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The Effect of Functionalized versus Unmodified Graphene Oxide on Polyimide Nanocomposite Properties

A thesis submitted in partial fulfillment of the requirement
for the degree of Bachelor of Science in Chemistry from
The College of William and Mary

by

Natalie Vaughan Hudson-Smith

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May 4, 2015

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Abstract

Polyimides are a commercially useful material, typically used in air and space applications due to high heat resistance, impressive mechanical strength, and self-extinguishing properties. In recent years, graphene has come of interest in the material science world. However, the pristine, carbon-honeycomb allotrope is extremely hydrophobic, chemically unreactive and it is therefore difficult, if not impossible, to disperse graphene nanoparticles as single nanosheets into polar solvents used typically used for polymerization and synthesis. Focus has shifted to graphene oxide (GO); the honeycomb structure of graphene with oxygen-containing functional groups on the surface. Incorporation of GO into polyimides is shown to improve mechanical properties, increase gas barrier properties and to increase water solvent resistance along with other solvents. Functionalization of GO sheets with monomer components of the chosen polymer results in further improvements of these properties. Here we demonstrate that tailoring of GO to be compatible with polyimide resins is a valuable technique in enhancing GO-polymer composite properties.

I. Introductory Material

a. Polyimides

Polyimides are a family of high performance polymers which demonstrate many unique properties that are vital for industrial applications. These thermoset polymers demonstrate excellent mechanical strength as well as being resistant to both heat and chemicals. Polyimides are resistant to organic solvents, oxidation and acidic environments.[i] As thermoset polymers, polyimides do not melt but degrade at high temperatures though they are typically stable up to an impressive 520°C.[i] Thermoplastic polyimides are also available. Polyimides are found in industrial applications such as electric motors, missiles, jet engine blades, aircraft wire, and molded pistons and seals. Other applications of polyimide films include Kapton® tape, produced by DuPont and used to seal and label experiments that are processed through high temperature. Recent space and air applications of polyimide films include applications used in both the Mars Explorers Curiosity and Spirit[ii] as well as usage in the European Space Agency's Rosetta space probe [iii] and the sun shield of NASA's James Webb Space Telescope.[iv]

b. Graphene Oxide

In recent years, due to the 2010 Nobel Prize in Physics awarded to Andre Geim and Konstantin Nososelov, graphene has gained attention as a strong, durable yet lightweight material. It would be advantageous if the properties of graphene, such as the extremely high modulus of 1 terapascal (TPa), an ultimate strength of 130 gigapascal (GPa) and gas impermeable honeycomb network[v] could be lent to polymers by means of creating graphene-polymer nanocomposites. However, the pristine, carbon-honeycomb allotrope is extremely hydrophobic, chemically unreactive and it is therefore difficult, if not impossible, to disperse graphene nanoparticles as single nanosheets into polar solvents used typically used for polymerization and synthesis.

However, this increased interest in graphene's exceptional strength has revitalized interest in an analogous compounded, graphene oxide.* Graphene oxide has the same honeycomb structure as graphene but with oxygen-containing functional groups on the surface of the planar structure. These oxygen-containing functional groups are ketones, 6-membered lactol rings, alcohols, epoxides and hydroxyl groups.[v] It is therefore a much more polar material. Graphene Oxide was first produced in 1859 by Brodie.[v, vi] Graphene oxide, produced by the later developed Hummer's Method[v], can be incorporated into water or organic solvents[v] commonly used in polymer precursor resins to create graphene oxide-polymer composite materials.

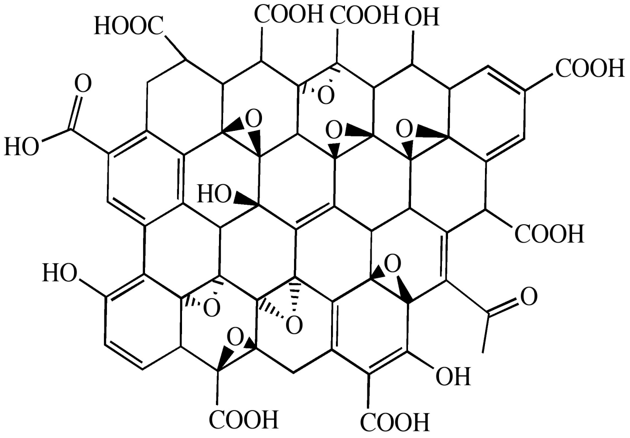

Figure 1: General structure of graphene oxide

c. <u>Composite Materials</u>

A range of Graphene Oxide (GO)-Polymer composites and nanocomposites systems have been made previously for polyurethanes, nylons, and many other polymer systems as well as a

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* Note: Some literature uses graphite oxide or graphitic oxide to denote the identical compound.

number of polyimide systems.[vii] As well, reaction of monomers or small molecules with reactive oxygen-containing groups on the surface of the GO has recently become a means of producing enhanced improvements and dispersion quality. Concentrations of nanoparticles in polyimide systems have range from 0.03%[viii] to 30%[ix] by weight. The effect of small loadings (<1%) make up a large majority of the literature on this topic. It is known from the literature, and from experience in our laboratory, that higher loadings introduce an increased risk of agglomeration of GO nanoparticles. Higher loadings of GO particles can also affect the optical transparency of polyimide films[viii] which may be undesirable if the film is to be used in applications such as solar charge battery technology, glass substrates for liquids crystal displays[viii], or other applications that demand the high performance and thermal stability of polyimides but optical clarity as well.

In terms of mechanical properties, significant increases in Young's Modulus and tensile strength have been demonstrated. In 2011, Wang et al[x], at loadings of 0.3 to 5%, found a 6.4 times increase in tensile modulus and a 240% increase in tensile strength for GO sheets reacted with 4-4'-oxydianiline in a polyimide system comprised of 4-4'-oxydianiline and 3,3’,4,4-Benzophenonetetracarboxylic dianhydride. In 2012, Shi et al[viii] found an increase of stress intensity by 29% and Young's Modulus by 25% with an addition of 0.12% by weight GO in a polyimide system comprised of 4,4'-bisphenol A dianhydride, 4-4'-oxydiphthalic anhydride and diaminophenyl methane. In 2013, Zhu et al found an increase of the Young's Modulus by 282% in a 30% by weight composite in a polyimide system comprised of the monomers pyromellitic dianhydride and 4-4'-oxydianline.[xi] Again in 2013, Park et al found an increase in Young's Modulous from 4.5 to 6.8 GPa (or a 51% improvement) and an increase in tensile strength from 75 to 123 megapascals (or 64%) with the addition of 0.5% by weight of surface functionalized graphene oxide in a polyimide system comprised of pyromellitic dianhydride and 4-4'oxydianaline.[xi]

Increased gas or vapor barrier properties are desirable for polyimide films. In 2013, Zhu et al determined that incorporation of GO nanosheets reduced the oxygen transmission rate (OTR) through the polyimide film.[ix] Also in 2013, Park et al found a significant decrease in water vapor transmission rate from 150 to 40 g/m^2 day by inclusion of functionalized GO sheets into their polyimide system.[xi] In 2014, Chang et al[xii] found that gas barrier properties imparted to the composite material by the inclusion of GO particles resulted in excellent anticorrosive properties in a polyimide coating.

For electronic applications, electrical or thermal conductivity may be a desirable material property. Increases in electrical conductivity of composite polyimide films compared to standard, pure polyimide films were found by Zhu et al, Heo et al, Park et al, and Wang et al.

The improvements in mechanical, gas barrier and electronic properties appears to result in a small decrease in thermal stability. Heo et al[xiii] demonstrate an increase in thermal stability in that there is a slight increase in the onset of thermal degradation with their composite materials which they attribute to the high thermal stability of graphene sheets. However, Zhu et al show a decrease in thermal stability corresponding to increasing loading of GO sheets which they attribute to “pyrolysis of labile oxygen functional groups”[ix] which remain in the composite materials.

With the understanding of these trends in the literature and the understanding of already characterized polyimide composite systems, it was decided to synthesize and characterize composites of GO in a polyimide system comprised of BTDA and 4-4'ODA monomer and composites of GO functionalized with 4-4' ODA monomer in that same system. Characterization methods include mechanical, water vapor transmission, water gain analysis and thermal stability. Additionally, a thermoplastic polyimide system has been synthesized and will be the subject of analogous experiments to functionalize GO with the diamine monomer of the thermoplastic system and characterize the properties of resulting composite thermoplastic polyimide films.

II. Methods

a. Synthesis Methods

1. Polymer Synthesis

The polymer focused on in this experiment is a thermoset aromatic polymer of the monomers Benzophenone-3,3':4,4'-tetracarboxylic dianhydride (BTDA) and 4-4' Oxydianiline (4-4' ODA).

Figure 2: Left: Structure of BDTA Right: Structure of 4-4' ODA

Like most thermoset aromatic polyimides, this polymer system is prepared in two distinct steps. First, a solvated poly(amic acid) resin is produced. This resin is later spread in a 100 x 15 mm soda lime glass petri dish and subjected to a high-heat (300ºC) curing cycle to remove solvent and complete the imidization process and yield a thermoset polyimide film.

Before polymerization, BTDA must be dried in a vacuum oven at 150ºC for 5 hours in order to remove atmospheric moisture. The solvent for the poly(amic acid), dimethylacetamide

(DMAc) must be stored and sealed properly to prevent acquisition of atmosphere moisture as well.

Equimolar amounts of 4-4' ODA and pre-dried BTDA are dissolved readily in DMAc to make two solutions of 12% solids by weight. The dissolved BTDA is added to a three-necked resin kettle, followed by the 4-4' ODA solution. A mechanical stirrer keeps the solution spinning and the resin is flooded with N_2 to keep out oxygen and moisture from the reaction apparatus.

After 48 hours the resin is removed from the resin kettle and stored to be used for curing films in the future.

To obtain a solid polyimide film, the poly(amic acid) resin is pipetted into a soda lime petri dish to obtain a thin and even layer of liquid resin. This dish is then placed into a Thermolyne 47900 Furnace for a cure cycle at which the resin is ramped to 100ºC, held at 100ºC for one hour, ramped to 300ºC over the course of two hours, held at 300ºC for one hour and then returned back to room temperature. After room temperature is reestablished, the finished circular film can be easily peeled by gentle lifting with a razor blade and cut to the desired shape for the impending characterization and sample testing.

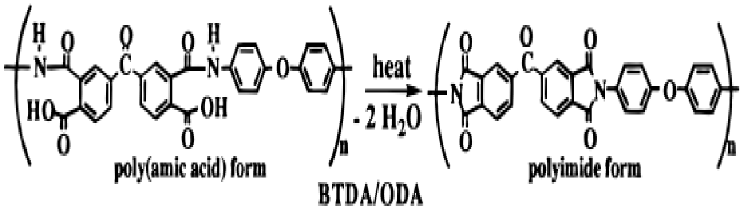

Figure 3: Imidization step occuring during heat cure cycle[xiv]

2. <u>Preparation of GO</u>

Graphene Oxide was obtained by two versions of the Hummer's method, denoted

Hummer's Method and Improved Hummer's method. The GO samples from these methods are denoted as GO and GOi in sample names. The Improved Hummer's method has proved to be advantageous in practicality. It does not produce any toxic gases and controlling the temperature of the reaction is more easily achieved.

