2016

Electrical Response of Functionally Graded Graphene-Nylon Segregated Composites Under Quasi-Static Loading

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ELECTRICAL RESPONSE OF FUNCTIONALLY GRADED
GRAPHENE-NYLON SEGREGATED COMPOSITES
UNDER QUASI-STATIC LOADING
BY
KIMBERLY I. McCARTHY

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN
MECHANICAL ENGINEERING AND APPLIED MECHANICS

UNIVERSITY OF RHODE ISLAND

2016

MASTER OF SCIENCE
OF
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2016

ABSTRACT

This research examines the fabrication and electro-mechanical properties of functionally graded graphene-nylon segregated composites. A novel production technique was expanded upon to produce segregated nylon-pellet and graphene nano-composites with low percolation threshold for electrical conductivity. This particle templating procedure effectively disperses graphene within the nylon pellet matrix and is hot-press melted into three-inch diameter discs. While ideally structured for electrical transport, these specimens are mechanically weak along the polymer grain boundaries. To enhance the mechanical properties, a double-rotary shearing step was added to increase mechanical strength without significant sacrifice to electrical properties, signifying the shearing method is a viable trade-off fabrication approach. Lastly, a production technique for fabricating graphene-nylon textiles with conductive properties was investigated. Graphene-coated nylon yarn in a polymer matrix proved to have high electrical conductivity.

Chapter one is an introduction to graphene and related studies and applications. The nylon-pellet graphene material fabrication and testing are explored in chapters two and three respectively. Chapter four addresses the nylon-yarn and graphene composites. Electrical conductivity was measured using a high resolution four-point probe method. Three-point bend and tensile testing experiments were used to evaluate mechanical properties.

ACKNOWLEDGMENTS

First and foremost I would like to extend my sincerest gratitude to Dr. Arun Shukla for his inspiring guidance and encouragement throughout my graduate research. I am especially grateful for his willingness to take me on as a part-time student and for his patience and support throughout the process. He is an exceptional professor and mentor and has fostered a wonderful, supportive team environment in his laboratory.

Furthermore, I would like to thank Dr. D.M.L. Meyer, Dr. Arijit Bose, Dr. David Chelidze and Dr. Mayrai Gindy for agreeing to serve as my committee members. Dr. Arijit Bose provided valuable advice and encouragement during my work with graphene and nylon. Dr. D.M.L. Meyer was inspirational in my decision to pursue Mechanical Engineering as an undergraduate ten years ago.

I am sincerely thankful for the mentorship and tireless support from Dr. Nicholas Heeder, whose doctoral research is the foundation for the work I am continuing here. I greatly appreciate the generous assistance from Abayomi Yussuf, along with Chitanya Gopu and Savannah Gregor. The help and encouragement from all of my Dynamic Photo Mechanics Laboratory colleagues throughout the years is sincerely appreciated, including Michael Pinto, Prathmesh Parrikar, Emad Makki, Helio Matos, Payam Fahr, Chris Shillings, Sachin Gupta, Craig Tilton, Frank LiVolsi, Sandeep Abotula, Shyamal Kishore, Daniel Clarkin, Nicholas DeNardo, Koray Senol, Carlos Javier, Jefferson Wright, Erin Gauch, Murat Yazici, and İdris Karen. I would also like to thank Indrani Chakraborty from chemical engineering. In addition, I would also like to thank Dave Ferreira, Joe Gomez, Jim Byrnes, Rob D'Ambrosca, AJ Bothun, Jen

Cerullo, Nancy Dubee and the rest of the mechanical engineering department faculty and staff.

I would like to acknowledge my late best-friend, Leah Ploutz, for her positive contributions to my life, including demonstrating the pursuit of a master's degree while working full time. However it was during the entirety of my own graduate career that I witnessed her true strength and the everlasting inspiration that will accompany me the rest of my life. I am thankful for the gift of friendship and I know she would have been very happy to know I have finished my thesis.

