVA-Borax-CNT system can effectively release and maintain the rate of the desired drug as it passes through the stratum conium of the skin, using it as a semi-permeable membrane. None the less, the PVA-Borax hydrogel model\textsuperscript{168,169} has been extensively studied and deemed very safe\textsuperscript{170}. Now, it has been demonstrated as a suitable platform for drug release for modification by carbon nanomaterials such as CNTs.
Chapter 3

Water Drop Tribology of Graphene Surfaces

3.1. Centrifugal Adhesion Balance (CAB)

Tribology\textsuperscript{171} (Greek word “tribos” meaning rubbing) is the multidisciplinary science of interacting surfaces in dynamic motion with one another. Under this section of surface science and engineering, the study of friction, lubrication, and wear fall under this. The main theme of tribology is centered on the nature of the surface. The surface of any material will always be less coherent than that of the bulk and therefore softer than the bulk. This stems from the surface layer (a few nanometers) has fewer nearest neighbors and this in dynamic equilibrium with the surrounding environment\textsuperscript{172}. Surfaces have roughness of nanoscale peaks and valleys (surface dislocations and grain boundaries included) called asperities\textsuperscript{173} (figure 4:1). When in contact with other surfaces, these asperities are in contact
with other asperities which can break off (debris) and plow into other surfaces causing wear damage at the nanoscale\textsuperscript{174}. This effect is compounded when surface area is increased because of more available events for asperity locking and interlocking. For MEMS\textsuperscript{175}, NEMS\textsuperscript{176} and other nanodevices\textsuperscript{177} with moving parts this is a concern as their enormous surface area to volumes leads to severe friction and wear events resulting in very limited service lifetimes\textsuperscript{178}. Traditional lubricants fail to reduce friction in these systems because the lubricants (like many liquids) become too viscous when confined to nanoscale thickness\textsuperscript{179}. Also at this small scale, a time-dependent character in friction is observed. This has led to new sub disciplines such as nanotribology\textsuperscript{180} to propose new theories about friction by considering intermolecular surface forces and testing equipment to measure these forces such as Surface Force Apparatus (SFA)\textsuperscript{181,182}. 

\textbf{Figure 4:1} Nanoscale schematic of tribological wear\textsuperscript{183}. 

\[ F_n = \sum f_n \]

\[ F_f = \sum f_f \]

\[ \mu = \frac{F_f}{F_n} \]
One of tribology’s founders, David Tabor\textsuperscript{185} observed the lateral force (frictional force) needed to slide two surfaces against one another is proportional to the contact area of the surfaces. The special case of the Amonton Law\textsuperscript{186} extends the idea of a rough surfaces’ contact area is linearly proportional to load. Interestingly, this is not obeyed by liquid drops sliding on solid surfaces\textsuperscript{187}; frictional forces decreases with normal force despite the fact contact area increases. Also importantly is the time the drop rests prior to moving affecting these forces. It is shown that $f_\parallel$ increases with the time the drop rests on the surface before the onset of sliding\textsuperscript{188}, $t_{\text{rest}}$. This time dependent behavior is related to the normal component of the Young Relation which increases pinning of the three phase contact line, hence increasing the retention force\textsuperscript{189}. In the past, it has been difficult to verify such claims due to experimental instruments\textsuperscript{190,191} (figure 4.2) not sophisticated enough to decouple normal and lateral forces since experiments were done on tilt stages where the angle of incline increased until the liquid drop moved but that changes two parameters at the same time (lateral and normal forces)\textsuperscript{192}. This is a cardinal sin, as in experimentation, you need to change one variable at a time. This chapter describes an instrument that can.
The Centrifugal Adhesion Balance (CAB)\textsuperscript{187} is illustrated in figure 4:2. CAB is a home-made device used specifically to measure the liquid drop tribology forces on surfaces where lateral forces, $f_\parallel$, is associated with drop friction moving on surfaces. CAB has an aluminum beam with two ends and center attached to a DC motor which rotates the beam normal to the gravitational field at full 360°. On one end of the beam is the counterweight to keep the beam balanced. On the other is a chamber with a sample mount, CCD camera goniometer, and tilt stage. This tilt stage is fixed but can be changed with respect to the beam at any angle, $\alpha$ (0° ≤ $\alpha$ ≤ 360°). This allows pendant and sessile liquid drop experimentation. A computer (not shown) controls how fast the beam rotates and records the movement of liquid drops on the sample surface. The sample chamber is enclosed during the run to the outside to prevent convection forces from interfering during the experiment.

Figure 4:2 Traditional method at calculating lateral forces on drops\textsuperscript{193}.
CAB uses centrifugal forces in combination with gravitational to allow independent manipulation of normal and lateral forces according to the equations:

\[ f_\parallel = m(\omega^2 L \cos \alpha - g \sin \alpha) \]
\[ f_\perp = m(\omega^2 L \sin \alpha + g \cos \alpha) \]

Equation 4:1 Normal and lateral force balance equations from a liquid drop in the CAB machine\(^{194}\)
Where \( f_\perp \) is the normal force, \( g \) is the gravitational acceleration, \( f_\parallel \) is the lateral force, \( \omega \) is the angular velocity, \( L \) is the distance from the center of rotation to the drop, and \( m \) is the mass of the drop. Unlike past apparatus\(^{188}\), the CAB allows for real-time monitoring of liquid drop movement while the experiment is in progress by the CCD camera. Another distinction of the CAB is drop sliding experiments can be done in pendant (\( \alpha = 180^\circ \)) and sessile (\( \alpha = 0^\circ \)) configurations. In a typical experiment (figure 4:3a, b), a single liquid drop of known volume is placed on a substrate by a pipette and allowed to rest at time \( t_{\text{still}} \). The \( t_{\text{still}} \) signifies the period which the centrifugal force is zero (CAB is motionless) followed by an active time, \( t_{\text{active}} \) during which \( \omega \) is gradually increased (by the computer controlled motor) until a critical angular velocity, \( \omega_c \) the drop begins to move along the substrate. Throughout the experiment, the liquid drop is resting pinned to the substrate surface and onset of movement is the end of the active time; therefore,

\[
t_{\text{rest}} = t_{\text{still}} + t_{\text{active}}
\]

Equation 4:2 time relation variables of a single drop during a CAB experiment

Not only does the CAB impart information about how liquid drops slide across surfaces, but also on the surfaces themselves. The way a liquid drop deforms while moving can yield information on the surface amphiphilic quality to liquids as well as chemical heterogeneity\(^{195}\). Two systems are reported here for graphene
substrates; sessile and pendant force drop experiments and compared to other surfaces.

Figure 4:4 Vector force balance on (a) liquid drop on a tilted substrate in the CAB and (b) schematic and optical photo of a 10µL drop on graphene 194.

DI water used for making drops was from Barnstead Nanopure Purification System which provides a specific conductance of $\leq 0.7 \times 10^{-6} \, \Omega^{-1} \, \text{cm}^{-1}$ at 25°C. Water drops were placed on the graphene substrate in a dust-free laminar flow hood (Terra Universal, ULPA filters) and a Transferpette electric pipette from Millipore for drop forming. All drops were measured at 6.0 µL DI and placed at the center of the substrate in the CAB chamber. To suppress the evaporation of the water, four smaller (1 µL) satellite water drops near the main (measured) drop (500 µm away) and sealed the chamber196. Optical images of water drops on the graphene and saline-coated silicon were taken using Micromaster® I microscope from Fisher Scientific. ParafilmM from Sigma-Aldrich was used as the goniometer sealing agent.
for all experiments performed using the CAB. HOPG grade SPI-1 (12x12x1 mm³) was obtained from SPI Supplies and slow cleaving of about 45 min for 1.4 cm² of HOPG surface to obtain 1.4x6 cm² few layers. All liquid drop substrates were silicon wafers with diameters of 76.2±0.3 mm, orientation: <110>±0.9°, resistivity 0.0034–0.0046 Ω cm, and thickness: 381±25 mm used in all experiments from Virginia Semiconductor. The silicon wafers were cut into a 1.4x6 cm² size substrate, rinsed with ethanol, then with DI water and dried in a StableTemp vacuum oven (model: 5053-10 from Cole-Parmer) at 100 °C for 30 min. Then, the silicon substrates went through a 45 min cleaning using an ultraviolet/ozone Procleaner (model: Procleaner 110) to remove any organic impurities on the surface. From the ultraviolet/ozone cleaner, the silicon substrates were immediately placed in a 1% volume solution of octadecyltrimethoxysilane (90% technical grade obtained from Sigma Aldrich) in toluene (99.5% ACS Reagent obtained from Sigma Aldrich), where it remained for 3 hours at 70 °C. The surface was then washed with excessive amount of DI water for at least 10 min, and was placed in a DI water bath for about 45 min. Finally, it was dried in the Cole-Parmer vacuum oven at 80 °C for 15 min. The liquid drop on graphene along with its vectored representation is shown in figure 4.4.

### 3.2. Graphene Fabrication

The type of graphene used in the liquid drop tribology is from CVD grown graphene made by a protocol developed by Srivastava\textsuperscript{197}. In an typical CVD
Experimental setup shown in figure 4:5a, a 25 μm thick Cu thin film (CVD grown bought from Sigma Aldrich) was placed into quartz tube and the pressure was reduced to $10^{-2}$ Torr before flowing in Ar/H$_2$ at a pressure of $\sim$8-9 Torr. The films were heated to 950°C in Ar/H$_2$ ambient and maintained for 30 minutes to remove any oxide layer formed. Then Ar/H$_2$ flow was stopped and hexane vapor evaporated from a liquid precursor (flow rate $\sim$ 4 mL/h) was passed in the quartz tube for 20 minute reaction growth of the graphene. During the reaction time tube pressure was maintained at 500 mTorr and stopped after 20 min and allowed to cool to room temperature. Then the Cu films with the as-grown graphene films on them were spin-coated with a thin layer of PMMA (poly methyl methacrylate) on a HOLMAC spin coating machine (4000 rpm, 150V) for 15 minutes (figure 4:5b). The sample was dipped in a 100 mL dilute nitric acid (.5M) bath was used to dissolve the Cu foil for 30 minutes. After dissolution, the PMMA-supported graphene was carefully washed with DI water to remove any precursors and gently transferred (stamped) onto a <111> orientated silicon wafer (also from Virginia Semiconductor) with 300 nm SiO$_2$ layer. Prior to transfer, the Si substrate was rinsed with acetone three times, ethanol alcohol two times and DI water, and then dried using N$_2$ gas. The PMMA film was removed by dipping in a 100 mL acetone bath for 3 hours, leaving behind pure graphene on silicon wafer substrate intact (figure 4:5c).
To evaluate the number of graphene layers a Thermo Scientific DXR Raman Microscope was used at 531 nm wavelength at 0.1 mW low power to reduce sample heating. The Graphene samples on silicon substrates were placed inside the
microscope and run at standard temperature and pressure. OriginPro 8.5 was used for data analysis. All samples used the same Si substrate and laser wavelength.

![Raman spectra showing sharp D, G, and 2D peaks](image)

**Figure 4:6 Raman analysis showing sharp D, G, and 2D peaks**

The Raman spectra are plotted intensity versus frequency. For CVD grown graphene, three distinct regions are considered: 2D (2695 cm\(^{-1}\)), G (1595 cm\(^{-1}\)), and D (1350 cm\(^{-1}\)) bands (figure 4:6). The G-band is the primary mode in both graphite and graphene because it is a measure of the planar configuration sp\(^2\) carbon. This peak is resonant and usually independent of excitation laser frequency. The D band
is known as the disorder or defect band that represents a ring-breathing mode from sp² carbons. Weak in graphite and graphene; the D-band intensity is directly proportional to the level of defects in the sample¹⁹⁹. Unfortunately, it cannot reveal types of defects such as kinks, holes, or wrinkles²⁰⁰. The 2D band (also called the G’-band) is the second order of the D-band (two phonon scattering process) and unlike D-band does not need defect proximity to be active therefore does not represent defects. Both G and 2D bands are used to determine graphene layers. For 2D, the band shifts to higher values and the G shifts to lower ones. Taking the intensity ratios of the G and 2D bands gives an indication of the number of layers of graphene. For ratios ~.38 is single, .64 two, and .828 few layer graphene sheets²⁰¹.