3. Preparation of Unfunctionalized GO Dispersion

Good incorporation between GO nanoparticles and the polymer matrix requires a common medium to encourage even dispersion of particles within the matrix. The solution was to disperse GO particles, both functionalized and as produced, in the same solvent system as the polymer, DMAc.

In order to disperse unfunctionalized, or unaltered, GO particles into the system solvent, GO produced by a modified Hummer's method is sliced into small pieces, about the size of large salt grains. These GO pieces are then dried in a Precision brand oven at 100ºC for one hour to remove atmospheric moisture.

The GO pieces are massed and then placed into a clean Erlenmeyer flask. A recorded mass of DMAc is added to the flask which is then sealed tightly with a rubber cork and laboratory film. The sealed flask is sonicated in a Fisher Scientific FS110D water bath sonicator until a homogenous dispersion is achieved. The concentration of the dispersion is calculated in mg GO per grams of total dispersion.

Atomic Force Microscopy scans performed by members of Dr. Hannes Schniepp's Nanomaterials and Imaging Lab showed that size of GO and GOi particles dispersed in this manner were approximately 1 micron or less, with few particles approaching or exceeding 2 microns.

4. Preparation of Functionalized GO Dispersion

Literature suggests that taking advantage of the reactive oxygen-containing species on the surface of the GO sheets allows for tailored functionalization of the nanoparticles for specific polymers.[x,vii] In order to achieve this for the BTDA/4-4' ODA polyimide system, the diamine 4-4' ODA is selected as the monomer with which the GO sheets will be functionalized. The sonication procedure utilizing the Fisher Scientific FS110D water bath sonicator for the creation of a homogenous GO dispersion in DMAc is followed. Then, a mass of 4-4' ODA corresponding to a 15mmol 4-4'ODA per gram of GO[x] ratio is massed and dissolved in DMAc. These solutions are combined under N_2 and reacted under reflux at 60°C for 24 hours to yield a dispersion of functionalized GO, written as 4-4' ODA-GO.

For both GO and 4-4'ODA-GO dispersions, a mass of poly(amic acid) resin is measured out and the mass of the solid component is calculated. The mass of GO or 4-4' ODA-GO dispersion required to make a dispersion of a certain percent is calculated and added to the polyamic acid resin solution. The following GO-particle composites by weight have been prepared for both unfunctionalized and functionalized systems; 0.01%, 0.03%, 0.06%, 0.1% and 0.5%. The two solutions mix readily due to a common solvent. The solution is spread into a soda lime petri dish and subjected to the same heat cure cycle as for the neat polymer. The composite films can then be lifted from the glass and cut into samples to characterize the material.

b. Characterization Methods

1. Mechanical Properties

Mechanical properties for polymer samples are determined by the use of a stress vs strain curve.

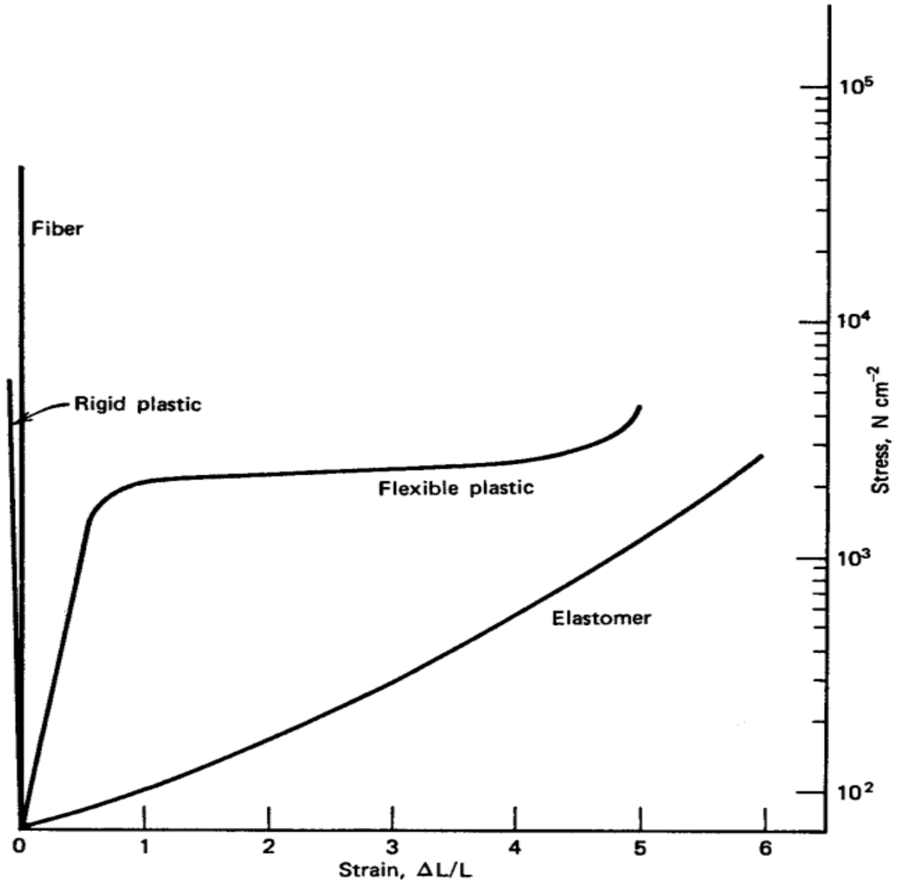

Fig. 1-10 Stress–strain plots for a typical elastomer, flexible plastic, rigid plastic, and fiber.

Figure 4: Typical stress vs strain curve shapes for a variety of materials[i]

The Young's modulus defined by the initial stress divided by ΔL/L where L is the length of the sample. It can be defined as $E = \sigma/\varepsilon$ where σ is stress and ε is strain.[i] The tensile strength is defined as the maximum stress prior to tearing the sample.

Previously, mechanical testing was accomplished by the use of a Materials Testing System (MTS) for were polyamide-11 and polyamide-12 dog bone shape samples which were significantly thicker samples (around to 0.5 cm) of solid polymer. Unlike polyamides, our polyimides are produced as a very thin (2-14 mm), orange but transparent film that are very stiff.

Due to the thinness of these films, the use of the MTS proved difficult as punching dog bones from film using a press and custom die was often unsuccessful. The MTS system also used pressurized grips that often allowed the thin film to slip during mechanical testing. Due to these instrumentation problems, mechanical testing was then done using a rheometer fit to plot the same stress vs strain curves as the MTS system.

A TA Instruments AR 100 rheometer instrument was fitted with adjustable grips. Software from TA Instruments, Rheology Advantage, was capable of plotting a stress vs strain curve from which data could be extracted and further analyzed in MatLab. With the rheometer, ASTM D882-73 procedure was followed in which the speed of separation was determined by the following equation;

$$A = BC$$

where A is the rate of grip separation measured in millimeters per minute, B is the initual distance between the grips, and C is the initial strain rate. The initial strain rate C is provided for material types by the ASTM D882-73 procedure. For polyimide applications, it is 0.01 min^{-1}.

Mechanical testing samples were cut by hand with a razor using a ruler as a guide to make strips of uniform width. Width and thickness of the film was measured with an iGaging EZ-Cal digital micrometer and recorded. Strips were placed into the rheometer grips and secured firmly but with not so much pressure to cause tearing at within the clamps. The length of the stretching portion of the strip was easily recorded by the rheometer as the 'starting gap' so that the proper stretching speed could be accurately calculated. Samples were anchored at the bottom and pulled from the top. This is the inverse method from the MTS system but produces the same data. The length of the strip versus newtons of force was recorded by the instrument.

Data taken from Rheology Advantage was analyzed in MatLab and combined into a table in order to compare neat polyimide, GO-polyimide, 4-4' ODA-GO-polyimide and DuPont Kapton ® as a commercial comparison.

2. Water Vapor Transmission

Reduced gas or vapor transmission is a desirable property for any polymer or composite material that may be used as a film or cover. Polyimides are largely produced as films and the concept of a durable, transparent but gas tight film is extremely desirable. As an indication of this property, it was decided to measure the rate of water vapor transmission to determine if the gas/vapor barrier properties of the polyimide film were improved by the introduction of graphene oxide and functionalized graphene oxide nanoparticles into the system.

The procedure for characterizing water vapor transmission rates was followed the guidelines of ASTM E96-95: Standard Test Methods for Water Vapor Transmission of Materials. This procedure is appropriate for testing water vapor transmission through plastic films and other materials. A desiccator which maintained approximately 70% humidity by use of a saturated NaCl solution present in the base. This humidity was maintained for the duration of the experiment. The high humidity provides both a quicker experiment and a more reliable level of humidity than using the ambient humidity.

Samples were cut by hand into approximately 1.5 x 1.5 cm squares. Width, length and thickness dimensions were measured with a digital micrometer and recorded.

For each sample, a small cylindrical vial, with a height of approximately 45 mm and an outside diameter of approximately 15 mm, was cleaned with pressurized air and labeled. The outside and inside diameters of the vials were measured with a digital micrometer and recorded.

Vials were labeled with permanent sharpie and the mass of the labeled vials was recorded.

The vials were filled to approximately 3/4ths capacity with the desiccant Drierite with color indicator obtained from Acros Organics. The mass of the Drierite and the vial was measured and recorded.

The rim of the vials were given a thin coating of vacuum grease to create a seal between the polyimide film samples and the glass and to prevent air passage through these gaps. Square samples of the polyimide films were placed on top and the mass of this entire system was measured and recoded at t=0. A schematic of this set up is shown in Figure 5.

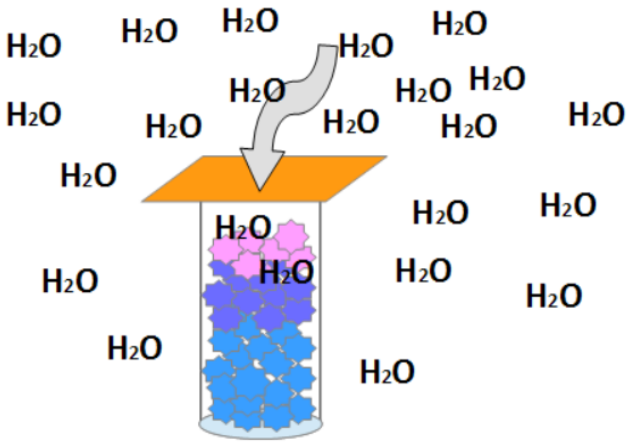

Figure 5: Schematic showing the set up for a single WVT sample. Polyimide film shown in orange.

Samples were kept in the desiccator serving as a humidity chamber and massed at least once a day. Times of measurements and masses were recorded. Data was transferred to Microsoft Excel. Graphs, with the thickness of films taken into consideration and corrected for by ratio of thickness, were produced to aid with data analysis.