I am deeply grateful for my fiancé, Mario, who is a rock of support and whose encouragement was instrumental in beginning graduate school. I am indebted to my sister, Michelle, for a lifetime of support and whose own passion of her studies inspired me to pursue mine. Lastly, I dedicate this dissertation to my parents, Bill and Emily. I cannot thank them enough for the immeasurable love and support throughout my life and their encouragement to pursue my goals. Thank you for helping me cultivate this moment.

PREFACE

This research examines the fabrication and electro-mechanical properties of functionally graded graphene-nylon segregated nano-composites and the feasibility of graphene-nylon yarn.

Chapter 1 provides background information and a review of relevant literature. An overview of the research and experiments are discussed, along with major conclusions.

Chapter 2 examines the fabrication of graphene and nylon-pellet composites. A novel production method was expanded upon to most efficiently and effectively coat the nylon pellets with graphene. The steel mold went through several evolutions before it was able to produce adequate specimens.

Chapter 3 discusses the behavior of the material fabricated in Chapter 2. Electrical and mechanical experiments were conducted to evaluate tradeoffs of the graphene-nylon pellet composite material.

Chapter 4 investigates the feasibility of producing electrically viable graphene nylon-yarn composites for future growth in smart textiles.

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CHAPTER 1

INTRODUCTION

Graphene is a single atomic layer of carbon atoms arranged in a honeycomb lattice. This two dimensional material is the strongest material ever reported in nature and its electrical and thermal conductivity is very high [1]. For this reason, graphene research and its many diverse applications has gained much attention since its discovery in 2004 [1],[2]. Innovative manufacturing methods make it possible to procure graphene nanoparticles in a variety of sizes and capacities. Research involving integrating these nanoparticles into efficient structures can develop into broad ranges of use. The potential applications for graphene-polymer nanocomposites include industries such as automotive, aerospace, construction, and electronic [3]. Graphene nano-composites can form a three-dimensional electrical network if effectively dispersed within the matrix material. Polymers used as matrix material in carbon-based nano-composites have been extensively studied [4-7]. Studies have shown even a low graphene content in polymer composites exhibits outstanding electrical conductivity compared with conventional filled polymers [8]. The electro conductivity of the composite material depends on efficient dispersion of graphene in the filler, and this can be managed with low graphene content when using a segregated composite structure [9-11].

The first part of this research investigates segregated graphene-nylon pellet composites, while the second part is discussed later on and examines graphene-nylon textile composites.

Previous work by Heeder et al. investigated the electrical conductivity of polystyrene-graphene segregated composites [12]. The novel production technique demonstrated “is simple, commercially viable, and does not require hazardous chemicals. It provides the means to form highly organized conductive networks throughout insulating polymeric materials” [12]. A further innovative step to the material production process uses shear manipulation to distort the segregation of the material. The result is a functionally graded material that is nearer to ideal conditions for both mechanical and electrical properties [13].

In advancement from the previous study discussed above which created one-inch diameter samples with a single face distorted exclusively, this research uses three-inch diameter samples and distorts both the top and bottom of the sample discs. Furthermore, the composite will contain nylon as the matrix material instead of polystyrene. Both polymers are among the most commonly used thermoplastics in commercial industry.

A material fabrication procedure was regimented to achieve the ideal conditions for specimen repeatability. Once the nylon-graphene composite material was efficiently mixed, it was placed into a mold and heated to the appropriate melting temperature before being compacted under pressure. If the sample was categorized as “organized” it was then quenched in a bath of cool water. If the sample was categorized as “sheared”, it was sheared on the top and bottom surfaces during the

compacting step before quenching. The objective of the shear manipulation is to form an area with an integrated structure to improve mechanical properties by allowing the matrix material to form cohesive bonds. Although this disrupts the electrical networks and diminishes electrical properties, the areas of the sample that remain segregated still have highly conductive characteristics. In this way a sample can possess both ideal electrical and mechanical properties.

The specimens were experimentally tested to determine electrical and mechanical properties. The electrical conductivity for each specimen was established using a differential four-point probe method. The material resistance was calculated by passing a constant current through the specimen and measuring the voltage drop across the known width of the specimen. For mechanical testing, an Instron machine was used for quasi-static three-point bend testing and tensile testing of the material at a slow loading rate. The Instron is equipped with a data acquisition system to record load, deflection, and time.