In order to confirm single and few layer graphene films and quality, TEM was done using a JEOL 1230 High Contrast Schottky-type field emission gun with a charge-coupled device Gatan model 794 camera. Power was at 120 eV and thermally induced drift was accounted for. Graphene sample TEM preparation was similar to the aforementioned Si substrate mounting procedure, except holey TEM carbon grid was used as a substrate. Images shown in figure 4:7 a and b are good uniform quality with little or no defects with one, two and > three graphene layers. AFM was not done as a compliment to TEM since AFM cannot discriminate between defect types²⁰².
Figure 4: TEM of (a) single and (b) few layer graphene.\textsuperscript{194}
3.3. Discussion

Experiments are started with plate tilt angles at $\alpha = 0^\circ$ for sessile and $180^\circ$ for pendant drops with the computer controlling the motor’s angular velocity $\omega$. A velocity profile with respect to time for a single run is shown in figure 4:8a. $\omega$ acquired by is plotted against experimental time from the moment ($t = 0$) the drop (V = 6 µl) is placed on single graphene surface and $t_{\text{still}}$ is the period of time during which the CAB remains perfectly still (i) - (ii) in figure 4:8b with $= 0$. $t_{\text{active}}$ is the time which $\omega$ is increased until $\omega_c$ (ii) - (iii) where the receding and advancing drop angle edges are recorded.
Figure 4:8(a) CAB water drop velocity profile and (b) water drop morphology during experimental run.

From the angular velocity profiles and using equations 4:1 the lateral adhesion forces acting upon the liquid drop can be determined. This is plotted with lateral forces with respect to time up to and including the critical time for drop movement.
Figure 4:9 Drop retention force as a function of time for a drop of hexadecane on a mica surface. The open triangle is sessile and closed triangle pendant drops.

The observed time effect for hexadecane drop on a mica surface is shown in figure 4:9 for both sessile and pendant drops. Easily, it can be seen that pendant drops have almost 30% more force needed to move a drop than that of sessile drops. Another is this plateau of the force after a critical time where after a certain $t_{\text{rest}}$ the linear relation between $f_{||c}$ breaks down and becomes independent no matter how high $t_{\text{rest}}$ is. These observed higher $t_{\text{rest}}$ values the larger the lateral forces needed for drop sliding is counter to what traditional views held by Tabor or
any other established classical friction theories for drops. To ensure this behavior is
not unique to mica substrates and hydrocarbon drops, other systems were tested
and compared in figure 4:9. As seen in figure 4:10 a-d, a similar trend is seen across
three different substrates and liquid drops.

Figure 4:10 Time effect experiments for different systems showing $f_{hc}$ as a
function of $t_{rest}$.

Though classical theories fail to explain this liquid drop lateral force time
effect behavior$^{203,204}$, one possible solution would be to invoke Shanahan-de Gennes
deformation of the contact area between the liquid and first few layers of the surface. This approach shows that the unsatisfied component of the Young equation can cause substrate surface deformation, which is proportional to \( \frac{\gamma \sin \theta}{r} \), where \( r \) is drop radius, \( \gamma \) is surface tension of the drop, and \( \theta \) is the contact angle of the drop-
surface makes. This surface deformation is a molecular re-orientation of the surface in response to the liquid drop. This molecular re-orientation at the solid surface enables stronger intermolecular interactions of the re-oriented solid molecules with the liquid (hence higher \( f \)). In layman's terms, the liquid drop is “hugging” the first few layers of the surface. The vector direction of this force is opposite to the gravitational force, which may explain why pendant drops require more force than sessile for movement. Though there is no way of directly knowing in what fashion the surface molecular re-orientation, this is the best theory to date. To stress the point, sessile drops have a bigger contact area with the surface than pendant drops, even though \( f \) are higher for pendant drops than sessile and should be insignificant for hard surfaces. However, the data says otherwise. The previous surfaces were chemically heterogeneous in which functional groups could re-orient with respect to the drop's influence and Shanahan-de Gennes does take this into account. Graphene, which is tested next, is chemically homogenous and therefore a test to this theory.
Figure 4.11 Schematic representation of the time effect showing a plot of lateral force, $f_{\parallel}$, required to slide a drop on a non-graphene surface, as a function of the drop-resting time, $t_{\text{rest}}$. $f_{\parallel}\text{pl}$ is the lateral force in the plateau region and $t_{\text{pl}}$ is the time for the lateral force to reach the value of $f_{\parallel}\text{pl}$. (b) Lateral force, $f_{\parallel}$, required to slide water drops on HOPG (solid grey squares) and graphene (other symbols) substrates as a function of $t_{\text{rest}}$.

For non-graphene surfaces (figure 4.11a), the time for molecular re-orientation was measured between 10 to 20 minutes. However, for the graphene surfaces shown in figure 4.11b is a completely different case from other surfaces tested. Different symbols correspond to different graphene layers, drop volume, and normal accelerations ($a_{\perp} = (g \cos \alpha - \omega_{c}^{2}L \sin \alpha)$): solid black diamonds, $V=4\mu l$, 1 layer, $a = 0.1 \pm 0.05 g$; solid green circles, $V=6.5\mu l$, 1 layer, $a = 0.22\pm 0.04 g$; hollow red triangle and hollow blue triangles, $V = 7\mu l$, 2 layers, with hollow red triangles, $a = -0.14\pm 0.06 g$, and hollow blue triangles, $a = \pm 0.1 g$; solid red triangles and solid blue triangles, $V = 7.5 \mu l$, 2 layers with solid red triangles, $a = 1 g$ (sessile) and solid blue
triangles, $a = -1 \text{ g (pendant)}$; and solid grey squares, $V = 9.5 \mu l$, HOPG substrate with $a = 1 \text{ g (sessile)}$. The time effect dependence of $f_\parallel$ is not observed within the minimal time resolution of the experiment, unlike the data shown in figure 4:9. To note, the minimum time of resolution for the CAB is in the microseconds. Ideally, graphene is an atomically homogeneous sp$^2$ carbon lattice surface$^{209}$. If molecular reorientation events occur, it can only be expressed in the realignment of the electronic orbitals, which are very fast events – on the order of attoseconds$^{210}$. But if this is the culprit of drop pinning at the surface, then the slightest force to slide the drop, should have allowed the liquid molecules at the three phase contact line to induce orbitalic re-orientation on the solid surface molecules nearby and hence the sliding of the drop$^{211,212}$. In other words, there would be no force retaining the drop to the solid surface, while it is experimentally shown (figure 4:10b) that this is not the case. Another mechanism to hold drops to a surface is via defects on the solid surface$^{213,214}$. The liquid is either energetically attracted to those defects compared to the rest of the surface, or repelled$^{215}$. This can create a serrated three phase contact line which the drop is pinned to the defects either by adhering to them or by adhering to the rest of the surface to avoid them. Energetically, it costs less energy to avoid them$^{216}$. The defects on a graphene surface can emanate from the borders at the places where different domains of graphene that nucleated during CVD growth$^{217}$. Such junctions can provide a morphologically different region from the sp$^2$ carbon network and a “defect” for the water drop to pin on$^{218}$. Studies carried out for understanding evolution and morphology of the CVD grown graphene sheets
revealed explicit domain structure\textsuperscript{219}. Boundaries of the domains have mismatch in the atomic structure of the two meeting graphene layers as well as Bernard stacking of the graphene layers as they overlap each other\textsuperscript{220}. Further imperfections on the size scale of the droplet (10 micron) are also expected, e.g., ripple and point defects. The strength of the interaction with these defects has no time dependence and hence why we see straight horizontal lines with zero apparent time dependence\textsuperscript{221}.

While the regions of defects are difficult to resolve \textit{in-situ}, such serrated three phase contact line can be enhanced using optical microscopy as the drop evaporates\textsuperscript{222}. Figure 4.12 shows that indeed the three phase contact line of a graphene surface is serrated on a micron scale upon evaporation, while that of a non-graphene surface is not.
Figure 4:12 Optical images of water drop three phase contact line of (a) silicon and (b) graphene surface. The three phase boundary appears smooth on silicon whereas the boundary is serrated. Different light contrast corresponds to different light optimization for the different drop contact angles.
The absence of time effect in the drop retention force shown in figure 4:11b is therefore a manifestation of the absence of any surface molecular reorientation that can lead to a stronger solid-liquid intermolecular interaction in the graphene surface. Metals, ceramics, and other hard surfaces zero contact angle with any liquid because of the high energy surface to break bonds. Graphene, also being a hard material, seems to be an exception to this rule. The deformation at the three phase contact line that leads in other surfaces to molecular re-orientation of the solid molecules, can only lead to topographic deformation in graphene, but not molecular re-orientation. The two energetically different states of graphene, the part inside the sheets and near their edges, have chemical difference; the edges have dangling (sp³ character) bonds which are terminated by hydrogen atoms quickly after growth, while inside the sheets are composed of the classic sp² carbon lattice. All of these structures are already on the surface and the mechanical strength and high electrical conductivity of the graphene coating prevent any other functional groups located deeper in the substrate to re-orient such as to reach the surface.

In addition to the previous observation on graphene substrates regarding the time dependency of \( f\parallel \), another interesting phenomenon observed in figure 4:10 is the similarity between \( f\parallel_{pl} \) for sessile (\( a_\perp = +1g \)) and pendant (\( a_\perp = -1g \)) drops. For non-graphene surfaces, the \( f\parallel_{pl} \) for pendant drops are distinctively higher than for sessile drops. In the case of surfaces that consist of chemically heterogeneous molecules the pinning force emanates from the enhanced intermolecular interaction associated with the deformation at the three-phase contact line. For pendant drops,
higher $f_{pul}$ retention forces was attributed to is gravity induced facilitated three phase contact line deformation. For the graphene sheet, however, the deformation of the surface does not affect its intermolecular interactions with the liquid. Therefore, the forces associated with sliding pendant and sessile drops are similar.

To conclude, using the CAB, it is shown experimentally that the retention force of water drops on graphene surfaces does not depend on the drop resting time, in contrast to any other known system. It is also observed the forces required to slide sessile and pendant drops on graphene sheets almost have the same values. Both of these tribological observations are attributed to the chemical stability of graphene surfaces, which sustains the same morphology and chemical composition on the surface regardless of the Shanahan de-Gennes type surface deformation. The retention force of the water drops on graphene surface is therefore only attributed to the boundaries where domains of graphene that nucleated at two adjacent nucleation sites meet. This gives rise to a unique serrated three phase contact line on graphene surfaces. The three phase contact line is pinned along the serrated structure of these domains and not to the Shanahan de-Gennes deformed ridge, and since the domains were on the surface historically, there is no time dependence to the drop retention force on graphene.
Layer by Layer (LbL) Assembly of Polyamide Graphene Nanocomposites

4.1. Graphene oxide and Functionalization

As previously discussed in the introduction, the unique aspect of GO as a filler is its ability to be chemically modified to yield different properties in the composite which is absent in other nanofillers such as clays. A new, safer type of GO protocol synthesis dubbed Improved Modified Hummers (IMH) developed by the Tour Group was used for nanocomposite synthesis. This protocol is safer than Hummers’ and Staudenmaier’s since it uses fewer oxidants and requires no pre or post-oxidation step. Though more oxygen functionalities, it has almost the same electrical conductivity and the basal plane is less disrupted. All chemical treatments, washes, and filtration were done in a fume hood. In a 500 ml Erlenmeyer flask, 360 mL of H₂SO₄ and 40 mL of H₃PO₄ (9:1 ratio) were mixed with 3g of graphite.
powder (BayCarbon Inc., SP2, 200 mesh size) with 18g of KMnO₄. A slight
temperature spike was observed from 35 to 40°C. The reaction vessel was heated to
50°C and magnetically stirred for 12 hours. The solution was allowed to reach room
temperature and poured over 400 mL of iced DI water. After the iced melted and
allowed for reach room temperature, 3 to 6 mL 30% H₂O₂ was added. This was
done to bind the permanganate ions out of solution. The solution color changed
from dark brown to light brown followed by fizzing. Next, the solution was
centrifuged for 4 hours at 4000 rpm and the supernatant decanted away. The
remaining slurry was then filtered in a Millipore glass filtration vacuum setup with a
.1 micron 40 mm PTFE membrane and washed in the following sequence in order:
800 mL of DI water, 400 mL of 30% HCl, 400 mL of DI water, 400 mL of ethanol and
400 mL of dimethyl ether. The centrifuge process was repeated again and
transferred back to the filter setup where 400 mL of ether wash and vacuum dried
for 24 hours at room temperature. Approximately 6g of fine, light brown-silvery film
product adhered to the membrane was obtained. Throughout the chemical
treatment, the color of graphite went from black to light/dark brown. The GO film
was ground up using a ball and mortar in an N₂ gas glove box. Attenuated Total
Reflection Fourier Transform (ATR-FTIR) spectroscopy was used to measure the
groups present in GO and an idealized model was constructed based on that
information shown in figure 5:1 a, b. OH groups have signature bands from 3000 to
3500 cm⁻¹ but so do water molecules. It is impossible to totally remove water from
GO due to it being so hydrophilic, so XPS and XRD were done. Easily seen are the
epoxy groups at 850 and 1200 cm\(^{-1}\); alkoxy at 1060 cm\(^{-1}\); phenolic at 1278 cm\(^{-1}\); carbonyl at 1720 cm\(^{-1}\) and tertiary alcohol at 1375 cm\(^{-1}\). All spectra signals were verified using this paper\(^{225}\).