3. Water Gain Analysis

Solvent uptake is a concern for polymers. Uptake of moisture or any other fluids present while the material is in use may result in swelling or polymer deformation. The amount of mass of solvent gained can be easily measured by submerging strips of polymer into a solvent or liquid and massing the strips, after their surfaces have been dried, at established time intervals.

The procedure for characterizing the rate of water absorption was followed the procedure designated in ASTM D750-98: Standard Test Method for Water Absorption of Plastics. Strips of polyimide sample, including loaded and unloaded samples, as well as commercial Kapton ® were cut into 1 x 3 cm strips. The strips were left in a 100°C oven for an hour in order to remove any deposited ambient humidity. As this temperature is much below the final cure temperature for BTDA/ODA polyimide and this polymer is designed to be heat resistant, this procedure does not influence the polymer behavior in any appreciable way.

Strips were then submerged in deionized water in scintillation vials. At intervals of approximately 10 min, 20 min, 1 hour, 1.5 hours, 3 hours, 6 hours, 12 hours, and 24 hours, strips were removed, dried by hand on WypAlls and KimWipes and massed on a 4-digit Sartorious balance. Masses at each time interval were recorded and the data was transferred to Microsoft Excel for analysis. Data was plotted as as a simple mass vs time plot.

4. Thermal Stability Analysis

Polyimide films like Kapton are known for their thermal stability. It is of interest to determine if the introduction of GO or functionalized GO nanoparticles to form a composite material is beneficial, benign or detrimental to the thermal stability of the film. Previous results found in the literature, namely from Heo et al. suggest that the incorporation of these particles will be detrimental for thermal stability even for composites of functionalized GO particles due to aforementioned, “pyrolysis of labile oxygen functional groups”[xiii] present in the composite materials.

To determine the extent of the effect of GO incorporation on thermal stability, it was decided to perform thermogravimetric analysis on a functionalized loaded sample type and on neat material as a control. Due to cross-linking, thermoset polyimides do not melt but rather degrade under high temperature but rather begin to degrade.

On a TGA Q500, thermal analyses were run. Commercial polyimide material, DuPont Kapton ®, begins to decompose at 520ºC.[xv] It was decided to go past the onset of degradation. A procedure to jump to 100ºC, ramp 10ºC/minute to 550ºC and hold isothermal for 5 minutes to the termination of the procedure was selected. The platinum TGA pan was cleaned by flame and tared before each run. TGA samples were cut by hand and had an average mass of 4.690 mg.

III. Results

a. Mechanical

Addition of GO particles showed improvement of the Young's Modulus, indicating increased stiffness of the material as seen in Figure 6. An important observation is that the composites of 4-4' ODA-GO (orange and blue bars towards the bottom of the bar graph) have a significantly higher percent increase of the Young's Modulus compared to unfunctionalized GO composites (shown in shades of purple). For example, 0.01% ODA-GOi-PI and 0.01% ODA-GO-PI demonstrate percent increases of 28% and 39% , respectively. This can be compared to the 0.01% GO-PI which shows a decrease of 6%. A concentration 0.1% GO-Pi demonstrates an increase of 27% in the Young's Modulus.

Hue saturation of the bars is correlated to percent by weight of loaded GO particles;

darker cos have higher loadings, the highest being 0.5% GO-polyimide. Neat samples made in lab are shown in black and commercial DuPont Kapton ® is shown in gray. These controls allow comparison of composite materials to both non-composite in-lab synthesized polyimides and industry standard polyimide films.

Addition of 0.01% ODA-GOi shows a 28% increase in the Young's Modulus. However, when agglomerations appear in the 0.03% ODA-GOi samples, a decrease of approximately 5% is found. The 0.1% ODA-GOi sample also shows agglomerations but boasts an increase of 82% in the Young's Modulus. In the second set of functionalized samples, ODA-GO, improvement is shown at all loadings. 0.01% ODA-GO demonstrates the highest improvement of this family with an increase of 45%. 0.03% ODA-GO and 0.06% ODA-GO show improvements of 22% and 39%, respectively.

For unfunctionalized GO, increases in the Young's Modulus are found at loading starting at 0.03%. At 0.03% GO, there is a 16% increase in the Young's Modulus. At 0.06% GO, a 11% increase is shown in Young's Modulus. At 0.1% and 0.5% GO loadings, increases of 27% and 21% are shown.

These results show that the functionalized particles are capable of producing increases in the Young's Modulus at lower loadings than the unfunctionalized require for comparable improvements. The 0.01% ODA-GOi composite sample boasts a 28% increase in Young's Modulus and the 0.1% GO composite sample shows a 27% increase in Young's Modulus. A similar increase is produced by monomer functionalized materials but with 10 times less of the amount of loading material. A summary of these ratios and improvements by percentages can be found in Table 1 and represented visually in Figure 6.

	Kapton	Neat	0.01% ODA-GOi	0.03% ODA-GOi (agglomerations)	0.1% ODA-GOi (agglomerations)
Average	2088	2274	2911	2171	4141
Neat/Sample Ratio	0.92	1.00	1.28	0.95	1.82
Percent Change	-8.18	0.00	28.01	-4.53	82.10

	0.01% ODAGO	0.06% ODAGO	0.1% ODAGO	0.01% Load GO	0.03% Load GO
Average	3301	2775	3155	2143	2635
Neat/Sample Ratio	1.45	1.22	1.39	0.94	1.16
Percent Change	45.16	22.03	38.74	-5.76	15.88

	0.06% Load GO	0.1% Load GO	0.5% Load GO
Average	2526	2881	2742
Neat/Sample Ratio	1.11	1.27	1.21
Percent Change	11.08	26.69	20.58

Table 1: Mechanical results numerical comparison against neat samples

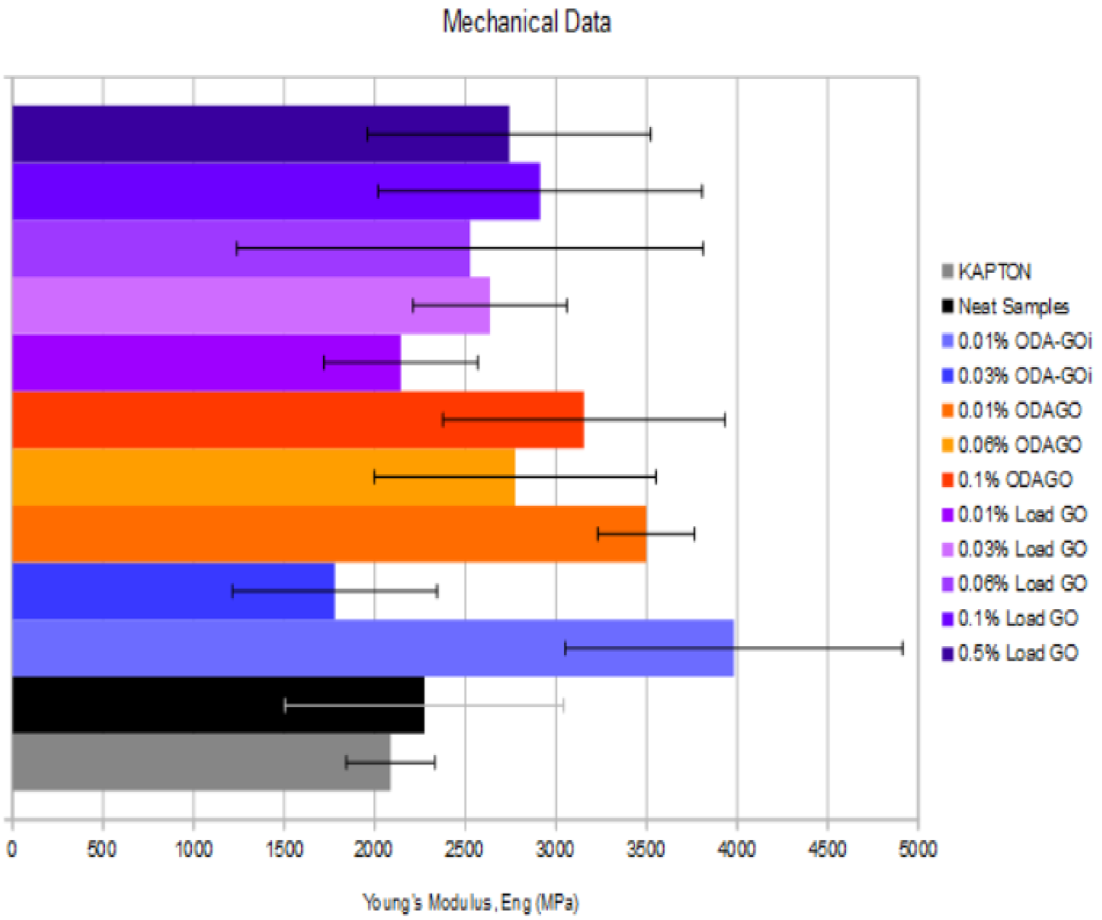

Figure 6: Mechanical results showing Young's Modulus in Mpa – GO-polyimide samples (purples), ODA-GO-polyimide (orange and blue), polyimide (black) and Kapton ® (grey)

b. Water Vapor Transmission

Data from Water Vapor Transmission tests shows that the incorporation of small amounts of GO particles decreases the amount of water vapor that passes through the polyimide film. Comparison of composites containing functionalized and unfunctionalized GO particles shows that the functionalized GO particles result in a much larger decrease in the amount of water vapor transmitted compared to the unfunctionalized particles. This indicates a stronger interaction and quality dispersion within the polymer matrix. See Figures 7-9.

4-4' ODA-GO-PI samples demonstrated water vapor transmission masses much below the neat samples while GO-PI samples demonstrated some films that were comparable to the neat, though the majority of them are well below the neat system. All sample types were run against DuPont Kapton® film samples. Our samples produced in lab were unable to out-perform DuPont's commercial material in terms of water vapor transmission. We believe this is due the quality of DuPont's industrial manufacturing process. Figure 7, showing the time vs mass gained plot for ODA-GO-PI demonstrates the best decrease in the amount of water vapor transmitted through the sample film. We believe that functionalization of GO particles with an appropriate monomer is key to producing samples with the best improved gas barrier properties at low loading percentages.

In Figure 7, the mass of water vapor gained, corrected for the thickness of the film, is plotted against time. The neat sample in Figure 7 is shown in black. An important observation is that the polyimide composites containing functionalized GO particles, ODA-GO-PI, appear to level off after approximately 20 hours and the rate at which water vapor transmits through the material is greatly reduced. Figure 13, a bar graph, represents visually the amount of water vapor transmitted through the film after 77 hours. In Table 2, it is read that the 0.01% ODA-GO-PI, 0.06% ODA-GO-PI, and 0.1% ODA-GO-PI allowed for the transmission of approximately 12.4%, 9.1% and 8.6% of the amount of water vapor transmitted through the neat sample in the same period of time.