As postulated, a significant increase in electrical conductivity could be achieved with a small amount of graphene when compared with plain nylon. The organized specimens had the highest conductivity, but were considerably weak mechanically. The sheared specimens had slightly lower electrical conductivity but were appreciably stronger, indicating the shearing method is a viable trade-off approach.

The second part of this research examines combining graphene nanoparticles with nylon yarn to form smart textiles. “Wearable electronic devices, such as e-textiles, are of great interest due to their potential applications in portable electronic

devices, in multifunctional fabrics, including healthcare units and wearable displays, and even in warfare. [14] Graphene-oxide (GO) is commonly used as it absorbs into textiles more easily, however it does not have high electrical conductivity so efforts are typically made to transform it into reduced graphene-oxide (RGO) [14-17]. Textile industry standard productions, such as wet spinning, are often used [16],[17]. It has been found that dispersing graphene in an acetone bath results in high electrochemical performance because it “prevents the adulteration effects of impurities into the system.” [17]

A preliminary investigation was done to determine the feasibility of producing nylon smart textiles. A method of combining graphene with nylon yarn was explored. The graphene used was pure, few layered graphene as opposed to graphene-oxide, and a hand-mixing method was used that involved an acetone-graphene solvent and dry graphene powder. The graphene-nylon yarn was then preserved in a polyurethane matrix. The electro-conductivity of the graphene-nylon yarn composites were electrically evaluated and found to be within the same order of magnitude as the sheared graphene-nylon pellets from the first part of this research.

CHAPTER 2

MATERIAL FABRICATION

Graphene is a two-dimensional atomic matrix of carbon and is the basic structural element of its other allotropes; graphite, carbon nanotubes, and fullerenes (also known as bucky balls). Although graphene refers to a single atom thickness of carbon and graphite is multi-layered carbon, “few-layered graphene” can be considered to be in-between with a thickness still in nano-scale. In this thesis, “few-layered graphene” will be used interchangeably with “graphene”. Few-layered graphene was selected for use in this study to produce a viable electro-conductive pathway through the macro-composite of nylon pellets.

The graphene selected for use in this research was xGnP Grade M from XG Sciences. Per the manufacturer’s data sheet, the non-oxidizing proprietary process makes the graphene ideal for electrical conductivity. Each graphene nanoplatelet is approximately 6nm thick with a surface area unit mass of 120-150 m²/g. The electrical conductivity parallel to the nanoplatelet surface is 10⁷ S/m, and the conductivity perpendicular to the surface is 10² S/m.

Nylon 6-12 is a polyamide thermoplastic commonly used in commercial industry and was selected for this research as the composite matrix material to be combined with graphene. One current use of nylon 6-12 is for automobile fuel lines by combining with carbon black to form a composite material. The nylon is sufficiently robust yet elastic enough to provide durable ductility in an everyday vehicle. The

electrical conductivity of carbon black, which is derived from the incomplete combustion of hydrocarbons or petroleum products, acts to discharge static and prevent static ignition of the fuel.

ZYTEL® LC7601 NC010 from DuPont was selected as the nylon for this research. LC stands for long chain, indicating flexibility. NC signifies that the material is white in color. The cylindrical pellets on average measured 0.131 inches high by 0.085 inches in diameter and had a mass of roughly 0.0168g. The flexural modulus is 540 MPa. The electrical conductivity is on the order of 10^{-12} S/m, depending on the nylon's water absorption. The melting temperature range is between 220-230°C (425-445°F). This high melting temperature and large desired sample size posed a production challenge, as will be discussed later. Nylon is susceptible to moisture absorption so the manufacturer recommends dehumidifying and drying the pellets at 80°C (175°F) for 4 hours before use. The Nylon pellets were placed in an oven and dried in accordance with manufacturer's instructions, then stored in air tight containers until use. Appendix A includes more details on the materials and Appendix B includes the steps for specimen production, which is also described below.