Figure 5:1 Functional groups of GO by (a) FTIR and (b) GO model.
As noted before, IMH imparts more oxygen functionality in GO than other protocols having more sp$^3$ than sp$^2$ character making GO an insulator. But surprisingly the basal plane is relatively intact. For functionalization purposes, not all of the oxygen bearing groups is used and some are even a hindrance such as OH groups in free radical reactions. Therefore, removing unwanted functional groups in GO while leaving the remaining ones for later reactions is needed. Using chemical reduction can tune these functional groups to specific ratios and consequently the physical properties of the GO (and therefore nanocomposite films). This is preferred over rapid thermal reduction because of gas pressure damage from volatized functional groups.$^{226}$ A good amount of control is needed to remove specific functional groups to which enough of them for GO to remain soluble in polar organic solvents. To setup this experiment, the fine brown powder of GO was dispersed along a .1 micron pore PTFE membrane (47 mm diameter) and put into a Pyrex vacuum desiccator along with an open beaker 50 mL of hydrazine hydrate. This beaker was put below the membrane holding GO to ensure uniform gas diffusion. After that, the desiccator was sealed and pumped down to remove air (100 mTorr). Different time intervals were taken from 30 minutes to 1 week of vapor exposure and analyzed by both XPS and FTIR how the different functional groups are affected.
Figure 5:2 Hydrazine reduction of (a) carbonyl, (b) phenol, (c) alcohol, and (d)-(f) epoxide groups on GO.

Noticeable changes in the FTIR spectra of the functional groups on GO shown in figure 5:2. The first two hours of exposure, GO still retained its hydrophilic nature able to form stable suspensions in water up to 1mg/mL concentrations but crashed after 3 hours. After that, carbonyl groups showed a drop in spectra intensity at 1720
cm$^{-1}$ and vanished after 8 hours. Similar trend was seen for phenol groups, but vanished at 16 hours. Epoxide groups have two peaks that took different rates of reductions; completely vanishing after 22 hours. Alcohol groups took the longest to vanish at 108 hours. The reason for such long times could be attributed to steric hindrance of the other groups being reduced first.

Selectively removing and reacting functional groups is of interest for composite processing. To this end, GO was reduced and then functionalized in a two-step, one pot reaction described in figure 5:4. This protocol borrows from Tour et al diazonium salt reactions with graphene$^{227}$ and McLaughlin’s efficient reduction of nitro groups$^{228}$. In a 500 mL Erlenmeyer flask, 225mg of GO was dispersed in 1 wt% aqueous solution of sodium dodecylbenzenesulfonate (SDBS) surfactant (2.25g of SDBS, 222.75g of DI water)$^{229}$. A Fisher Scientific Misconix Sonicator 3000 was used to homogenize the solution for 1 hour. The solution pH was changed to 10 by using small drops of 1 M NH$_4$OH and measuring with pH paper (Hydrion). The solution was then reduced with 60% hydrazine hydrate (2.25 mL) at 80$^\circ$C for 24 hours magnetically stirred and then allowed to cool to room temperature. Functionalization was carried out by pre-dissolving 15g of solid 4-Nitrobenzenediazonium tetrafluoroborate (Sigma Aldrich, 294438) with a minimum amount of water, added drop-wise to the solution and stirred at room temperature for 1 hour. The mixture was the poured into a Millipore glass filter setup with a 0.1µm Teflon membrane and washed in water twice and then acetone three times. The product was resuspended in DMF to remove any excess SDBS and unreacted
diazonium salt. The product was isolated into a drying dish and dried under vacuum at 60°C overnight. The product weight was about 22 to 24 mg.

Figure 5:3 Functionalization and reduction of GO.

The second part of this reaction (Figure 5:4b) describes the reduction of the nitroarenes to anilines. Using a reflux condenser, 1g of elemental sulfur was added to 2g of NaHCO₃, 30mg of f-GO in 50 mL of DMF were reacted at 130°C for 5.5 hrs. The solution was then allowed to cool to RT, filtered, and dried overnight in a vacuum furnace. FTIR and XPS in figure 5:5 analysis confirm successful functionalization and reduction. Asymmetric (1513 cm⁻¹) and symmetric (1343 cm⁻¹)
1) stretches in figure are assigned to the -NO$_2$ group (Figure 5:5). After reduction, a broad peak due to minimal H-bonding in the solid at 3200 to 3300 cm$^{-1}$ is assigned as -NH stretch, and the weak peak at 1590 cm$^{-1}$ is assigned as -NH$_2$ deformation. High resolution XPS scans of the N1s core-level, showed that the nitrogen binding energy shifted from 406 eV (-NO$_2$ group) to 400 eV (-NH$_2$ group). The nitrogen binding energy shift thus indicated the functional group conversion.
Figure 5:4 ATR-IR spectra (a) A, (b) B core-level N1s spectra of A (red) showing the NO\textsubscript{2} peak at 406 eV and after reduction to B (blue) indicating the reduction to NH\textsubscript{2} (400 eV).

4.2. LbL Nanocomposite Assembly

Self-assembly\textsuperscript{230,231} (SA) has been investigated as an alternative manufacturing strategy to the limited, top-down ones traditionally used. SA encompasses a very diverse chemistry and physics to assemble larger structures
from molecules or atoms. Nature uses SA almost exclusively to make nacre, DNA, cells, wood, and mammal teeth. Researchers have spent decades trying to bio-mimic\textsuperscript{232} Nature’s superior SA protocols in the laboratory with some success\textsuperscript{233,234}. The few strategies that do show promise are Langmuir Blodgett\textsuperscript{235,236} (LB) and self-assembled monolayer\textsuperscript{237,238} (SAM) techniques. The LB performs well for building up multilayer thin films and other structures but suffers greatly from expensive instrumentation and not all non-amphiphilic materials are compatible with this strategy, severely limiting the types of structures made. The SAM strategy has a wider variety of compatible materials but it is difficult to make free standing structures – a great drawback because the substrate usually hinders said structure’s physical properties. Layer-by-layer (LbL)\textsuperscript{239} is bio-inspired absorption strategy is a straightforward and relatively inexpensive nanofabrication process for multilayer formation and allows a wide variety of materials to be incorporated suffering none of the disadvantages of LB or SAM assembly. Of the many hierarchal structure shapes LbL can make, thin films are only considered here because of important connection to transistors, electrodes, gas barriers, and displays.

Decher\textsuperscript{240,241} experimented in electrostatic self-assembly (ESA) in the 1990s but reports have been made earlier. A generic schematic of the LbL process is outlined in figure 5:6. The main driving force is based on the electrostatic attraction of oppositely charged molecules – polyanions and polycations. A solid substrate with positively charged planar surface is exposed to a solution of anionic polyelectrolytes for a short time (30 seconds to 30 minutes). An electrostatic
potential gradient is setup and eliminated when charge neutralization takes place and the adsorption of a polyanion single layer onto the surface results. At high solution concentrations or low concentrations and longer times, a charge resaturation occurs, leading to a charge reversal – which happens when the polyion has a higher stoichiometric charge number relative to the substrate. This step is self-limiting and the thin film now has a negative charge. Polyanion solution is usually labeled as “-“ and polycation as “+”. A pair of these, “+-“ is called a bilayer. So an LbL film made of 5 bilayers, “+-+-+-+-+“ would have 10 layers total.

Figure 5:5 General schematic and mechanism of LbL assembly\textsuperscript{242}. 

![Diagram of LbL assembly process](image-url)
The process repeats when the substrate (with the polyanion single layer) is exposed to a solution cationic polyelectrolyte solution and then cycle restarts again with the polyanion solution, etc. Sometimes a wash cycle of water or some other good polyelectrolyte solvent is used to rinse away surplus adsorbent. This cycle of alternating surface charges builds up thin films one layer at a time, affording precise depositions from nanometer to micrometer range\textsuperscript{243}. Because the process involves adsorption from solution, there are few drawbacks with respect to substrate size and morphology. This makes LbL strategy scalable and second only to Atomic Layer Deposition\textsuperscript{244} (ALD) in terms of control; however, LbL does not need high vacuum equipment and can be done at room temperature and pressure. A variety of organic and inorganic materials are compatible with LbL process unlike the very limited LB process. Thin films have been made from clays\textsuperscript{245}, proteins\textsuperscript{246}, DNA\textsuperscript{247}, CNTs\textsuperscript{248}, graphene\textsuperscript{249}, and colloidal nanoparticles\textsuperscript{250}. Functional thin films have been made for MEMS\textsuperscript{251}, biosensing\textsuperscript{252}, drug delivery\textsuperscript{253}, and electro-chromic applications\textsuperscript{254}. The charged solid substrate can be even three dimensional and can act as a sacrificial template to create nanotubes\textsuperscript{255}, spherical hallow capsules\textsuperscript{256}, and micro/nano-gels\textsuperscript{257}. Unlike SAM and LB process, the solid substrates used in LbL are relatively tolerant to micron-sized surface defects – an ability not found in CVD. This lies in the entropic conformation properties of the polyelectrolytes ability to bridge over surface pits, cracks or any other surface defects\textsuperscript{258}. Though the driving force for layer assembly is in the kinetic interaction of opposing charge groups on constituent components, a total account of the interplay of mechanisms and effects on film
quality involved is still under investigation with just very general rules on deposition.