In Figures 8-12, plots for unfunctionalized GO polyimide composites, GO-PI, are shown and summarized in a bar graph in Figure 14. For GO-PI samples, the greatest decrease in water vapor transmission is observed at 0.1% GO loading. The 0.1% GO-PI sample allowed for the transmission of 10.3% of the amount of water vapor transmitted thought the neat sample in the same period of time. Though GO-PI composite films show reduced water vapor transmission, they do not show decreases as dramatically as the ODA-GO-PI films and the trend is less apparently. Finally, the amount of water vapor transmitted does level off after 30 hours in the both GO-PI samples as it does in the ODA-GO-PI samples (see Figure 7).

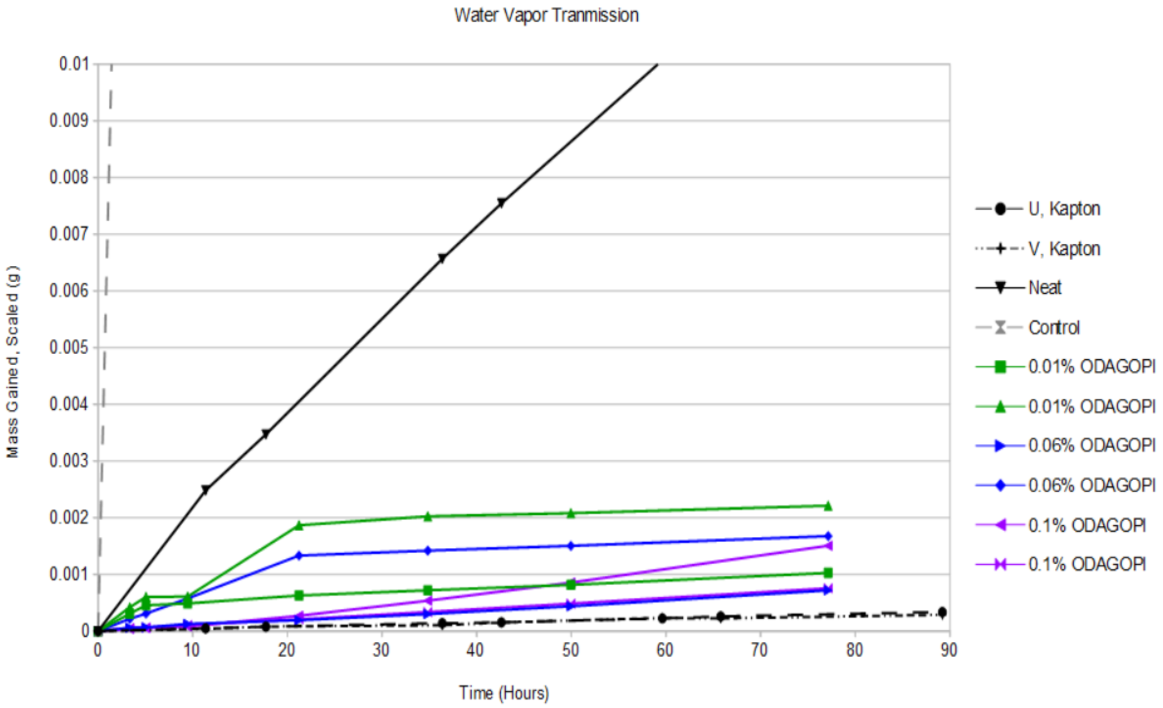

Figure 7: Time vs Water Vapor Mass Gained for three functionalized loadings (shown in colors) compared to in-lab synthesized neat polyimide material (black, averaged results, duplicate samples)

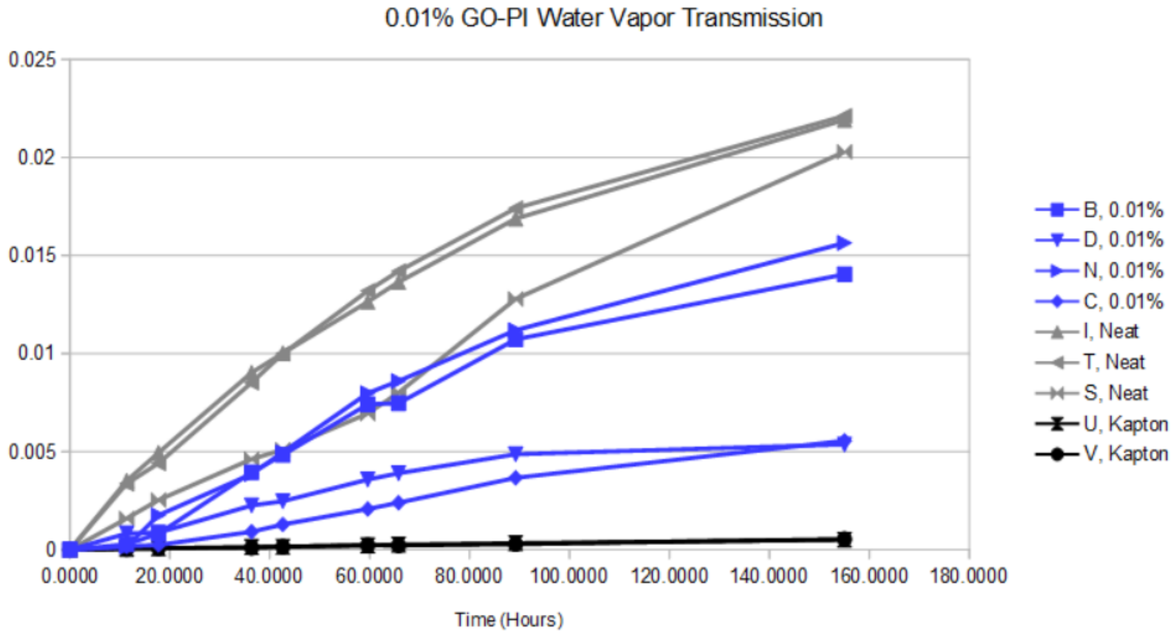

Figure 8: 0.01% GO-PI WVT Results. 0.01% GO-polyimide (blue) compared to in lab neat samples (grey) and DuPont Kapton ® (black). Dupont Kapton ® samples ran so consistently such that only one is visible; they are overlapped.

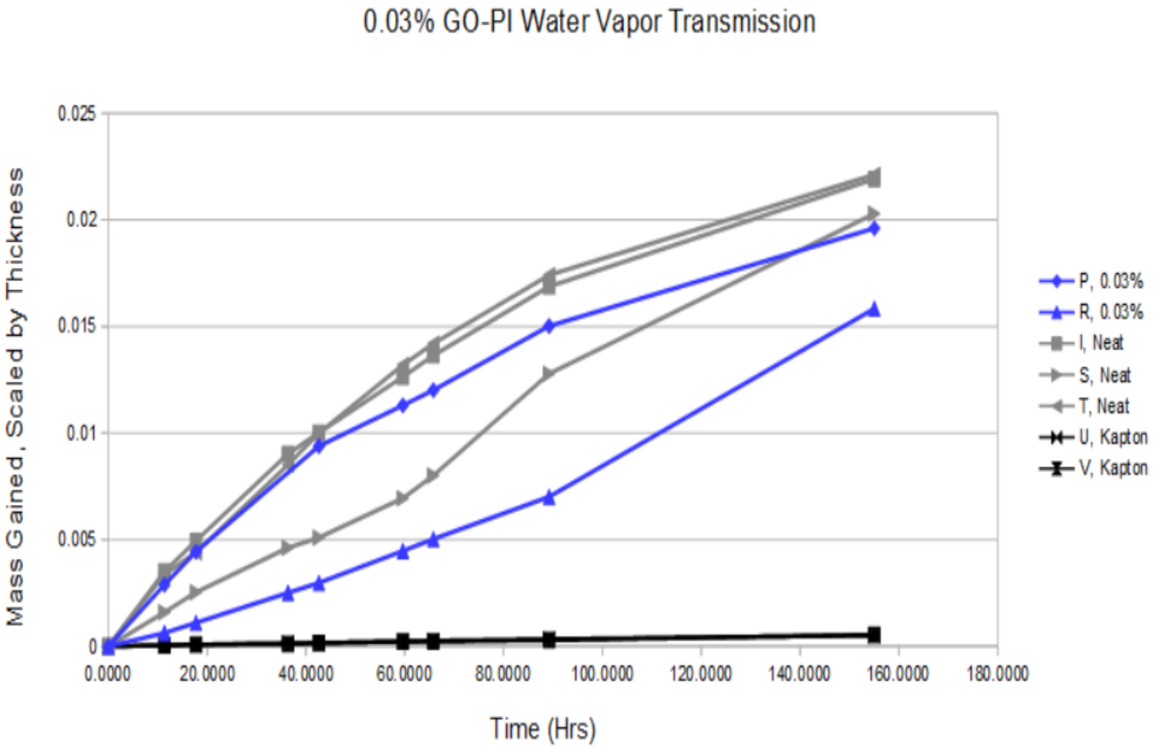

Figure 9: 0.03% GO-PI WVT Results. 0.03% GO-polyimide (blue) compared to in lab neat samples (grey) and DuPont Kapton ® (black). Dupont Kapton ® samples ran so consistently such that only one is visible; they are overlapped.

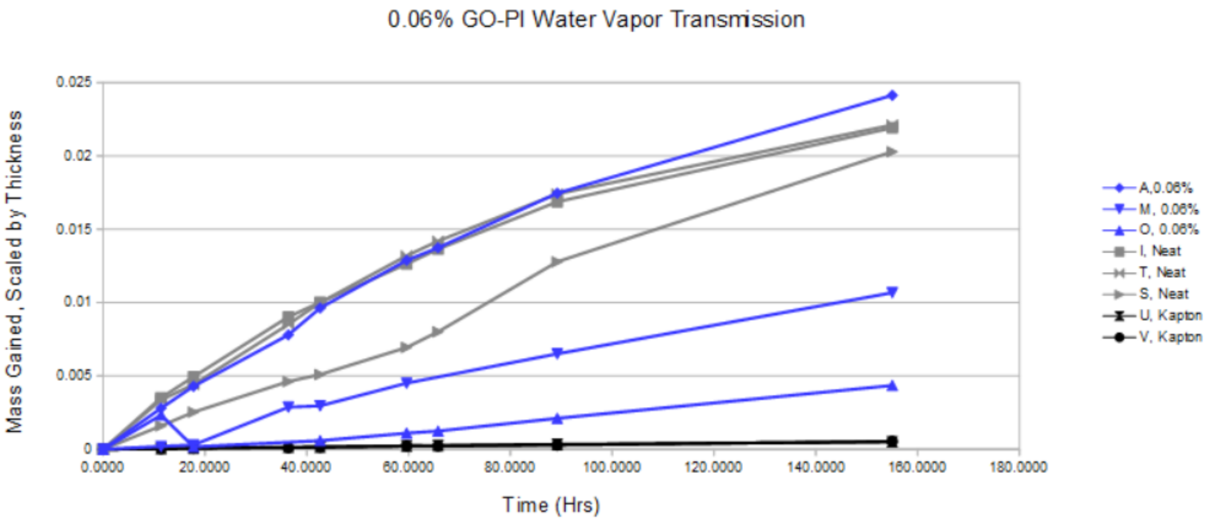

Figure 10: 0.06% GO-PI WVT Results. 0.06% GO-polyimide (blue) compared to in lab neat samples (grey) and DuPont Kapton ® (black). Dupont Kapton ® samples ran so consistently such that only one is visible; they are overlapped.