To utilize graphene most efficiently, it is advantageous to identify the percolation threshold, or least amount of graphene to nylon ratio for electro-conductance. By distributing graphene along the outer surface of the nylon pellets before melting into a sample, a conductive network is created along that pellet's surface. It can then be conductively linked to the adjoining neighboring pellet, and so on. In this way, only a small amount of graphene was needed in relation to nylon. Several samples of varying percent volume ratios of graphene to nylon were created

and electrically tested. The conductivity increased significantly at 0.3% volume ratio of graphene. 0.3% volume graphene was also the percolation threshold of Heeder's research [12].

Once the appropriate ratios of graphene and nylon were measured, both were placed in a glass jar and shaken vigorously. Graphene adhered to the surface of the nylon pellets likely due to electrostatic attraction. A 3-inch diameter by ½ inch disc specimen contains roughly 3,270 nylon pellets. Photos of the nylon pellets before graphene coating and after graphene coating are shown in Figure 1.

Figure 1: (A) Uncoated white nylon pellets. (B) Nylon pellets coated with 0.3% graphene.

The nylon-graphene mixture was then placed in a steel mold and heated to melting temperature of 200°C, compressed, and cooled before removal. The result resembled a 3D honeycomb lattice network of dark graphene around white nylon pellets as shown in the figure below in a 1-inch diameter sample.

Figure 2: One-inch diameter sample disc of nylon-graphene composite cut to reveal inside conductive networks.

There were several iterations of the 3-inch diameter steel mold before the optimized mold was developed. The final mold setup is shown in Figure 3 and consists of a hollow cylinder die with two pistons on the top and bottom. The mold sits on a height-adjustable framed pedestal consisting of a steel plate, two threaded rods with nuts, and a threaded anvil base. A spherical steel sphere bearing is placed between the bottom piston and the anvil base, and another steel sphere bearing is placed on top of the top piston to make contact with the hydraulic press. The graphene coated nylon pellets are placed into the mold die which is heated by four heater cartridges. The cartridges fit into bored holes in the top and bottom pistons. The mold temperature is read by a thermocouple that fits into a small drilled hole on the outer diameter of the hollow cylinder die. Once the thermocouple reads 200°C, the heating cartridges are removed and a hydraulic press is used to apply 10 tons of compression to the top piston. Quickly and while under compression, the top and bottom pistons are rotated by hand relative to the center die using an adjustable pin spanner wrench to

latch onto the bored holes on the top and bottom pistons. This performs the shearing of the top and bottom faces of the sample.

Figure 3: Final mold assembly for double rotary shearing.

Figure 4: Preliminary mold concept showing thrust bearings on top and bottom pistons.

Steel material was selected over aluminum for the mold to withstand repetitive heating and quenching in a bath of cold water. Quenching is necessary to cool the nylon before it is allowed to overheat.

The following is a discussion of lessons learned when manufacturing several iterations of the mold. The first hollowed cylinder die was made from stainless steel and had an inner diameter of approximately 3 inches, an outer diameter of 4 inches, and was 3 inches high. The gap between the die inner diameter and the pistons was only a small fraction of an inch, but this was wide enough to allow leakage of nylon-graphene material to escape from the mold as shown in Figure 5. When torque was applied to the top and bottom pistons, the small gap permitted the pistons to tilt to one side and created a moment arm so that the bottom edge of the piston scored the inside of the die. Repairing the score by machining the die and pistons surfaces to smoothness only widened the gap further and created a cycle of damage that required more repair than the previous.

Figure 5: Initial mold design showing material leakage through gap between piston and die.

The mold leakage and scoring issue was corrected by machining a new die and two new pistons to a tighter diametrical gap of only 0.004 and 0.006 inches (0.002 and .003 inches radially each side). The final hollow cylinder die was created from high strength 17-4 PH stainless steel to inhibit scoring, and the pistons were created from 316 stainless steel. It was observed that at room temperature with fully polished surfaces, the descent time of the piston being released into the die was observably slower to allow air to escape from the tight gap.