For polymer LbL, the solution thermodynamics between solvent and polyelectrolyte as what Flory and Huggins$^{259}$ describe seem to be one of the main factors of LbL assembled films. An extended chain polyelectrolyte deposits a thinner, smoother layer than bulky compact globules. Molecular weight, ionic strength, and polyelectrolyte charge density also affect LbL film properties. Generally, higher molecular weight increases deposition time and higher charge density results in thicker films. Other film formation mechanisms such as hydrogen bonding have been shown to aide in film formation. The modularity of LbL process allows covalent bonding (even click chemistry$^{260,261}$) reactions to occur during or film formation, with the aim to increase film stiffness. The last few years, LbL assembly has become an umbrella including new LbL techniques. Spray LbL$^{262}$ (SLbL) is the merging of spraying technology with LbL to make films sprayed on one layer at a time. Spin-assisted LbL$^{263}$ (SpLbL), the merging of spin solution casting with LbL is another also falls under this category. In many ways, both new techniques resemble ALD, but without the expensive ultra-high vacuum apparatus and an order of magnitude faster than traditional LbL.
The LbL system under investigation is a combination of hydrogen bonding LbL process and in-situ polymerization between aligned GO sheets parallel to the thin film pane and polyamide for strong, smooth conductive thin film. This idea is bio-inspired from examining the layered structure of sea shells (figure 5:7). The shell of *Haliotis tuberculata* and other gastropods is composed of nacre – an organic/inorganic composite material. Nacre has sheet-like micron sized calcium carbonate crystals orientated in one direction and separated from one another by an organic compound composed of protein. To bio-mimic this in the lab, a clean, smooth, charged rigid substrate is needed for LbL assembly. To this end, microscope slides (25mm × 75mm × 1 mm, Premiere) and silicon substrates were cleaned with piranha in a 3:7 volume ratio of H$_2$O$_2$ to H$_2$SO$_4$ solution for 10 minutes, rinsed with DI water and dried with dry N$_2$ gas. The substrates were then functionalized with 3-aminopropyl triethoxysilane (APTES) by immersing in a 1:9 volume ratio of APTES.
and toluene solution for 1 h at 23 °C. After 1 h, the substrate was rinsed with freshly
distilled toluene, sonicated in toluene for 10 minutes and rinsed with MeOH
followed by drying with N₂ gas. The LbL PAA-f-CCG composite films were fabricated
by manually alternated dipping of the substrate into Pyromellitic dianhydride-
oxydianiline polyamic acid (PAA) and f-CCG solutions. The APTES functionalized
microscope slide was immersed in a 1 wt % solution of PAA for 1 h (step a, figure
5:7). The slide was rinsed with copious amounts of NMP to remove the excess PAA
(step b) followed by drying with dry N₂ gas. Step b was followed by immersion in a
0.1 wt % f-CCG solution in DMF (step c). Finally, the slide was rinsed with DMF (step
d), followed by drying with N₂. Steps a-d comprises the deposition cycle resulting in
a bilayer deposited on the substrate after each round. The manual LBL assembly
was performed for 10 cycles.
Manual LbL process is very tedious so an automated solution was employed. A modified Asymtek dispensing machine (Asymtek Model d-583) (figure 5.9) was fitted with a clamp for glass slide attachment followed the protocol described in figure 5:8. The layers were assembled by immersing the APTES-functionalized glass slides in a 1% PAA solution for 10 min followed by rinsing for 2 min in a beaker with NMP (3 times), and flush drying with N₂ gas. This is then followed by immersion into the f-GO solution and subsequent rinsing. The whole assembly was repeated 40 times. The imidization of the LbL assembled films was conducted after LbL assembly in a Linberg/Blue M gravity oven at 100 °C for 1 hour followed by
heating at 225 °C for 1 hour. The fabricated composite film samples were characterized by X-ray photoelectron spectroscopy (XPS) using a Phi Quantera SXM Scanning X-Ray Microprobe with a pass energy of 26 eV, 45° takeoff angle and a 100 µm beam size. Raman spectroscopy was performed using Renishaw Raman scope using a 633 nm He-Ne laser. FTIR analysis was performed using a Nicolet FTIR fitted with attenuated total reflectance (ATR) attachment. Atomic force microscopy (AFM) images were obtained using Digital Instrument Nanoscope III in tapping mode. Differential Scanning Calorimetry (DSC) was performed using a Q-600 from TA Instruments. Gas used on DSC was N₂ gas and a ramp rate of 5°C/min.

Figure 5:8 Automated assembly and resultant thin PI-CCG film.
4.3. Discussion

Graphene oxide-polyelectrolyte LbL assembled films was first reported by Kotov\(^{265}\). Self-assembly of poly (diallyltrimethylammonium chloride) (PDDA) and GO was driven by the polycationic charge densities of the PDDA and the polyanionic nature of the GO by adjusting pH. The approach using GO allowed for ordered incorporation of graphite sheets in ultra-thin polymer films. Reduction of the samples was accomplished by either hydrazine, or other reductant chemicals, or electrochemically, rendering conductive sandwich structures. Since Kotov’s paper, many other LbL films have been assembled with GO as a filler\(^{266}\). Along this same line of thought, the fabrication of thin films comprised of f-GO and polyimide (PI) were fabricated. PI is known for its good thermal and chemical stability and strong mechanical properties but poor gas barrier properties. For example, clay types of monomillutrite have a plate-type structure that improves gas barrier properties. GO, with a similar structure, may be as good as or better than clays in producing composites since graphene is known to be an impermeable membrane even to helium and capable of withstanding high pressures. This composite system could further enhance the barrier and gas selective properties of polyimides, in addition to improving structural reinforcement and electrical conductivity.

To take advantage of the desirable thermal mechanical and electrical properties of the graphene sheets, in-situ reduction of GO within the polymer matrix is usually employed. For polyimides however, the use of GO and its subsequent reduction would have harmful effects for many PIs including PAA. PAA is
susceptible to hydrolytic chain scission and PI is vulnerable to ring opening by hydrazine. Also, reduction by dehydration of GO during imidiazation might produce too much water, leading to oligomerization of the PAA. To circumvent this problem, f-GO was employed in order to have a reduced form of graphene sheets without the need for chemical reduction. In addition, reduced GO (RGO) is not soluble by itself and the driving force for assembly is less controllable by itself, thus GO was made into f-GO by aryl salt functionalization. Pyromellitic dianhydride-oxydianiline polyamic acid (PAA) is produced from two monomers by a condensation polymerization reaction: pyromellitic dianhydride (PMDA) and 4, 4’-oxydiphenylamine (ODPA) in shown in figure 5:9.

![Pyromellitic dianhydride-oxydianiline polyamic acid (PAA) condensation reaction](figure59.png)

**Figure 5:9 Condensation reaction of PAA from dianhydride and diamine.**

The addition of the two monomers at ambient temperature in dipolar aprotic solvents (DMAc, NMP) leads to an intermediate polyamide called poly (amic acid) (PAA) by nucleophilic attack of the amino group (its unshared pair of electrons) on the carbonyl carbon of the anhydride group. This reaction is the bonding between the carbonyl carbon and nitrogen; resulting in the formation of a cyclic configuration with the pi electrons shifted to the oxygen. Requirements for this
reaction are a one to one stoichiometric ratio of monomers (used to maximize this reaction) and high purity monomer content. This first step of this two-step reaction occurs usually within 24 hours of mixing. In the second step, heat (generally 200 to 300 °C) is applied to activate imidiazation by cyclodehydration between the amide and acid groups, closing the ring and releasing water. This process is used in industry for bulk iridizations. However, chain degradation is caused by two events: water release during reaction and unyclized amic-acid groups. In the f-GO PI thin films, heating was done in two stages: one at 100 °C to evaporate solvent and water and the second at 225 °C to promote imidiazation (figure 5:10).

\[
\begin{align*}
\text{PAA} & \to -\text{H}_2\text{O} \\
\text{Heat} & \to \text{Kapton (PI)}
\end{align*}
\]

**Figure 5:10 Thermal imidization and ring closing of PAA.**

The most utilized driving force in LbL assembly has been the attractive complementary charges of polyelectrolyte systems. But the technique has now been extended for other driving forces such as charge transfer, hydrogen bonding, biological recognition, hydrophobic interactions and van der Waals forces. An attractive feature of the process arising from these interactions is that the rinsing steps remove the excess layers due to non-interaction or repulsion. The interactions
exploited in this work are the acid-base interaction between the aniline group of the f-CCG 2 and the carboxyl functionality of the PAA chains.

LbL assembly is driven by the hydrogen bonding between PAA and f-GO. During thermal imidization, the possibility of covalent reaction between the amine groups of the f-GO and the acid groups of the PAA. While this could inhibit imidization, the graphene sheets would be grafted to the PI chains forming a strong, gas barrier thin film composite. The initial assembly of layers was monitored by XPS after adsorption of each layer on a 200-nm SiO2 coated silicon wafer. Figure 5:11 shows the survey scans obtained on a Si substrate after (5:11a) piranha treatment (5:11b) APTES functionalization (5:11c) deposition of PAA and (5:11d) deposition of CCG. There is significant increase in the nitrogen content after APTES and PAA assembly. For figure 5:11, the carbon/nitrogen ratios are estimated to ~ 6.8. After the deposition of graphene however, the ratio increase to 71 due to the increase in carbon fraction from the graphene framework.
**Figure 5:11** XPS survey scans on Si substrate after (a) piranha treatment, (b) APTES assembly, (c) PAA deposition, and (d) f-CCG (2) deposition. Note the increase in carbon fraction in (d).

XPS analysis of the film showed that the imidazation at 225°C is complete with the C1s core-level spectrum resembling that of bulk polyimides (Figure 5:12). The peak assignments are as follows: 284.8 eV (C=C, C-H); 286 eV (C-O) and 288 eV (imide peak).
Raman analysis of the 40 bilayer film (figure 5:13) showed imide peaks in agreement with the results reported by Pethe. The imidized thin films showed the following Raman bands: 1200 – 1300 cm\(^{-1}\) (C-O-C stretch), 1397 cm\(^{-1}\) (imide C-N stretch), and 1660 cm\(^{-1}\) (imine C=N stretch) and 1790 cm\(^{-1}\) (symmetric C=O imide stretch). The narrow peak at 1350 cm\(^{-1}\) is assigned to the diamondoid peak (D-peak) of the f-CCG while the graphitic peak (G-peak) is not evident as it overlaps with the imine C=N stretch (shoulder). The spectrum was collected with the pinhole engaged to minimize the fluorescence starting at 1500 cm\(^{-1}\) and extending to 3300 cm\(^{-1}\).
AFM analysis was performed on the thin film after the 40 bilayer depositions (Figure 5:14). After piranha treatment and APTES functionalization, the glass substrate shows a rough morphology, (Figure 5:14a). The thickness of APTES deposited during salinization, based on ellipsometry, was estimated to be ~5 nm. The in-plane structure of LbL film after 40 bilayer depositions is shown in Figure 5:14b. The mean roughness measured is about 2.7 nm, although some aggregated...
flakes are visible. Section analysis (Figure 5:14c) showed that the large flakes have heights reaching up to ~9 nm and the coverage of graphene sheets.

![AFM micrographs](image)

Figure 5:14 AFM micrographs of (a) APTES treated glass slide (phase mode), (b) in-plane morphology of 40 bilayer LbL assembled films, and (c) section analysis of the 40 bilayer film.

The inhomogeneity of the film surface is also evident on the SEM micrographs obtained. Figure shows a representative example of the surface.
obtained after 40 depositions. Based on the section analysis of the deposited films, the estimated thickness is about 28 nm.

Figure 5:15 SEM micrographs of 40 bilayer film (a) in-plane structure showing rough morphology and (b) cross-section image.
Dynamic Scanning Calorimetry (DSC) was used to determine the glass transition ($T_g$) and crystallization of the LbL thin films (figure 5.16). The 40 bilayer nanocomposite were obtained using a TA Instruments Q20 Series in a N$_2$ environment. Temperature was ramped at 10°C/min from 25 to 300°C at 1 min isothermal. A 40 bilayer imidized PI film without CCG was used as a control. The $T_g$ values were determined from the mid points of the corresponding glass transition regions. From figure 5.16a, the control sample shows the main melting point at 218°C and a second, minor one at 211°C. These are $\alpha$ and $\gamma$ crystal phases respectively. For the nanocomposite (figure 5.16b) $\alpha$ signal shifts to 221°C and $\gamma$ signal is not present. The CCG appears to have stabilized $\alpha$ phase in favor of $\gamma$ or that the CCG has reduced $\gamma$ crystallites to such a small scale where DSC cannot detect. This has been reported before and x-ray diffraction techniques revealed a weak $\gamma$ signal. The $T_g$ enhancement for the LbL films: 62°C for PI LbL control and 115°C PI-C; CG LbL. Though $T_g$ modification by nanofillers is well-reported, the LbL process itself plays a critical factor. Kotov et al reported how the structural organization of nanofillers courtesy of the LbL process maximizes polymer-nanofiller interactions compared to other nanocomposite processing methods. In addition to the LbL process effect, the imide and hydrogen bonding between CCG and PI chains further constrains polymer motion to a high degree leading to enhanced thermal transitions.
Nature inspired process such as LbL has been demonstrated using all organic materials in a reasonable time. Thin films have been successfully made comprising of CCG and polyimide using LbL assembly largely driven by acid-base interaction of the aniline moiety on the \( \text{f-CCG} \) and the carboxylic acid groups on PAA and the use of \( \text{f-CCG} \) circumvented the use of reducing agents such as in-situ hydrazine. This could to applications such as piezo-electric devices and coatings for selective gas permeation\(^{268}\). The LbL assembled CCG-PI films may find potential application in fuel cell membranes\(^ {269}\).
Chapter 5

Fluorinated Graphene Oxide

5.1. Synthesis

As the previous chapters have demonstrated, when graphene is imbued with hydroxyl, carbonyl, epoxy, and phenol functionalities, GO can be an extremely versatile precursor for composites and devices. This versatility is a consequence of GO’s ease of tuning the sp³/sp² ratio, the C:O ratio, or highly selective functionalization protocols. However, there are few reports on imparting inorganic functionalities in graphene²⁷⁰. While considerable progress have been made in merging boron-nitride (BN)²⁷¹ with graphene by CVD and fluorine²⁷² doping of graphene by gas phase reactions, yield is fantastically low. This is concerning as graphene doped with inorganic elements such as the halogens would greatly expand graphene’s repertoire of applications²⁷³. One remedy would be to copy GO’s ability
to be manufactured in bulk by using graphite and then dope it with inorganic elements. In 1934, Ruff et al heated graphite in a stream of F₂ at 420 to 260 °C to make nonstoichiometric fluorinated graphite (FG) of the chemical formula, (CFₓ), where x = .25 to 1.12. Depending on the amount of fluorine content, FG retains the layered structure of graphite but in a puckered morphology with sp³ C-F and sp² graphite domains (figure 6:1).