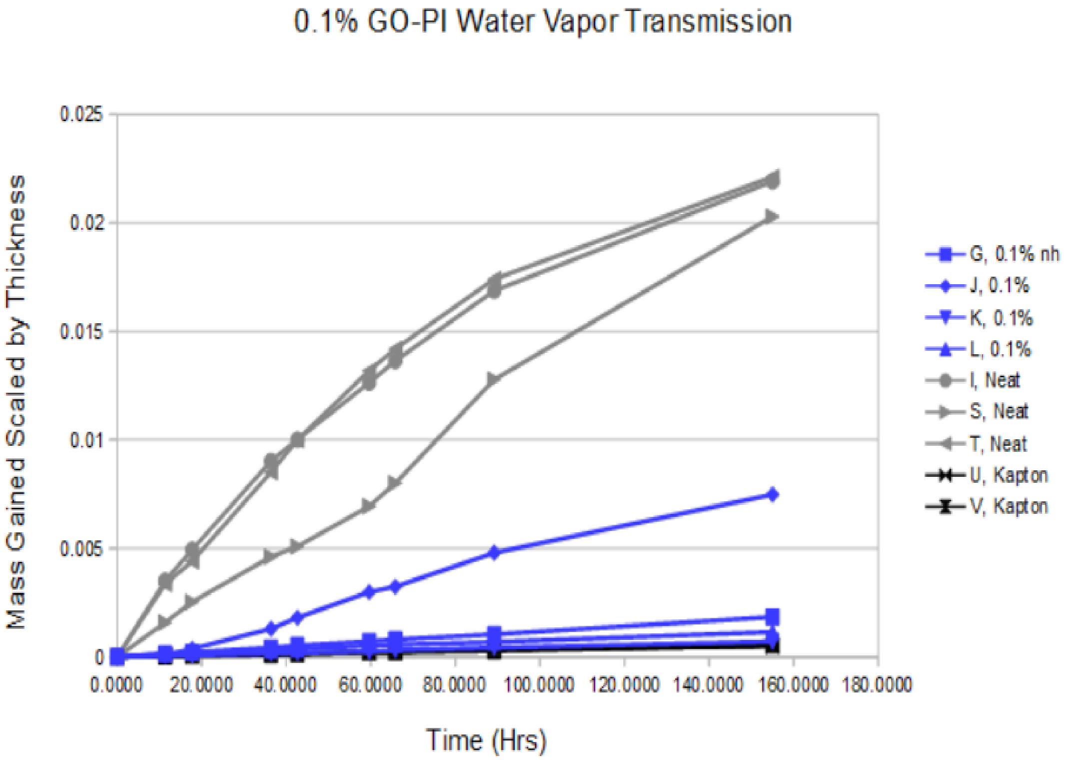

Figure 11: 0.1% GO-PI WVT Results. 0.1% GO-polyimide (blue) compared to in lab neat samples (grey) and DuPont Kapton ® (black). Dupont Kapton ® samples ran so consistently such that only one is visible; they are overlapped.

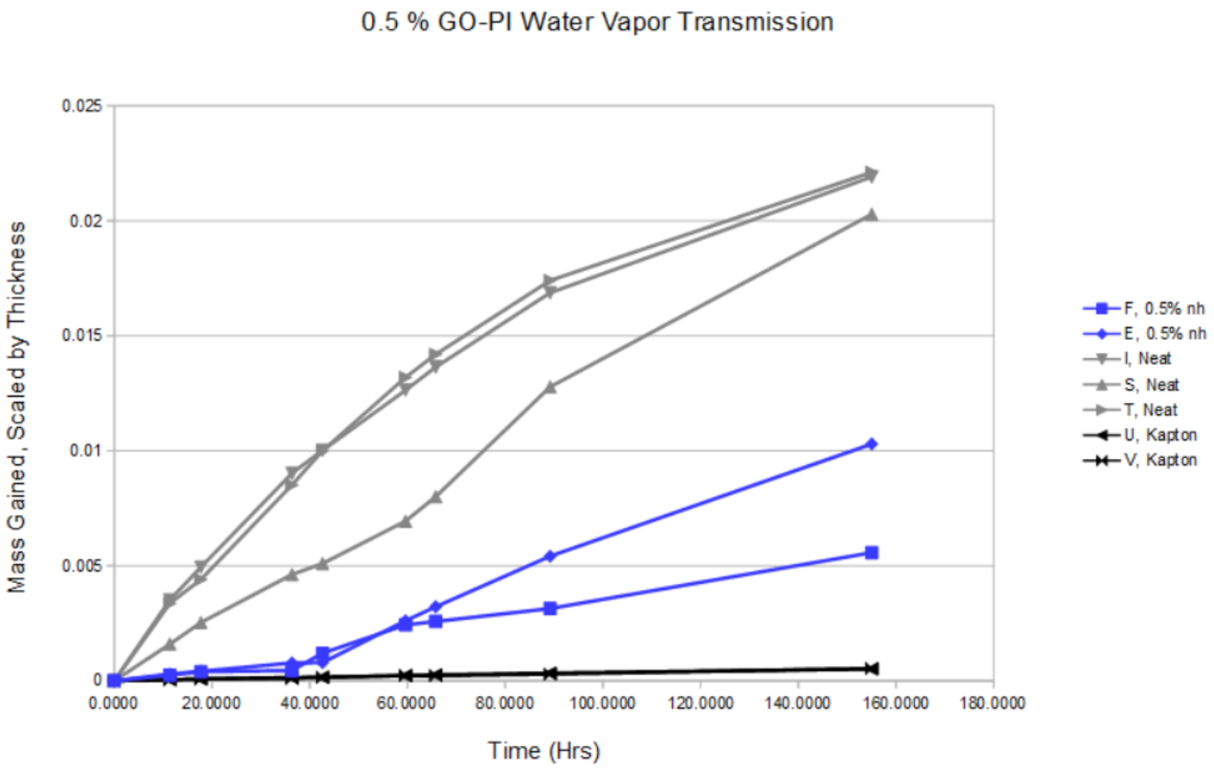

Figure 12: 0.5% GO-PI WVT Results. 0.5% GO-polyimide (blue) compared to in lab neat samples (grey) and DuPont Kapton ® (black). Dupont Kapton ® samples ran so consistently such that only one is visible; they are overlapped.

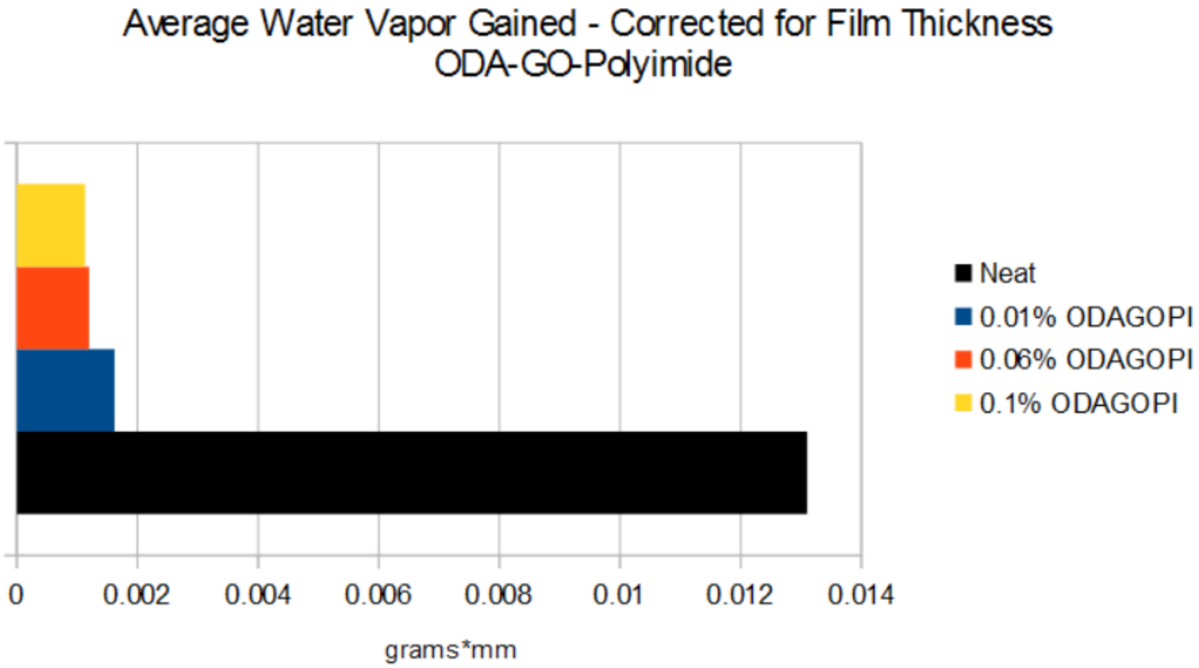

Figure 13: Visual Comparison of amount of water vapor gained corrected for thickness after 77 hours for functionalized GO particle composites (ODA-GO-PI) compared to neat polyimide (black).

	Neat	**0.01% ODAGOPI**	**0.06% ODAGOPI**	**0.1% ODAGOPI**
Average	0.0131	0.0016	0.0012	0.0011
Neat/Sample Ratio	1.0000	0.1237	0.0915	0.0863
Percent of Neat Transmission (%)	100.0000	12.3664	9.1450	8.6336

Table 2: Table showing ratio of average water vapor gain after 77 hours for functionalized GO particle composites (ODA-GO-PI) compared to neat polyimide samples

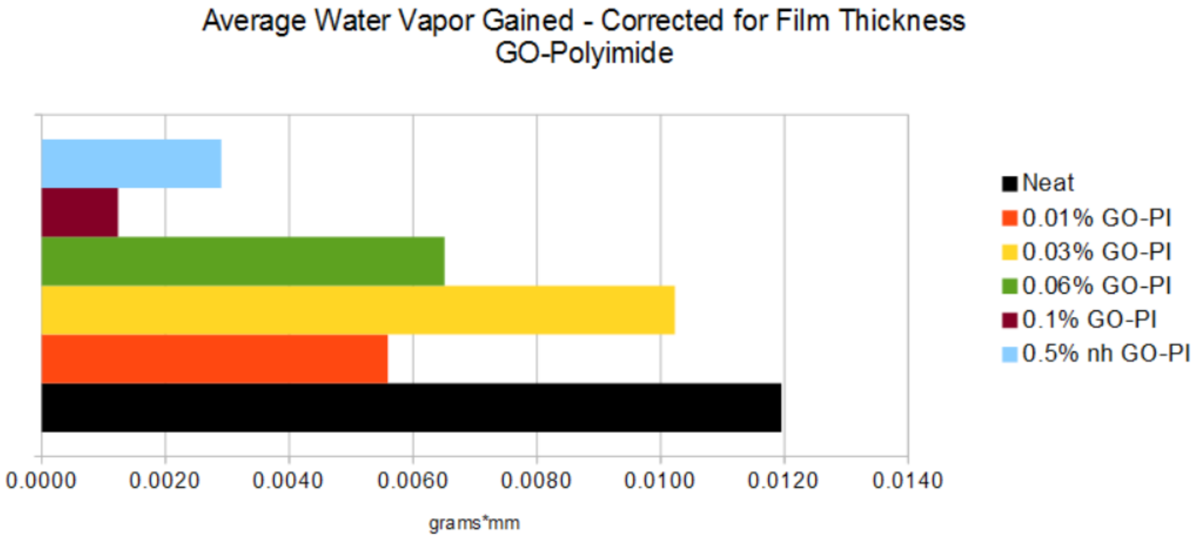

Figure 14: Visual Comparison of amount of water vapor gained corrected for thickness after 65 hours for unfunctionalized GO particle composites (GO-PI) compared to neat polyimide (black). Visually non-homogenous samples denoted by 'nh'.