The heater cartridges were housed within the machined cavities in both the top and bottom pistons. Both pistons also had four blind holes at 90° radial spacing to accommodate the spanner wrench pin during rotation. Manual rotation of the pistons was expected to be difficult, so flat aluminum bronze bearings were preemptively selected to mount between the sliding surfaces of the top and bottom pistons, and the stationary base or hydraulic press. This bearing setup proved insufficient so a miniature thrust ball bearing turntable was attempted on both top and bottom pistons. Though this second bearing design was considerably improved, manual rotation was still difficult and the final design of a single large ball bearing on both top and bottom pistons accomplished the task. The very small surface area contact of the single ball bearing made the mold unbalanced, but the mold frame held the mold steady.

The mold frame pedestal plate uses four dowel pins protruding upwards for a loose fit into the mating four blind holes in the bottom of the die. This prevented the mold die from turning during rotation and also permitted easy removal from the frame after heating was completed. The plate frame is mounted by two threaded rods to allow height adjustment with respect to the anvil base.

Several preliminary specimens were created to pinpoint the temperature reading needed to melt the nylon just enough to form a cohesive bond but not too much that the segregated templating of the conductive networks were lost and the material was burned. The mold took approximately four hours to reach the desired thermocouple reading of 200°C (392°F), though the inside of the mold likely saw a slightly higher temperature closer to nylon's melting temperature of 220-230°C (425-445°F). The factors contributing to the lengthy heating time included the large amount of metal being heated and the ambient room temperature. A mylar thermal blanket was used to enclose the heated mold and prevent heat from escaping into the room for more efficient heating. During the winter months a space heater was required in the enclosed room or the mold would never reach the desired temperature. A temperature controller system was preemptively selected and programed to maintain the desired temperature range, but was not needed since it was concluded that the heating cartridges needed to be removed from the mold immediately after the sample reached 200°C to prevent the specimen from burning or melting excessively and losing its conductive pathways. If the mold and specimen was immediately quenched in a cool water bath, it would form internal or external bubbles as shown in Figure 6. Removing the heat source and Mylar blanket and allowing the mold to cool by convection for approximately five minutes reduced the air bubbles. Figure 6 shows the internal voids in a sample, likely caused by trapped air bubbles.

Figure 6: (A) Initial trial of organized sample showing internal and external voids. (B) Organized sample that was allowed to cool gradually and did not form voids.

The specimens that were radially sheared had smear patterns that varied depending on the degree and direction of piston rotation. All specimens used for testing were sheared on top and bottom in opposite directions approximately 360° . Figure 7 below illustrates the basic pattern resulting from shearing. In the top view, the greatest shearing occurs on the outer periphery of the disc since this area essentially travels the most for a given degree. The interior remains relatively un-smeared. The side view shows more smearing on the top and bottom with the center again remaining relatively un-smeared.

Figure 7: Smear patterns of sheared specimen with top and bottom faces sheared 360° in opposite directions.

A sliced section view in Figure 8 shows internal smear patterns. Specimen (A) was only sheared approximately 45° and has an interesting smear pattern that varies between being organized on the outer circumference and center, and smeared in the remaining areas. Specimen (B) was sheared approximately 360° and has areas of extreme smearing with moderate smearing in the interior of the sample. In both cases, the interior remains relatively organized because the center has the least travel distance when the piston is rotated. Figure 9 depicts a sketch of the shearing pattern.

Figure 8: Section view of sheared specimen showing smear pattern for (A) 45° shear top and bottom, and (B) 360° shear top and bottom.

Figure 9: Sketch of sheared specimen pattern for moderate shearing.

Each 3-inch sample disc was cut to different dimensions depending on the method of mechanical testing. Figure 10 shows ½” wide specimens cut for three-point bend testing. Figure 11 shows ¼” wide specimens used for tensile testing.

Figure 10: (A) Dimensions for cutting $\frac{1}{2}$ inch wide specimen for use with three-point bend testing. (B) Actual specimen after cutting.

Figure 11: (A) Dimensions for cutting $\frac{1}{4}$ inch wide specimen for use with tensile testing. (B) Actual specimen after cutting.

The samples needed to be cut in such a way that the nylon would not melt across the freshly cut surface and block the electro-conductive pathways. Samples that were roughly cut with a band saw or milling machine did not display consistent

electrical results and the data was excluded. Consistent results were achieved by using a thin spiral blade on a milling machine at 340 rpm. Compressed air was used on the sample during cutting, and only a small amount of material was cut at a time. A total of three-passes were used to cut through the $\frac{1}{2}$ inch sample.