![Figure 6:1 Unit cell of (a) graphite and (b) FG. Closed dots are carbon atoms and open circles are fluorine atoms.²⁷⁵.](image)

This configuration is due to the highly polar covalent nature of the C-F bond. This morphological frustration between this and the planar sp² carbons leads to this boat-like or puckered stacked conformation. Compared to pure sp² graphene, FG has a C-C bond of 0.005 nm longer than graphite and the C-C-C bond is 2° smaller²⁷⁵. Interestingly, FG share a few of the applications used for graphite such as solid
lubricants and battery materials\textsuperscript{276}. Unlike, GO, FG has no oxygen-based functional
groups limiting the ability to be solution processed. To this remedy this, applying
the same acid-oxidant treatment used for GO to FG is explored for high yield.

To a 500 mL flask, 4 g of fluorinated graphite polymer CF\textsubscript{x} where x = .25 (Alfa
Aesar, 42537) was dispersed in a 9:1 volume mixture (360:40 mL) of H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{3}PO\textsubscript{4}
and stirred magnetically at 50 °C for 2 hours (figure 6:2). 18 g of KMnO\textsubscript{4} (Aldrich)
was then added to the mixture in parts of 3. During KMnO\textsubscript{4} addition, a whistling
sound was observed along with an increase in temperature spike at 90° C and the
color of the solution had changed from black to dark brown after which the mixture
was left to stir for 12 hours at 50° C. After 12 hours, the temperature and mixing was
turning off and allowed to reach RT. The mixture was then poured slowly over DI
water ice (500mL in a 2L flask) and then added 10 mL H\textsubscript{2}O\textsubscript{2} in parts of 2 and stirred.
During this step, an effervescence and evolution of yellowish-brown color was
observed and the solution color turned white, and then yellow indicating oxidation.
Simultaneously, a fluffy dark brown solid phase was observed to precipitate out to
the bottom of the solution and grayish slurry floating at the top surface of the
solution. The two phases were allowed to phase separate overnight, after which
both phases had formed, as pictured in figure 6:2 top and bottom

Figure 6:2 Schematic of FGO process with isolated phases (top) HFGO in THF and (bottom) in FGO in DI water.

To ensure this was not some experimental quirk, the experiment was repeated over 7 times, and each time 2 distinct phases were observed in figure 6.3. FG is hydrophobic due to the rich C-F bonding and just going by visual inspection of the two phases, there is a redistribution of fluorine content – one rich and the other poor in fluorine. Therefore, the top phase is called Highly Fluorine Graphite Oxide (HFGO) and bottom phase Fluorine Graphite Oxide (FGO). HFGO was scooped out of solution using a Teflon spatula by hand and filter washed with 400 mL of DI water with an Omnipore 0.1 μm membrane. After which, HFGO was washed with 200 mL
of ethanol and 200 mL of ether and allowed to vacuum dry for 24 hours. For FGO, as much of the supernatant was decanted as possible and the wash-filter process was repeated again. Both phases where then dispersed in the appropriate solvent (FGO in water and HFGO in Tetrahydrofuran (THF)) and centrifuged (6000 rpm, 2 hours), after which they were isolated and washed with 200 ml of 30 wt% HCl, 200 mL ethanol and soaked in diethyl ether. In appearance, FGO is a dark brown powder which forms homogeneous colloidal suspensions in water, while HFGO has a light gray color and repels water. HFGO weight roughly 2g while FGO weight roughly at 4g.

Figure 6:3 After 30 hrs of adding DI water and H₂O₂. Both phases remained stable.
One of the very first tests of the two phases is the measure of solubility in various solvents that are used commonly in solution polymer nanocomposite processing. Figure 6.4 shows the stability in THF, NMP, and ethanol for HFGO and FGO after 3 hours. Overall, both phases demonstrated good stability in said solvents.

![Figure 6:4(a) solubility of FGO after 10 hours and (b) HFGO after 3 hours](image)

**5.2. Characterization**

HFGO and FGO morphology is revealed to see how close it is to GO. High-resolution TEM and SEM (figure 6:5) of FGO and HFGO showed their morphology to be in the form of sheets with a well-defined basal plane and edges. Both types have a sheet size between 500-800 nm which is on the order of that reported for GO.
Figure 6:5 TEM images of FGO (a) and HFGO (b) show sheeted structures, with both nanomaterials existing as 2D nanosheets upon exfoliation having defined geometries on the basal plane and edges.\textsuperscript{277}.

The AFM of HFGO in figure 6:6 confirms the sheet like structure found in TEM and SEM. Though mostly smooth, the variations in thickness (1 nm max) could be from the functional groups imparted by the acid-oxidation treatment.
Figure 6:6 AFM of (a) HFGO and (b) side view\textsuperscript{277}.

XRD of both FGO and HFGO is shown in figure 6:7. The spectra show evidence of a stacked structure of the nanosheets and degree of order before and after
synthesis. Tetracarbon monofluoride (C₄F) has a similar structure and its models have been proposed that suggest a layered structure of C₄F. C₄F contains regular distorted regions of graphitic sp² planes with three C-C sp³ bonds and one covalent C-F sp³ bond and structurally isolated hexagonal regions with conjugation of three C-C bonds. The XRD of pristine fluorinated graphite polymer, which also has the chemical formula (CF₀.25)ₙ exhibits a sharp graphitic peak at 26° corresponding to the (002) plane of graphite while the remaining peaks are in agreement with those reported. The XRD spectra of both the exfoliated nanosheets, which have previously not been studied, show unique features different from²⁷⁸. The FGO phase has a prominent peak at 10°, which is also found in GO resulting from an increase in interlayer spacing from 3.3 Å to 6 Å due to functionalization of the basal plane. The remaining peaks are diminished, possibly due to the partial removal of other semi-ionic/covalent C-F bonds.
Figure 6:7 XRD shows a considerable increase in interplanar spacing, almost identical to that of GO after oxidation.\textsuperscript{277}

Raman analysis in figure 6:8 shows the restoration of the graphitic lattice in the FGO sample. In comparison, FG does not show graphitic D and G peaks due to a
highly distorted graphite lattice. The HFGO shows an XRD peak at 10°, indicating functionalization and exfoliation in solution, while its Raman spectrum shows less intense D and G peaks corresponding to a sp² lattice with slightly less ordering compared to the FGO phase.

Figure 6:8 Raman spectra of all three phases²⁷⁷.
Magic angle spinning (MAS) $^{13}$C NMR was used to provide a better look at the chemical composition of each phase and compared to paper$^{279}$. The NMR spectrum of FGO (Figure 6:9) is similar to GO, with the exception of a signal at 88 ppm that does not appear in the spectrum of GO. The 88 ppm signal is matched to a tertiary alkyl fluoride compound, as opposed to a secondary or primary alkyl fluoride or an aromatic fluoride, all of which would give significantly more deshielded $^{13}$C signals for the C-F bond that would be obscured by other signals. The other signals are typical of the epoxide, alcohol, alkene, aromatic, and carbonyl functional groups in GO. The relative signal intensities are believed to be meaningful, as a preliminary spectrum obtained with a shorter relaxation delay is similar. The signal at 88 ppm dominates the spectrum of the HFGO, which still shows the presence of epoxy, alcohol, and aromatic peaks, but there is no detectable carbonyl intensity in the sample. The relative abundance of each functional group, in particular the aliphatic C-F, is different in each structure, thus the naming of each phase. The ability of MAS at 15 kHz to effectively eliminate $^{13}$C-$^{19}$F dipole-dipole broadening has been demonstrated in work on fluorinated carbon nanotubes. High power $^1$H decoupling is still used to eliminate $^{13}$C-$^1$H dipole-dipole broadening. The reasons for the absence of any detectable scalar $^{13}$C-$^{19}$F coupling in the NMR spectra of FGO and HFGO are the same as in the NMR spectra of fluorinated CNTs. The tuning and matching characteristics of the NMR probe with FGO and HFGO provide another indication of the relative amount of structural alteration of the graphitic plane of the FG precursor. While FGO exhibits a modest change in probe tuning and matching for
both the 13C and 1H channels compared to glycine, HFGO exhibits almost no change, even more extensive functionalization of the graphitic plane has occurred.

**Figure 6:9 NMR spectra of (a) FGO and (b) HFGO**

ATR-FTIR spectra of both FGO and HFGO confirm data of the functional groups identified by NMR. The peaks at 1208 cm\(^{-1}\) in figure 6:10 are due to stretching vibrations of the C-F bond from tertiary sp\(^3\) carbons and a low intensity peak at 1730 cm\(^{-1}\) could be ascribed to a small amount of carbonyl groups in HFGO, which could not be detected in the NMR spectrum. The FTIR of FGO is identical to GO with a sharp peak at 1208 cm\(^{-1}\) indicating the presence of covalent C-F bonds with the remaining peaks has been accounted for in previous literature. HFGO shows the same peak at a considerably greater intensity and confirms an aromatic character (1620 cm\(^{-1}\)) with other organic groups.
Figure 6:10 ATR-FTIR of FGO (a) and HFGO (b).  

An XPS spectrum was done on both FGO and HFGO and deconvolution the C1s peak in figure 6:11. FGO shows a well-defined sp² domain with functional groups and C-F peak. HFGO shows a C-F peak and well-defined sp² domain but a much higher intensity than that in FGO, confirming much higher fluorine content in HFGO. From a structural point of view, this is also in agreement with FTIR and NMR data, both of which point towards similar structures for both FGO and HFGO with the latter having a significantly higher abundance of fluorine.
Figure 6:11 XPS spectra of (a) FGO (b) HFGO\textsuperscript{277}.

The company software from the XPS machine was able to give an atomic concentration account of both phases. Table 6:1 gives a breakdown of the relative concentrations of carbon, oxygen, and fluorine in HFGO and FGO with GO as a
comparison. This part of the data is in agreement with FTIR and NMR data, both of which point towards similar structures for both FGO and HFGO with the latter having a significantly higher abundance of fluorine.

Table 6.1 Summary of atomic percentages of C, F and O taken at three different sample areas. The chemical structure is similar to GO without the presence of fluorine in both compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C (%)</th>
<th>O (%)</th>
<th>F (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorinated Graphene Oxide (FGO)</td>
<td>76.60</td>
<td>17.80</td>
<td>5.60</td>
</tr>
<tr>
<td>Highly Fluorinated Graphene Oxide (HFGO)</td>
<td>64.61</td>
<td>11.45</td>
<td>23.00</td>
</tr>
<tr>
<td>Graphite Oxide (GO)</td>
<td>65.2</td>
<td>34.71</td>
<td>0</td>
</tr>
</tbody>
</table>

FG is very thermally stable structure and it would be of interest to see how well it stacks up to the two phases. To this end, a Q500 Thermal Gravimetric Analysis (TGA) from TA Instruments was employed. 100 mg samples from HFGO, FGO, and FG were placed in platinum sample pan and run from room temperature to 1000 °C in an argon gas atmosphere.
The FG curve in figure 6:12 agrees well with reported literature with the steep drop in weight around 600°C ascribed to gases release of C$_2$F$_4$. HFGO having 10 to 12% more oxygen than FG, degraded faster as C-F bond is stronger than the C-O bond. The drop at 250°C is most likely CO or CO$_2$ release and drop at 600°C could also be C$_2$F$_4$. Finally, FGO showed an almost linear decline with temperature indicating the oxygen rich functionality confirmed by XPS and FTIR.
UV-Vis spectroscopy of both FGO and HFGO showed well-defined absorption peaks in figure 6:12. The absorption spectrum of FGO is almost identical to GO, showing a peak at 225 nm corresponding to the pi transitions and small shoulder at ~300 nm due to the vibration transition of the carbonyl bonds. HFGO shows no match in shoulder at 300 nm, while showing a slightly less intense peak at 220 nm.
5.3. Discussion

From all the characterization, one possible mechanism for phase separation and formation of FGO and HFGO is proposed. The Modified Hummers Method results in complete oxidation and exfoliation acting upon the surface layers of the planar hexagonal FG. FG contains both semi-ionic and covalent C-F bond character. The semi-ionic bonds can be easily removed by the Modified Hummers Method and that part of FG is completely oxidized and settles down, forming FGO. The other part remains hydrophobic even after exfoliation due to the high content of polar C-F bonds, resulting in HFGO. Based on all characterization methods discussed in this chapter, a model of both phases is presented in figure 6:13.