	Neat	**0.5% nh GO-PI**	**0.06% GO-PI**	**0.1% GO-PI**	**0.03% GO-PI**	**0.01% GO-PI**
Average	0.0119	0.0029	0.0065	0.0012	0.0102	0.0056
Neat/Sample Ratio	1.0000	0.2427	0.5447	0.1033	0.8560	0.4680
Percent of Neat Transmission (%)	100.0000	24.2691	54.4661	10.3332	85.6031	46.8018

Table 3: Table showing ratio of average water vapor gain after 77 hours for unfunctionalized GO particle composites (GO-PI) compared to neat polyimide samples

c. Weight Gain Analysis

The excellent resistance of thermoplastic polyimide films to solvents is well known[i] but results from Weight Gain Analysis testing shows that it may be possible to improve these properties further. The 4-4'ODA-GO-Polyimide composite materials took up as little or less water than the neat and commercial Kapton ® samples. See Figures 15-22.

In order to better summarize these results, a bar graph showing the average amount of water weight gained (as percentage) at the longest time of immersion(24 hours) for each family of sample was created. See Figure 23. This bar graph shows that all composite materials gained less water weight than the neat system (grey). Only one composite system, 0.01% GO-PI gained more mass than the Kapton ®. Polyimides already demonstrate no higher than 4% mass gained by immersion in water in our experience with this testing method. The GO-PI film samples stayed consistently below 3% massed gained. The functionalized ODA-GO and ODA-GOi polyimide film samples stayed below 2% and 2.5% massed gained respectively. The functionalized systems gained much less mass on average than the neat systems, Kapton ® samples and the unfunctionalized GO composite polyimide films.

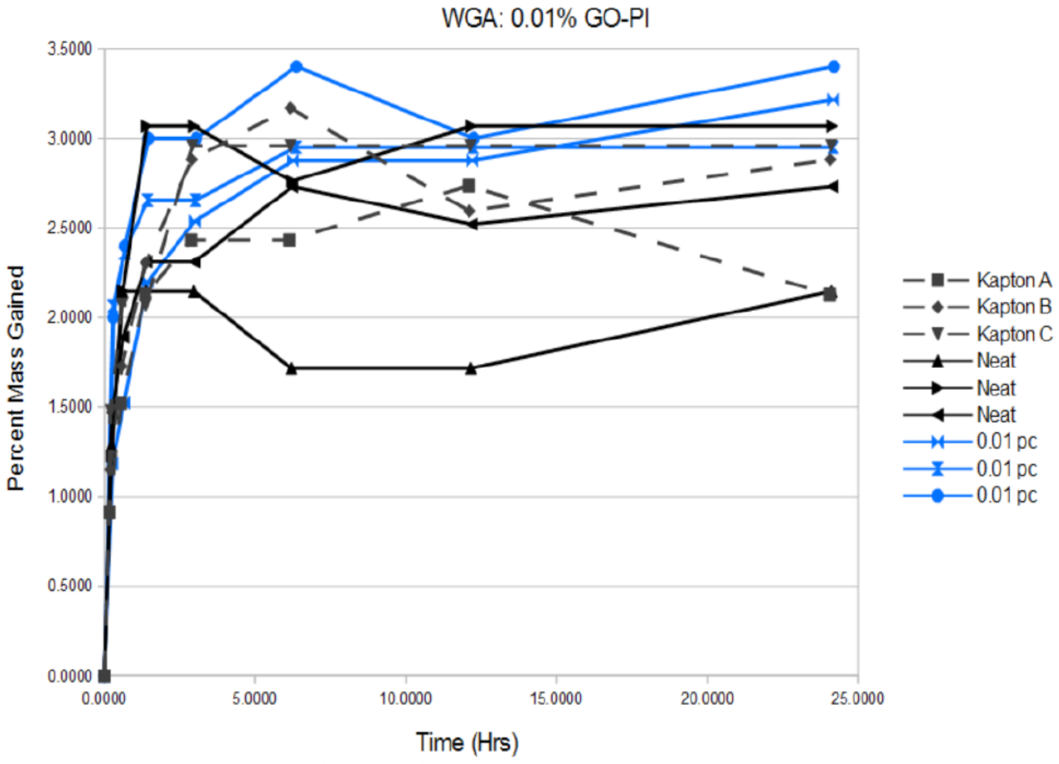

Figure 15: WGA Time vs Percent Mass Gained for 0.01% GO-PI Films compared to Kapton ® (grey) and neat samples (black)

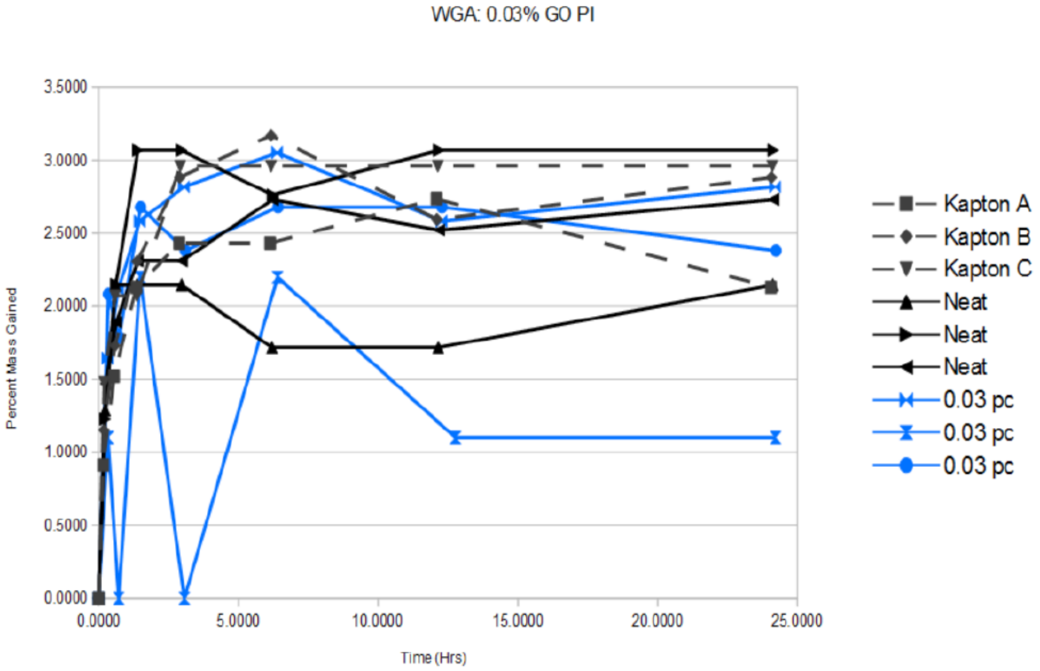

Figure 16: WGA Time vs Percent Mass Gained for 0.03% GO-PI Films compared to Kapton ® (grey) and neat samples (black)

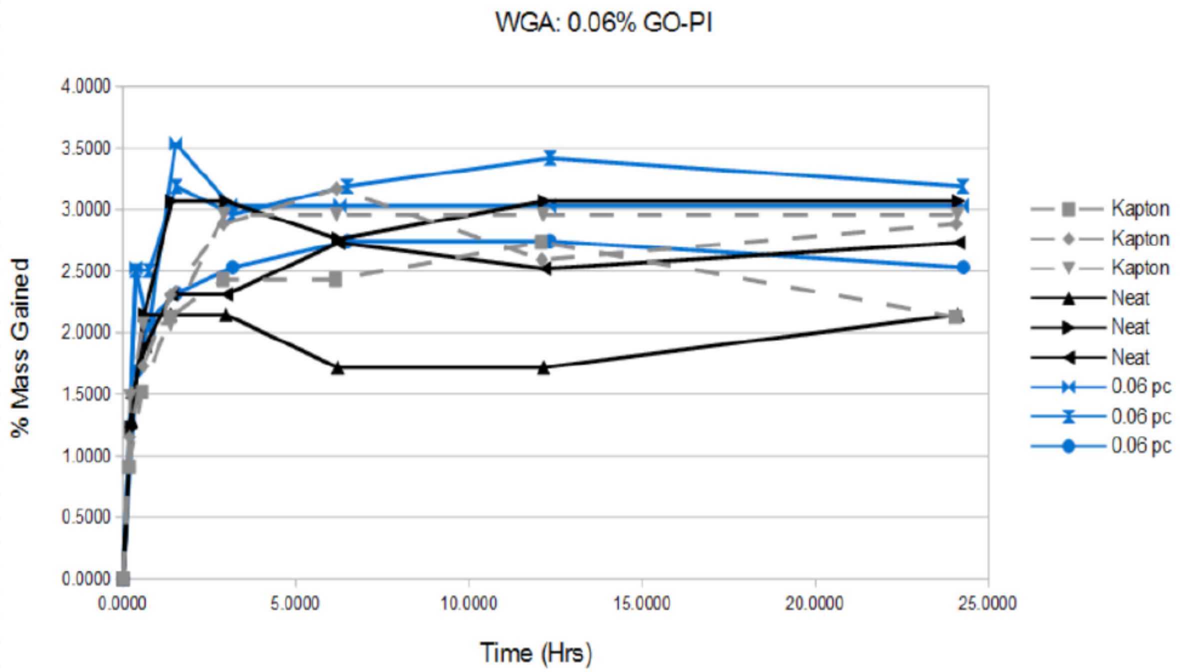

Figure 17: WGA Time vs Percent Mass Gained for 0.06% GO-PI Films compared to Kapton ® (grey) and neat samples (black)