Figure 6:13 UV-Vis of (a) HFGO and (b) FGO.277.

Figure 6:14 Computed model of (a) FGO and (b) HFGO.277.
Among the proposed applications of HFGO and FGO could be in piezoelectric polymer nanocomposites, cancer targeting agents, and electronic devices\textsuperscript{281}. Piezoelectric polymers such as Polyvinylidene fluoride (PVDF) can wet HFGO readily and maintain a dispersed state due to like fluorine groups enhancing actuation\textsuperscript{282}. Fluorine is MRI active\textsuperscript{283}, and having bio-inert nanoparticles with fluorine functionality could enhance early detection of cancer.
Chapter 6

Thermoplastic Polyurethane Graphene Nanoribbon Thin Film Composites

6.1. TPU-GNR Synthesis and Characterization

Thermoplastic Elastomeric Polyurethanes\textsuperscript{284} (TPUs) are linear block copolymers made up by alternating hard and soft segments formed by the reaction of diisocyanates with diols. Soft segments are composed of long chain diols and hard segments consist of diisocyanates and short chain extender molecules (figure 7.1a). Thermodynamic incompatibility results in phase separation and organization into hard and soft phases with an interphase phase separating the two at room temperature. The driving force for this separation is: melting points, polarity difference, and crystallinity. Hard phases have a higher melting point and polarity than the soft phase. The soft segments form an amorphous region that imparts elastomeric character while the hard segments consist of either glassy or
semicrystalline regions that act as physical crosslinks and impart stiffness and reinforcement (figure 7.1b). Because of this morphology, mechanical properties such as strength, elongation, and modulus can be tuned by changing hard/soft segment content leading to broad applications ranging from medical devices to deployable structures in space. Recently, nanocomposites formed from nanofillers (layered silicates, carbon nanomaterials) and TPU have been reported using various polymerizations and processing techniques that modify the TPU matrix for a host of properties such as improved barrier, electronic, and mechanical properties that no soft/hard monomer engineering can attain alone. This study aims investigate the viscoelastic and barrier properties of TPU with high aspect ratio graphene nanoribbons (GNR) made from Tour et al for the first time.
In a N₂ glove box, to a dry, 250 mL beaker, 250 mg of multi-walled CNTs where added to 150 mL 1, 2-dimethoxyethane (DME) and liquid 0.5 mL Na/K alloy (figure 7.2). The flask containing the mixture was then sealed with a septum and transferred out of the glove box where the reaction mixture was dispersed by a short 5 min Cole-Parmer ultra-sonication to yield a dark greenish to red suspension. After ultra-sonication, the reaction mixture was vigorously stirred at room temperature for 3 days. The reaction mixture was then quenched by the adding 20
ml 1-iodoalkane by a pneumatic syringe and left to stir at room temperature for one
day. 20 mL of Methanol was then added to sequester any excess Na/K alloy, and
then stirred at room temperature for 10 hours. For extraction, the reaction mixture
was filtered over a 0.45 μm pore size PTFE membrane and washed in sequence with
100 mL THF, 100 mL isopropanol, 100 mL H2O, 100 mL isopropanol, 100 mL THF
and 10 mL ether. Then a Soxhlet extraction apparatus was used with THF was used
for 3 days, and the product was dried in vacuum for 24 hours.
Commercial biomedical grade aliphatic, polyether based TPU (Tecoflex® EG 80A injection grade) was bought from the Lubrizol Corporation (Ohio, USA). Tecoflex EG 80A (around 35% of hard segments) having density of 1.04 g/cm³ and constituent formulation is methylene bis(cyclohexyl) diisocyanate (HMDI) hard segment and polytetramethylene glycol (PTMG) soft segment (molecular weight = 1000 g/mol) and chain extender 1,4 butane diol (BD). GNR-TPU nanocomposites were made by making a solution of THF and TPU (0.2 g/mL), adding GNR (.05 to 5 weight %), and magnetically stirring under 70°C for 5 hours. Finally, the solution was sonicated for 10 minutes and then drop cast onto 20mm diameter Petri Pyrex dishes. The samples were then transferred to a vacuum oven and baked at 80°C for 6 hours to ensure solvent evaporation.

To see how well dispersed the GNR is within the TPU matrix, nanocomposites and a control were immersed in a liquid nitrogen bath for 30 minutes and fractured. SEM was done on the newly fracture surface and is shown in figure 7.3. Clearly GNR is seen on the fractured surface and absent in the control sample.
Figure 7.3 SEM cross section of TPU-GNR composite (left) and control TPU (right).

To compare the thermal stability of GNR and the TPU-GNR nanocomposites, TGA was done from room temperature to 500 °C at a ramp rate of 2°C/min under an argon atmosphere. About 10 mg of each sample were tested in a Pt/ceramic pan. Figure 7.2, the GNR is extremely stable at high temperatures except in the 250° region where the drop can be attributed to hexadecane being boiled off from the GNR edges. This drop is shifted to higher temperatures as seen in the composites (0.05 to 5 wt %). An explanation is shift lies in the hydrogen bonding network between the TPU matrix and the hexadecane functional groups. With TPU control having no GNR filler hence no hexadecane groups to boil off, it is the most stable at this temperature range. However, starting at 350° (which is thermal decomposition for TPU), all TPU GNR composites has a slower rate of loss compared to control. This
verifies that even with the loss of hexadecane functional groups, the GNR still have a reinforcing effect.

Figure 7:4 TGA of GNR and TPU-GNR composites.

The Raman spectra (excitation at 514 nm) of GNRs are shown in figure 7.3 to determine graphene quality after the unzipping reactions. There is a relatively weak D-band 1350, a strong G band at 1580 and G+D at 2950 cm⁻¹. Just as in graphene, the D/G intensity ratio is a commonly used parameter to gauge the sp² graphitic quality of GNRs. In this measurement, the D/G ratio was around 2.5 to 2.8 indicating good amount of graphene quality. With GNR having more edge states than CVD grown graphene (or GO for that matter), sp³ character of the edge influences the D peak
strongly, hence an observed G+D peak but this nanofiller has more sp² character than previous used graphene fillers.

![Raman analysis of GNR compared to GO.](image)

**Figure 7:5 Raman analysis of GNR compared to GO.**

FTIR spectra of TPU and all TPU-GNR composites are shown in figure 7.4 and were used to see the amount of hydrogen bonding between GNR fillers and TPU. From figure 7.4a the relevant peaks are a large 1730 cm⁻¹ which is identified as the -C=O carbonyl groups that are free (non-hydrogen bonded) and a smaller one at 1715 cm⁻¹ from urethane N-H groups hydrogen bonded. Though the main peak is relatively unchanged, the smaller one almost vanishes at the highest GNR loading. In figure 7.4b, one peak, 3330 cm⁻¹ are the hydrogen bonded N-H stretching in TPU and an absence of 3460 cm⁻¹ free N-H stretching. This absence indicates all N-H groups
are all hydrogen bonded. The suppression of 1715 and 3330 cm\(^{-1}\) indicate phase separation of the hard polar domains in the soft TPU matrix by way of increased hydrogen bonding\(^{287}\). Indeed, it has been documented that certain nanofillers can reduce hydrogen bonding in the hard, polar phase such as clay silicate nanosheets which would explain reduced mechanical properties. The addition of GNR into TPU seems to have the direct opposite of this.
Figure 7:6 FTIR spectra of (a) Soft domain and (b) hard domain in TPU-GNR nanocomposites.
6.2. Dynamic Mechanical Analysis of GNR-TPU Films

Polymers exhibit viscoelastic behavior which is a mechanical property intermediate between energy-storing elastic solids and energy-losing viscous liquids. An example of this behavior would be Silly Putty. Rolled into a ball it can bounce like a ball and striking it with a hammer it shatters like a solid. At this end of the spectrum for small strains, the general form of Hook’s Law of Linear Elasticity explains this type of mechanical behavior. When left on a table for a few hours Silly Putty flows like a liquid. This is time dependent behavior and Newton’s Law of Viscosity describes this behavior. When crystalline metals and ceramics plastically deform, they deform by atomic or molecular displacements at specific crystallographic planes and directions. When polymers deform, they do not involve these movements but is a continuous displacement of atoms or molecules taking place over time. This deformation mechanism is related to the diffusion of atoms or molecules within a material. At higher temperatures, where diffusion becomes substantial, both crystalline and amorphous materials show a large amount of thermally influenced plastic flow behavior similar to that found in liquids. The viscosity of fluid results in a frictional energy loss, which manifests as heat energy dissipated. The more viscous a fluid, the higher is the frictional energy loss and therefore more heat energy released.

Newton’s Law of Viscosity and Hookean Mechanics are used to describe viscous and elastic behavior respectively but fail in describing viscoelastic properties. This is due to the inherent time-dependent behavior. To properly
characterize a viscoelastic material, one must apply a fixed timed sinusoidal
oscillation of an applied stress in the linear regime to the material and record the
material response. This is experimentally reproducible if the material is kept within
the linear viscoelastic region. During sinusoidal deformation, it can be shown the
applied stress and strain can be expressed as:

\[ \varepsilon(t) = \varepsilon_0 \sin \omega t \]
\[ \sigma(t) = \sigma_0 \sin(\omega t + \delta) \]

Equation 7:1 Relation between strain and stress in a viscoelastic material\textsuperscript{100}.

Where \( \sigma(t) \) is the stress at time \( t \), \( \varepsilon(t) \) is strain at time \( t \), \( \varepsilon_0 \) is maximum strain
amplitude, \( \sigma_0 \) is the maximum stress amplitude, \( \delta \) is the phase shift (also called
phase lag or phase angle) and \( \omega \) is the angular frequency of applied stress
oscillation. As noted before, viscoelastic materials exhibit a host of mechanical
properties between ideal elastic and viscous materials. At one extreme, the ideal
elastic material or Hookean limit will respond elastically with the oscillating stress
with both strain and stresses are in phase (δ = 0°). On the ideal viscous limit, strains and stress are out of phase (δ = 90°). From these two extremes, three material properties can be calculated that describe viscoelastic behavior:

Equation 7:2 Dynamic properties of a viscoelastic material.

\[ E'' = \left(\frac{\sigma}{\varepsilon_o}\right) \sin \delta \]
\[ E' = \left(\frac{\sigma}{\varepsilon_o}\right) \cos \delta \]
\[ Tan \delta = \frac{E''}{E'} \]

Where \( E' \) is the Energy Storage Modulus, \( E'' \) is the Energy Loss Modulus, and \( Tan \delta \) is Loss Tangent (also called Damping Factor). \( E' \) is a measure of the amount of elastic part of the material – the stored energy. \( E'' \) is a measure of the viscous part of the material – the energy lost or dissipated. The \( tan \delta \) is an indicator of how efficiently the material loses energy to molecular rearrangements and internal friction. Since it is a ratio of the loss to the storage modulus, therefore is independent of geometry affects \( tan \delta \) can be used as a check on the possibility of measurement errors in a viscoelastic test.

One of the most powerful but fairly unknown laboratory tools to measure viscoelastic properties of polymers and other soft materials is Dynamic Mechanical Analysis (DMA). DMA shares many similarities to rheology and static mechanical
measurements such as Instron testing. A mechanical force is applied to the sample in an oscillatory fashion in the linear viscoelastic region and the material response is recorded. Unlike Instron, DMA is a non-destructive characterization tool and unlike rheology, can both analyze liquid and solid samples. DMA applies an oscillating force to the sample and records the material's response to that force. From this, material properties can be calculated such as complex modulus and identify transitions associated to molecular motions. It is this reason that DMA is often called “mechanical spectroscopy” in some academic circles. These properties are often described as the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity) -the relaxation of the polymer chains. For example, if a polymer is heated so that it passes through its glass transition and changes from glassy to rubbery, the modulus will often drop order of magnitude. This drop in stiffness can lead to serious problems if it occurs at a temperature different from expected. One advantage of DMA is that it can obtain a modulus each time a sine wave is applied, allowing to sweep across a temperature or frequency range. So if running an experiment at 1 hertz (Hz) or 1 cycle/second, a modulus value would be recorded every second. This can be done while varying temperature at some rate like 2°C to 10°C/min so that the temperature change per cycle is not significant and record the modulus as a function of temperature. DMA is very useful in determining \( T_g \) and sub-\( T_g \) transitions in polymer samples. These transitions are normally too weak to be detected by traditional methods such as Dynamical Scanning Calorimeter (DSC) or Thermo gravimetric Analysis (TGA). These transitions are \( T_{\beta} \), and \( T_{\gamma} \). \( T_{\gamma} \) is
associated with highly localized bond movements, bending and stretching, and side chain movements, branches or pendant groups. The $T_\beta$ is moment where the free volume increases and larger chains are able to move in a concerted fashion.

Figure 7: TA Instrument’s Q800 series with tension clamp and TPU-GNR sample.

DMA was performed in a TA Instruments Q800 series apparatus shown in figure 7.6 in film tension mode. Rectangular film samples were cut into dimensions of 15 x 3.5 x 0.08 mm. Temperature was ramped from -100 to 100°C at 2°C/min rate with 1 Hz frequency and 1 % strain in an air atmosphere. Force track was set to
150% and preload force at 0.01N. Nanocomposite film samples were named according to their weight percent of GNR filler. For example, '0.02' sample name is a TPU GNR nanocomposites film with 0.02 weight percent GNR. 'TPU' is the control sample. Data was analyzed with TA Instruments’ Universal Analysis 2000 software package.

**6.3. Gas Permeation Testing of GNR-TPU Films**

The gas permeability of the TPU-GNR films was characterized by measuring the time necessary for a known amount of gas at ambient conditions to diffuse through the film into a dynamic vacuum better than $3 \times 10^{-3}$ mbar (figure 7.6). The pressure drop was measured by a gas type independent capacitive manometer. The reported effective diffusivities represent the average of three independent experiments for each sample and each gas. The gas chamber volume is 129 cm$^3$. 
Figure 7:8 Schematic drawing of the gas permeation apparatus.

The exponential decay function given in Eq. 7.1 was fitted to the pressure drop curves:

\[ p(t) = p_0 + A \cdot e^{-t/\tau} \]

Equation 7:3 Exponential decay function for fitting pressure curves.

Where \( p(t) \) is the measured pressure (mbar), \( t \) is the time (s), \( p_0 \) is the apparent
residual pressure (mbar), A is the initial pressure in the reservoir (mbar) and τ (s) is the time constant of the pressure drop. The effective diffusivity $D_{\text{eff}}$ (m$^2$s$^{-1}$) of the gases was calculated from the τ time constant according to Eq. 7.2:

$$D_{\text{eff}} = \frac{V_u \cdot l}{A \cdot \tau}$$

**Equation 7:4 Effective diffusivity $D_{\text{eff}}$ (m$^2$s$^{-1}$) calculation after determining τ.**

Where $V_u$ (m$^3$) is the volume of the gas reservoir, $l$ (m) is the thickness of the film and $A$ (m$^2$) is the area of the film. The CO$_2$ transmission rate analysis of samples adhered to ASTM standard F 2476. This is testing with an infra-red detector. The samples were mounted against the cell block (containing 2 cells A and B), while one side (outer side) was challenged with 100% CO$_2$ (the test gas), and the inner side is swept with dry nitrogen (carrier gas). As the permeate gas (CO$_2$) transmits through the film, the carrier gas transports the permeated CO$_2$ to the detector for quantification. The detector is essentially a heat sensor.

The IR light source is set at a frequency to oscillate water molecules (similar to a microwave oven), therefore as water molecules pass to the detector, the sensor measure the heat increase, thus knowing the heat 1 water molecule gives off at this frequency, the number of molecules are measured and the software computes the transmission rate. Then analyze for nitrogen transmission rate testing utilizing an instrument called the Multi Tran 400 which uses a TCD (thermal conductivity)
sensor. The test cells are allowed to accumulate for some specified amount of time, than the transmitted gas is analyzed and a peak is generated. The peak area is integrated, and compared against peak areas of known volumes of the test gas to get a transmission rate. OriginPro 8.5 was used for data analysis. TPU-GNR samples tested were neat, 1, and 5 percent GNR respectively, with no prior surface prep before testing.
6.4. Discussion

(a) 

(b) 

E' (MPa)

Tan δ

TPU
0.05
0.2
0.5
1
2
3
5

Temperature (°C)

Temperature (°C)
Figure 7:9 (a) $E'$ as a function of temperature showing all transition regions and (b) $\tan \delta$ as a function of temperature.

The storage modulus ($E'$) and $\tan \delta$ is shown in figure 7.7. All nanocomposites had higher modulus values especially at the glassy and rubbery transition. This indicates a reinforcement effect of the GNR upon the TPU matrix. In figure x, there is a steep drop in modulus at -75°C of all samples. This event can be ascribed to the soft phase $T_g$ of the TPU matrix. After this, the modulus reduction rate slows from -40 to 0°C which is found to be the soft phase crystallization in the control TPU. However, unlike other reports the nanocomposites exhibit a higher value of modulus in this temperature range than the control TPU. This may be due to the GNR having an inhibiting effect over crystallization which would lower the modulus but compensated by either chain immobilization or crystallite immobilization by GNR filler. There are several methods to determine the glass transition ($T_g$) by DMA of a given sample. This is not unusual as there are several methods for DSC too. Depending on industry standards or user preference; the peak or onset of the $\tan \delta$ curve, the onset of the $E'$ drop, or onset of peak of the $E''$ curve may be used. In this paper, the $\tan \delta$ is used. From figure y, the $T_g$ shifted steadily from -50°C of the control TPU to -43°C of the 5 wt% GNR/TPU composite. In addition, the $\tan \delta$ curve lowered and broadened by filler content resulting in reduced dampening capacity for the nanocomposites. This is a consequence of well-dispersed and delaminated GNR fillers restricting molecular motion of TPU chains.
Wide Angle X-ray powder diffraction (WAXRD) was performed using a Rigaku D/Max 2550 diffractometer with CuKα radiation ($\lambda = 1.5418$ Å) at 40 kV and 40 mA from 5 to 40° with 1°/min scan rate. The data obtained were analyzed and processed using the Jade 9 software package. The patterns only displayed a very diffused diffraction peak around $2\theta = 20^\circ$ which corresponds to the d-spacing of 4.45 Å 110 plane reflections. This broad peak is attributed to the short range ordering of hard segment domains indicating amorphous structure. The intensity is...
reduced with increased filler content which could mean GNRs are
reducing/destroying said ordering. This confirms what FTIR in figure 7.4 with
decreased hard domain signal in the form of N-H stretching.
(a) Graph showing pressure (mbar) over time (s) with different markers for TPU and various values.

(b) Similar graph with different markers.

(c) Graph showing pressure (mbar) over time (s) with markers for 0.5 and 1.0.
**Figure 7:11** Gas permeation curves of (a) N$_2$ gas (b) CO$_2$ and N$_2$ gas at longer times.

Figure 7.11 shows the gas permeability of TPU and TPU-GNR thin films under CO$_2$ and N$_2$. Figure 7.11a and b shows the incredible gas blocking properties of GNR above 0.5 weight % concentration. Samples .5 and 1.0 had to be taken at longer times to get a measureable D$_{eff}$ value. Table shows the calculated D$_{eff}$ values at the two gas types.

**Table 7:1: Calculated D$_{eff}$ ($10^{-9}$ m$^2$s$^{-1}$) of all composites.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>N$_2$</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPU</td>
<td>3.9</td>
<td>7.07</td>
</tr>
<tr>
<td>0.1</td>
<td>1.47</td>
<td>3.3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.65</td>
<td>1.25</td>
</tr>
<tr>
<td>0.5</td>
<td>0.23</td>
<td>0.37</td>
</tr>
<tr>
<td>1</td>
<td>0.04</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The influence of nanofillers on the gas permeability of polymers is explained within the model of tortuous paths developed by Neilson$^{289}$. According to this concept, the path of a small gas molecule must travel in a polymeric matrix will substantially increase in the presence of intercalated and/or exfoliated filler layers that possess high aspect ratios (>103). Since GNRs have an aspect ratio well about
this (over 1,000) this results in a noticeable decrease in the $D_{\text{eff}}$ of the nanocomposite. Another factor that could reinforce gas permeation is GNRs. GNRs have edge functionalized hexadecane chains which are used to hydrogen bond to TPU. Gas molecules that can hydrogen bond\textsuperscript{290} could bond to GNRs further retarding gas path movement within the nanocomposite.
In this thesis, Water Drop Tribology on graphene surfaces and non-graphene surfaces has been demonstrated for the first time. Graphene, a two dimensional, chemically homogenous material exhibits unique tribological properties apart from previous studied systems. Not only is the time effect not observed, but immune to substrate effects as shown by using HOPG for liquid drop experiments. The serrated three phase contact line gives a clue to the apparent time invariance to slide the drop via surface defects in the form of graphitic domain boundaries made during graphene synthesis. Surface defects are not accounted for in Shanahan de-Gennes type deformation, hence no time effect was observed. This also accounts for the similar retention force values from pendant and sessile drops. Future experiments would be to use graphene single domain crystals when graphene synthesis has advanced enough. In addition, graphene is not the only two dimensional surface;
boron nitride (BN), molybdenum sulfide (MoS₂), vanadium pentoxide (V₂O₅) and even graphene hybrids would be of high interest to measure liquid drop tribology phenomena. A possible application for this would be to tune retention forces and design droplet-fluidic devices.

Carbon nanocomposites presented herein hold promise for future work. LbL has proven to work well with graphene materials, specifically GNRs, to create mechanically strong polymer nanocomposites and inhibit gas permeation. Future work includes further understanding of GNR interaction with polymer chains. As described by Yakobson, GNRs exhibit thermally activated morphologic twisting as a consequence of the edge structure. This twisting could affect the polymer-nanofiller interface and needs to be investigated. A future direction for LbL-fabricated polymer nanocomposites is in using HFGO as nanofiller with piezoelectric polymers to create actuating nanocomposites. The fluorine-carbon-oxygen content can be turned in the Hummers process described and the sheet-like, polar structure can be amenable to LbL processing similar to graphite oxide. The hydrogel transdermal device shows promise for drug trials in the future. Its low cost makes it attractive and mechanism by which it operates tunable. However, full understanding of CNTs in relation to human health is still not fully understood unlike the PVA-Borax which is patently safe. This limits the device to pre-clinical trials. An alternative would be to use iron oxide (FeO) nanoparticles in place of CNTs to locally heat and disrupt hydrogen bond crosslinking in the hydrogel to release the drug.
References


290. Piccard, E., Vermogen, A., Gérard, J.-F. & Espuche, E. Barrier properties of nylon 6-montmorillonite nanocomposite membranes prepared by melt


Appendix A: Instrumentation

Below is a list of descriptions of the common analytical laboratory techniques extensively used throughout this thesis. Specialty, lesser known techniques such as DMA and CAB are reviewed extensively in earlier chapters.

A.1 Raman Spectroscopy

Raman Spectroscopy was used to characterize the quality and thickness of CVD grown graphene layers on silicon substrates. Raman relies on the Raman scattering of monochromatic light from the laser and records the shift of energy called the Raman Shift calculated by:
\[
\Delta \omega = \frac{1}{\lambda_o} - \frac{1}{\lambda_1}
\]

Equation 0:1 Raman Equation for bond vibrations by a photon of light.