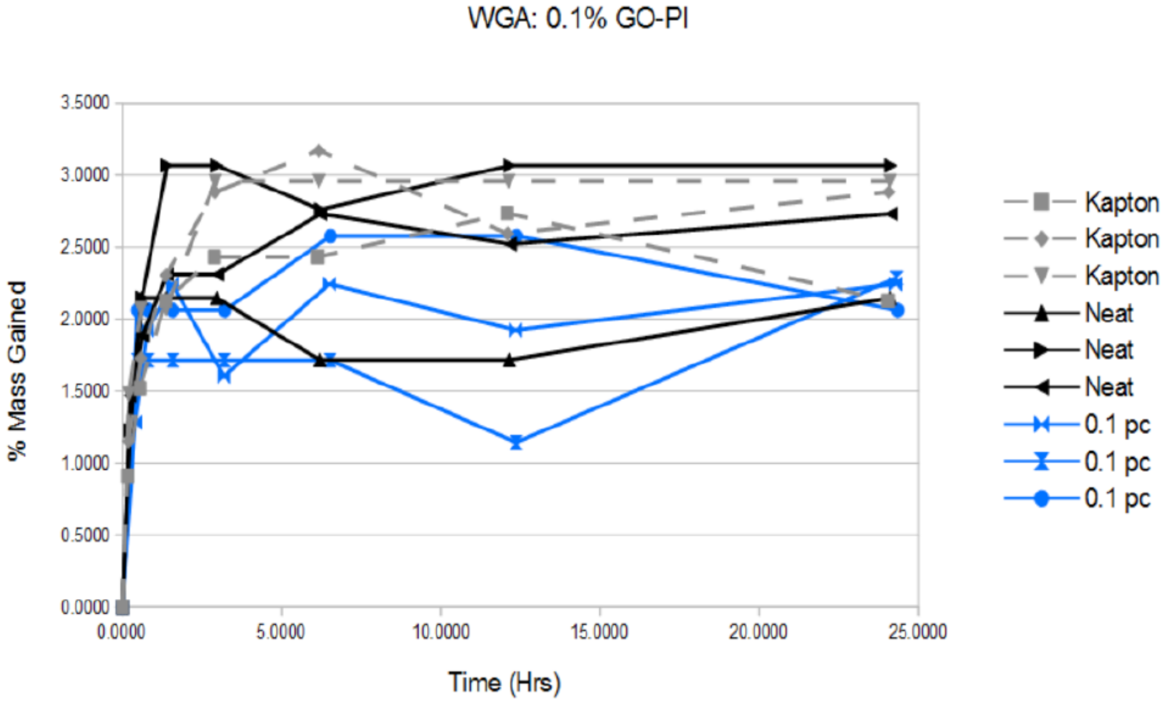

Figure 18: WGA Time vs Percent Mass Gained for 0.1% GO-PI Films compared to Kapton ® (grey) and neat samples (black)

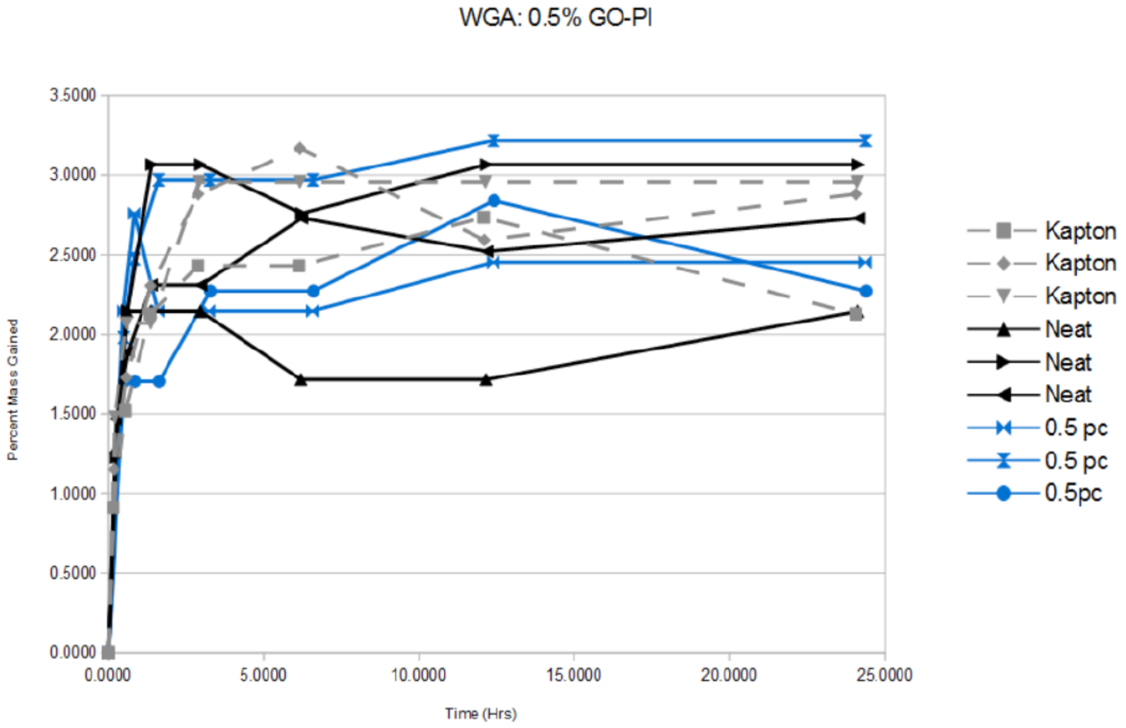

Figure 19: WGA Time vs Percent Mass Gained for 0.05% GO-PI Films compared to Kapton ® (grey) and neat samples (black)

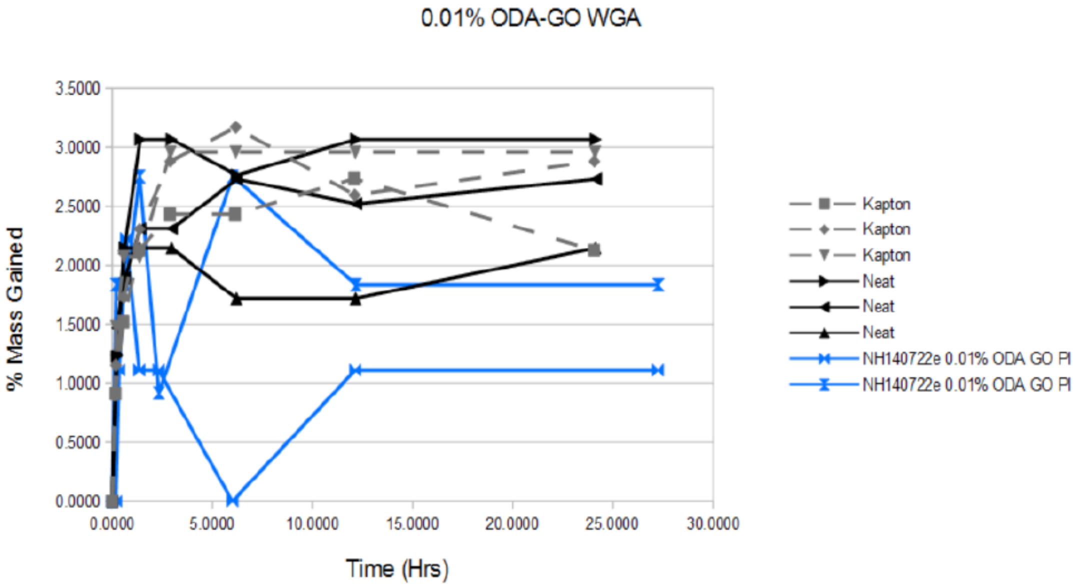

Figure 20: WGA Time vs Percent Mass Gained for 0.01% ODA-GO-PI Films compared to Kapton ® (grey) and neat samples (black)

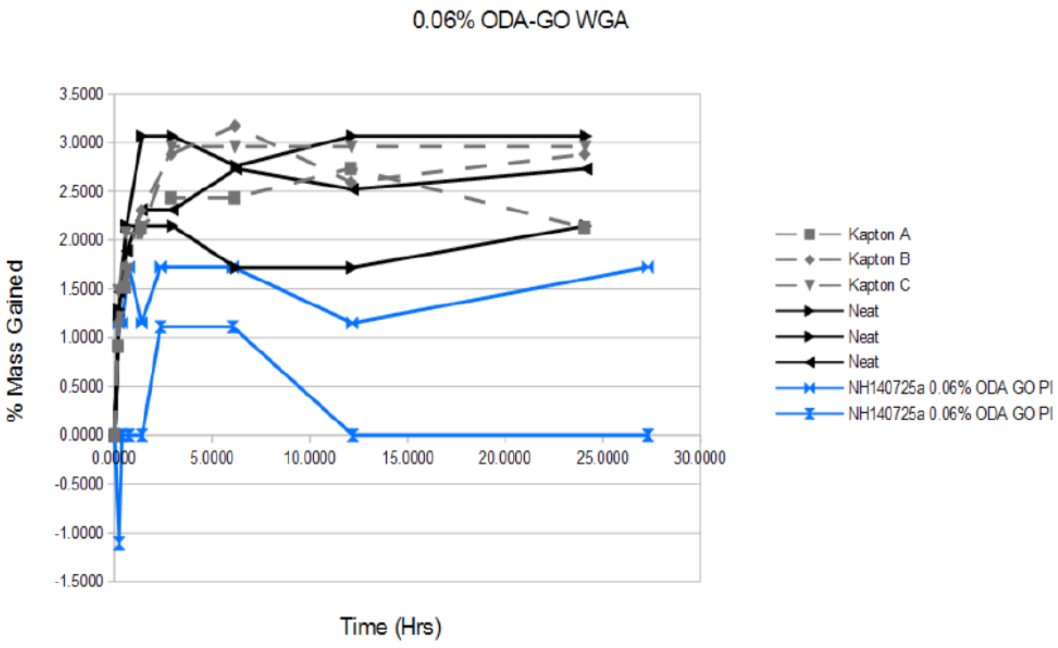

Figure 21: WGA Time vs Percent Mass Gained for 0.06% ODA-GO-PI Films compared to Kapton ® (grey) and neat samples (black)

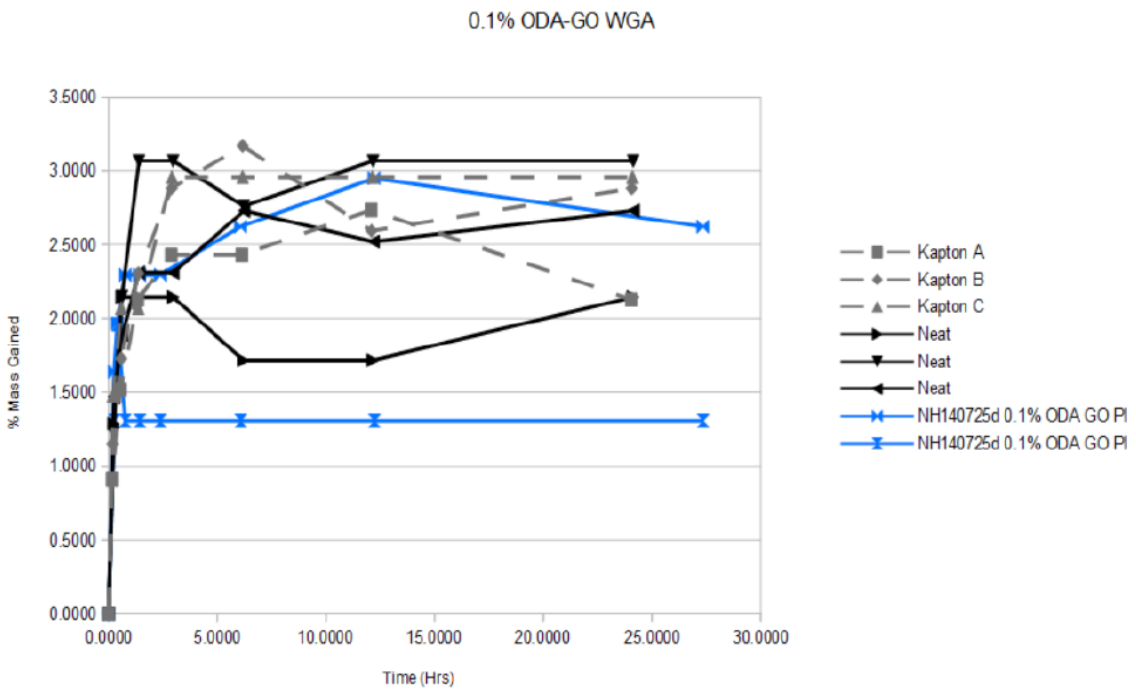

Figure 22: WGA Time vs Percent Mass Gained for 0.1% -ODA-GO-PI Films compared to Kapton ® (grey) and neat samples (black)