Where \(\Delta \omega\) is the Raman Shift (in cm\(^{-1}\)), \(\lambda_o\) is excitation wavelength, and \(\lambda_1\) is the Raman spectrum wavelength.

A.2 Scanning Electron Microscopy (SEM)

SEM is a nondestructive surface microscopy technique using a beam of electrons to create two dimensional images of sample surfaces from the backscattered electrons. The beam raster over the surface many times to create a black and white photo of the sample surface. This required UHV environment \((\sim 10^{-6})\) and the sample surface to be conductive. To that end, LbL and electrospun nanocomposite fibers were sputter coated with gold \((\sim 20\text{nm})\) thick layer before SEM imaging. A FEI Quanta 400 field emission gun SEM was used at various magnifications. Sample mounting was on Al pegs and samples were adhered by conductive carbon tape.

A.3 Transmission Electron Microscopy (TEM)

TEM is a nondestructive technique whereby a beam of electrons are transmitted through an ultra-thin sample under UHV at RT. Owing to the small de
Broglie wavelength of electrons, TEM can resolve down to the atomic level. Single layer graphene was measured under TEM using a JEOL 1230 High Contrast Schottky-type field emission gun TEM with a CCD Gatan model 794 camera. Power was at 120 eV and thermally induced drift was accounted for. Sample preparation was done by dispersing the graphene in 1:1 ethanol water mix and placing a single drop on an on 300µm holey mesh lacey carbon grids on copper support. After allowing drying, the grid was placed in the TEM chamber and measured. JEOL company software was used in image analysis.

A.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a nondestructive technique where infrared (IR) radiation is passed through a sample in which some IR radiation is absorbed and some transmitted. Molecules with covalent bonds absorb radiation, moving them to a higher energy state that causes molecules to stretch, bend, or rotate. For bonds with dipole moments, the incident radiation must equal the natural vibration frequency of the molecule. According to the equation:

\[ \nu = \frac{v}{c} \propto \sqrt{\frac{f}{\mu}} \]

Equation 0:2 IR active bond frequency relation.
Where \( \tilde{\nu} \) is wavenumber, \( \nu \) is vibration frequency, \( c \) is speed of light, \( f \) is force constant, and \( \mu \) is reduced mass. The force constant \( f \) contains information about bond order, strength, and depends on the electronegativity of the vibrating molecules. Along with \( \mu \), these two variables are unique to any given set of atoms and chemical bonds. In other words, the absorption spectrum is a physical property of the molecule; a molecular “fingerprint” identification. The term FTIR originates from the fact that a Fourier transform algorithm is needed to convert raw data (time domain) (interferogram) into an actual spectrum (frequency domain) with transmission percentage (or absorption) versus wavenumber.

The Nicolet 6700 FTIR Infrared Spectrometer was used for GO and GNR functional group identification with an ATR attachment. The ATR attachment enables to use solid samples directly with no further preparation. Resolution was set to .1 cm\(^{-1}\) at 64 scans to maximize S/N ratio and from 3000 to 500 cm\(^{-1}\) range. Before each sample, a spectrum was run with no sample in the chamber. The computer program also by Nicolet takes this as background spectrum to subtract from the sample spectrum to avoid contributions from ambient air. All samples were measured at standard temperature and pressure. OriginPro 8.5 was used for data analysis.

### A.5 X-ray Photoelectron Spectroscopy (XPS)

XPS is a nondestructive surface elemental analysis technique that uses monochromatic x-rays to eject inner shell electrons from the sample surface and
measures their energies. Unlike XRD, ultra high vacuum (UHV) is needed for the
detector to record incoming photoelectrons. Based upon the Photoelectric Effect,
XPS the binding energy of electrons by:

\[ E_k = h\nu - E_b - \phi \]

**Equation 0:3 Energy balance of a photon and surface work function.**

Where \( E_k \) the kinetic energy of the escaping electron is, \( h\nu \) is the x-ray photon energy, \( E_b \) is the electron binding energy, and \( \phi \) is the work function which is known from the instrument. Since \( E_b \) electrons depend on the energy of the electronic orbit and the element from which the electron is emitted, it can be used to identify the element present. The chemical environment the atom (such as compounds of different electro-negativity) is in effects \( E_b \) called chemical shifts and can be used to detect compounds and valance number in the sample. The spectra are plotted as photoelectron intensity versus binding energy with identifiable peaks representing elements and their electronic states. XPS can resolve elements at 3 and above but not below and usually discriminate the first few layers (8 to 12 nm) of the top sample surface.

A PHI Quantera XPS machine was used on GO and GNR to estimate degree of oxidation, reduction, and chemical functional groups at the surface. In order to reduce cross contamination, Pt substrates were used prior to analysis. Three to five
different areas on each sample were scanned (survey and elemental) to ensure a representative elemental scan of the surface.

Monochromatic Al K$_\alpha$ (1486eV, line width 0.85eV) radiation was used on all samples. Step size was set to 0.5 eV per point. Neutralizer was set to auto to prevent sample charging. Polymer nanocomposite samples were scanned the same way, except longer dwell time in the UHV chamber to eliminate out gassing. For data analysis, the PHI MultiPak software was used for peak identification and curve fitting. All samples were measured at room temperature and UHV ($10^{-9}$ torr). OriginPro 8.5 was used for data analysis.

### A.6 Wide Angle X-ray Diffraction (WAXRD)

XRD is a non-destructive technique useful for the analysis of solid crystalline or semi crystalline materials done at standard temperature and pressure. Most organic and inorganic compounds, minerals, metals, alloys, and a small number of polymers can form crystals. Amorphous materials cannot be identified by XRD, so most polymers and glassy materials would appear to have a diffuse, high noise pattern. XRD is not an elemental trace analysis technique; only crystalline structure and in some special cases, size. The use of diffracted x-rays is used to glean information about physical structure. XRD makes use of the wave properties of electromagnetic radiation that interact with the atoms or molecules in the unit cell of a crystal, and record the interference patterns in the form of peaks representing planes assuming elastic scattering by the Bragg Relation:
\[ n\lambda = 2d_{hkl} \sin \theta \]

**Equation 0:4 Bragg’s Relation for constructive diffraction.**

Where \( n \) is the order of diffraction of planes, \((hkl)\), \( \lambda \) is x-ray wavelength, \( d_{hkl} \) is the interplanar spacing of planes \((hkl)\), and \( \theta \) is the Bragg angle measured between the incident x-ray beam and crystal planes \((hkl)\). This sets both the limits of where to place a detector relative to the sample and type of x-ray wavelength for diffraction to be observed. Cu K\( \alpha \) wavelength at 1.54 angstroms is appropriate for most crystals and is used here. Positions of atoms in the unit cell affect the diffraction intensities, but not their directions and the scattered waves reach the detector is the result of the sum of all scatters. Even though the Bragg Law is obeyed, there can be no observable diffraction peaks. XRD plots the sum of diffracted x-rays from the sample as a function of \( 2\theta \). in the context of graphene oxide; XRD can be used to infer the amount of the degree exfoliation by the increase of d-spacing into single sheets. Stacked graphite has a c-axis peak at \( \theta \approx 26.3^\circ \) (.34 nm interlayer spacing) and shifts to lower values (higher d-spacing) and completely disappears when graphite is exfoliated into single sheets. For polymer nanocomposites, this is also true and a good measure how well dispersed the nanofiller is in the matrix.

Samples were measured on a Rigaku D/Max Ultima II configured with a vertical theta/theta goniometer, Cu Ka monochromatic radiation, graphite
monochromator, 20 micron beam diameter, and scintillation counter. X-ray source is a filament tube and CCD detector. All samples were placed on a glass substrate prior to measurement. Data analysis was carried out by OriginPro 8.5. All samples were measured at standard temperature and pressure.

**A.7 Differential Scanning Calorimeter (DSC)**

DSC is a destructive calorimetric technique that measures the heat flow into a reference and a sample (in mg) as a function of temperature of the sample. Both sample and reference are encased in aluminum pans. Temperature ramps with time linearly and the reference has a well-defined heat capacity over the temperature scanned. The underlying principle of DSC is from the sample undergoing physical transformations such as phase transitions. Phase transitions such as crystallization, melting, or glass transitions are either exothermic or endothermic transformations. This is manifested in heat flow in or out of the sample pan. This is detected by the DCS thermocouple and recorded as a spike or depression in the graph.

Polymers and their composites have been historically been characterized for their $T_m$ and $T_g$ as well as the heats of crystallization by DSC. The GO-PAA (Pyromellitic dianhydride-oxydianiline polyamic acid) LbL nanocomposites were tested in the DSC for $T_g$ and evidence of imidiazation. Pt pans were used in temperature range going from RT to 300° at 1°/min. Ambient pressure was used throughout the measurement. The reference pan was used an empty air. A TA
Instruments Q2000 DSC instrument was used. OriginPro 8.5 was used for data analysis.

A.8 Thermal Gravimetric Analysis (TGA)

TGA is a destructive thermo-analysis technique that measures the mass change of a sample in an oxidative or inert atmosphere while temperature is ramped. Sample weight or weight % is plotted versus sample temperature. A sample weight loss or gain can reveal many things about the sample. A weight gain could mean a chemical reaction or absorption from a component in the atmosphere. A weight loss could mean decomposition or evaporation of the sample. No weight change means the sample is stable or inert under those range of temperatures and type of atmosphere.

A TA Instrument Q500 TGA was used on GO and GO polymer nanocomposites. A ceramic pan was used for each sample under N₂ gas atmosphere. Temperature profile ranged from RT to 800°C at 2°/min. The pan was cleaned with Piranha solution before and after each use to remove organics or residual sample. For GO, the temperature was first ramped to 50°C, held for 30 minutes and cooled back down to RT before testing. This was done to remove water vapor from all samples. Sample weight was in the 5 to 15 mg range and was measured and monitored by the Q500’s quartz crystal microbalance. OriginPro 8.5 was used for data analysis.
A.9 UV-Vis Spectroscopy (UV-Vis)

UV-Vis is a non-destructive technique using ultraviolet-visible spectral region to irradiate liquid samples, excites their electrons, and measures their absorbance. Molecules with pi or nonbonding electrons are easier to see in UV-Vis because they absorb UV radiation more readily than other types. By seeing which wavelengths are absorbed and knowing the electronic transition rules, molecular structure can be determined. These transitions are plotted as absorbance as a function of scanned wavelength in the plots.

Another use for UV-Vis is the determination of solute concentration in a solution. According to the Beer-Lambert Law:

\[ A = \log_{10} \frac{I_o}{I} = \varepsilon cL \]

Equation 0:5 Beer-Lambert Law.

Where \( A \) is measured absorbance, \( I_o \) is incident light, \( I \) is the transmitted intensity, \( L \) is the path length through the sample, \( \varepsilon \) is the molar absorptivity, and \( c \) is the concentration. This method was used in the gel device concentration calculations.

A Shimadzu UV-3600 UV-VIS spectrophotometer was used to characterize the time release of sample drug, Rhodamine B in aqueous solution. Quartz cells were
used with containing water as a baseline and the other with Rhodamine B. Wavelength was ramped from 200 µm to 800 µm at .01 degree step size. UV-Vis spectra were taken a standard temperature and pressure. OriginPro 8.5 was used for data analysis.

A.10 Atomic Force Microscopy (AFM)

AFM is a nondestructive surface analysis technique with resolution power down to the nanometer level. Basic principle of operation is a Si tip of known dimensions mounted on a computer controlled cantilever brought into near contact with the surface. The tip experiences forces from the sample (electrostatic, Van der Waals) which causes a deflection in the cantilever in accordance to Hooke’s Law. A piezoelectric element in the cantilever transmits these forces into signals and converts them into a two dimensional image of the sample surface.

A Nanoscope III AFM was used to image the surfaces of LbL films and CVD grown graphene. Si tips were used with a scan area of 5µm by 5 µm at standard temperature and pressure. Tapping mode was used on all samples. LbL films no surface treatment was performed sans a N₂ jet to remove dust. For CVD graphene, an acetone-ethanol wash followed by N₂ jet was used to clean the surface. Origami 3.4 image analysis software package was used for image processing.