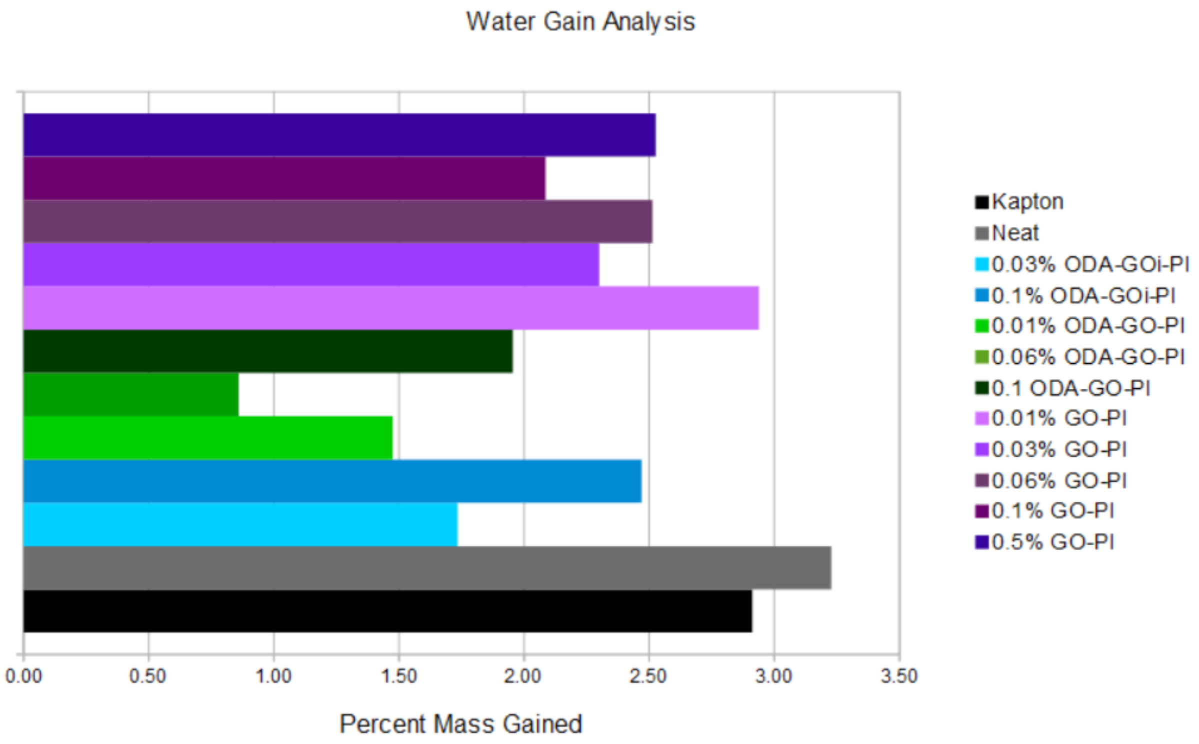

Figure 23: Bar graph showing the average amount of water gained as percent mass of original sample compared to Kapton ® (black) and neat samples (grey).

d. Thermal Stability

After being subjected to the selected heat cycle (jump to 100ºC, ramp 10ºC/minute to 550ºC and hold isothermal for 5 minutes until procedure termination), both polyimide samples showed black coloring and extreme brittleness, flaking apart upon touch and cracking easily, indicating thermal degradation of the polymer. The amount of mass loss during the cure cycle was determined in Universal Analysis and summarized in Table 3 below:

	Mass Losses (%)	
	Neat	**0.06% ODA-GO**
	13.25	17.58
	13.18	17.24
	14.25	17.01
	12.72	17.7
	-	18.78
AVERAGE	**13.35**	**17.66**
ST. DEV	0.64	0.68

Table 3: Summary of TGA Results

The results show that the 0.06% ODA-GO-Polyimide composite lost more weight than the neat polyimide sample produced in our laboratory. The decrease in thermal stability maybe be a tradeoff when producing these composite materials with improved mechanical, gas barrier and water resistant properties. However, it should also be noted that majority of the mass loss was lost at or after the temperature had reached 400ºC for both neat and composite samples so for normal use at temperatures up to 400ºC, the thermal stability of these composites in unchanged.

IV. Conclusion

Our experiments show that increases in the Young's Modulus can be achieved at extremely low loadings and that incorporation of GO particles functionalized with a monomer component of the system are more effective at yielding Young's Modulus increases at even lower loadings. A loading of 0.1% ODA-GOi resulted in a 82% increase in the Young's Modulus. A loading of 0.1% ODA-GO resulted in a 38% increase in the Young's Modulus. For unfunctionalized GO particles, a comparable increase in the Young's Modulus, was found at 0.1% GO to gain a 27% increase. Comparable increases with functionalized GO are achieved with much less GO incorporation. Improved performance even at lower loadings are advantageous economically, preferred for applications in which transparency is a concern, and lowers the likelihood of GO nanoparticles agglomerating during processing. The mechanical property improved at our lowest loading of 0.01% is the lowest loading percent found in the literature.

The Water Vapor Transmission results show that the composite materials have increased gas barrier properties compared to the analogous neat system synthesized in lab. The composite materials of functionalized particles out perform the composite materials of unfunctionalized GO particles. At 0.01% ODA-GO-PI, the composite film allows 12% as much water vapor to pass through as the neat sample synthesized in our laboratory allows. This represents a reduction factor of water vapor transmission of 1/8th. At 0.01% GO-PI, the composite film allows approximately 47% as much water vapor to pass through the film, a reduction factor of ½, as the neat sample synthesized in our lab allows. Functionalized and unfunctionalized GO particles both result in improved gas barrier properties compared to the neat sample but at significantly different levels of efficacy. We suggest that functionalization of GO particles results in improved gas barrier properties due to more favorable interactions between ODA-GO particles and the polyimide network.

The Water Gain Analysis results show that the incorporation of GO and ODA-GO particles decreases the amount of water uptake by a polyimide film sample. Polyimides already demonstrate no higher than 4% mass gained by immersion in water in our experience with this testing method. The GO-PI film samples stayed consistently below 3% massed gained. The functionalized ODA-GO and ODA-GOi polyimide film samples stayed below 2% and 2.5% massed gained respectively.

Improvement in thermal stability was not expected to result from the inclusion of GO or functionalized GO particles due to the introduction of labile oxygen-containing functional groups into the polyimide network. Our work showed a modest decrease in thermal stability at temperatures above 400ºC and is consistent with the results found by Heo et al.

In summary, very small additions of graphene oxide into the polyimide network on the scale of one part per thousand or less have significantly improved performance properties by factors of 20% (seen in the Young's Modulus) to a factor of 800% (found in gas barrier properties). The highest improvement factors are found in samples of polyimide composites in which the graphene oxide has been functionalized with the 4-4' ODA monomer. Clearly, reaction of graphene oxide nanoparticles with a monomer or small molecule compatible with the polymer system is the path for the most efficient improvement of polyimide properties by incorporation GO particles.

V. Future Work

Functionalization of GO particles and incorporation into a polymer matrix may be extended to other polyimides and other industrial polymers. Characterization experiments could be repeated and further experimentation could be performed to determine the effect of GO incorporation on other performance properties as a function of polymer structure. Future experiments include a plan to repeat mechanical testing of composite materials after the films have been subjected to temperatures at the higher range of their typical high-temperature use. This will allow us to determine if the improved mechanical properties observed are sustained after exposure to thermal stress. We also intend to repeat the method used for Water Gain Analysis with other common solvents to quantify the change in solvent resistance for other common solvents.

Current experiments being conducted in Kranbuehl lab as an extension of this project focus on composites of a thermoplastic linear polyimide and functionalized GO nanosheets with one of its component monomers. Synthesis and methods for functionalization with monomer and dispersion of GO follows in an Appendix. These materials have not been characterized due to the small amount of sample successfully synthesized thus far. The outlined synthesis for the thermoplastic polyimide system can be found in the Appendix.

VI. Appendix

a. Thermoplastic Polyimide Synthesis

The second system we have selected to work with, which will be the focus of much future work is the polyimide with monomers 1,3-bis(3-aminophenoxy) benzene (APB) and 2,2-bis(3,4-anhydrodicarbozyl phenyl) (6FDA). Unlike the aforementioned BTDA/4-4'ODA polyimide system, the APB/6FDA system is thermoplastic, as opposed to thermoset, and can therefore be stored as a dry solid, and then solvated to produced the desired film shape, thickness or form. This provides advantages in the logistical sense of storage and recycling of imperfect films.

Equimolar masses of APB and 6FDA are massed out and solvated into the solvent of choice. DMF and DMAc are both possible solvents. The solvent choice is not crucial at this juncture though DMAc is a better choice for preparations in which APB-GO particles are included. The amount of solid in resin is typically sits a 20% by weight but this number is very flexible and effects of multiple washes of vessels and the addition of APB-GO particles in later syntheses must be considered. For a typical synthesis, 3.965 g APB and 6.042 g 6FDA are used.

The solvated APB is transferred into a round bottom flask. The 6FDA solution follows. Pyrdine (3.225g) and acetic an hydride (4.200 g) are then added in order to catalyze the reaction to a linear, thermoplastic polyimide.[xvi]

The reaction is run under nitrogen gas, input into the flask over desiccant and through a mineral oil bubbler. Nitrogen leaves the system over desiccant. The reaction is stirred under N_2 for 24 hours and then removed. At this juncture, the APB and 6FDA are entirely polymerized but in solution. To yield a solid, easy-to-store polymer powder, the APB/6FDA solution in DMAc is poured into a large volume of methanol, a poor solvent for the system. Solid polyimide crashes out to the bottom and the methanol can be vacuum filtered out of the system and the rest dried at gentle heat under ventilation to yield a slightly off-white polyimide powder.[xvi]

An APB/6FDA film may be prepared by redissolving with a suitable solvent, spreading that solution out onto a glass film or glass petri dish and allowing the solvent to evaporate off either from ventilation or ventilation combined with gentle heat to obtain a thin, transparent polyimide film.

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