Exposure of the graphene electro-conductive pathways on either sliced end is essential. The next chapter will detail how the sliced ends of the samples were prepared for electrical conductivity testing. The chapter also describes mechanical testing.

CHAPTER 3

ELECTRICAL AND MECHANICAL EXPERIMENTS

This chapter discusses the electrical and mechanical experiments conducted on the graphene-nylon composite samples described in the previous chapter. Firstly, the electrical conductivity of each sample was tested to compare organized versus sheared samples. Secondly, the flexural and tensile properties were tested by three-point-bend and tensile test experiments.

The electrical conductivity of each sliced sample was evaluated by measuring the voltage drop across the known width of a sliced sample – from sliced end to sliced end. Figure 12 below shows a line of conductive silver paint applied to the center of the specimen on both cut ends, and a wire adhered to each painted surface. Black electrical tape and masking tape were used to ensure the wire made contact only with the conductive paint and not with any other portion of the sample. A sheared sample will have the greatest conductivity in the center where it remains relatively unsmearred as described in the previous chapter.

Figure 12: Organized graphene-nylon specimen illustrating silver paint and wire attachment.

Figure 13: Diagram of electrical conductivity testing on nylon-graphene samples.

The surface area of the silver paint did not significantly affect the voltage drop readings. An organized sample was tested a second time with both surfaces entirely painted with silver conductive paint and the voltage drop results were the same compared with the single small strip of paint. It is understood electricity will travel across all pathways and the measurement will come from the path of least resistance.

The wires were connected to a constant current source (Keithley Instruments Model 6221) and two electrometers (Keithley Instruments Model 6514). The voltage drop was measured using a digital multimeter (Keithley Instruments Model 2000 DMM) and recorded for current intervals ranging from 100 nA to 1 mA. The average resistance was found using Ohm's Law ($V = I \times R$) and conductivity was found by taking the inverse of the resistance. Below is a graph showing conductivity of sheared and organized nylon-graphene composites at 0.3% volume graphene.

Figure 14: Experimental results for electrical conductivity of organized and sheared specimens compared with plain nylon properties.

Compared with plain nylon, the sheared samples are on average nine orders of magnitude more conductive, and organized samples are on average ten orders of magnitude more conductive.

After electrical testing, samples were subjected to mechanical testing by means of three-point bend and tensile testing. Three-point bend testing examines the flexural properties of the graphene-nylon composite. An Instron was configured for three-point bend using two lower anvils spaced 60mm apart, and one upper anvil in the center. Samples were side loaded (perpendicular to mold pressure) at a rate of 0.1 mm/min. The figure below shows a loading direction diagram and a specimen flexing while undergoing three-point-bend, and finally a particle split in the center that indicates a “break” of the material.

Figure 15: Three-point bend testing. (A) Specimen is loaded perpendicular to pressing as shown in diagram. (B) Specimen undergoing three-point-bend. (C) Specimen at failure.

The flexural strength is the stress of the material just before yield during a flexural test. Figure 16 shows the flexural strength for organized and sheared samples. Compared with plain nylon, the organized samples have approximately one quarter the flexural strength. Adding the shear component to both faces of the specimen increases the flexural strength nearly four times so it is just shy of plain nylon's flexural strength.

Figure 16: Experimental results of flexural strength for organized and sheared specimens compared with plain nylon properties.

The average flexural strength and electrical conductivity data is normalized with respect to plain nylon's properties in the below figure. The graph shows the tradeoff between electrical conductivity and flexural strength for both organized and sheared samples. The segregated graphene network allows very efficient electron transfer, however it is very weak mechanically. The sheared network is just shy of the electrical performance of the organized specimens, but is significantly strong mechanically. This indicates the shearing method achieves a good balance in tradeoffs between electrical and mechanical performance.

Figure 17: Normalized electro-mechanical behavior of average experimental results for organized and sheared specimens compared with plain nylon properties.

For tensile testing, the thin ¼ inch cut specimens were used in an Instron with a clip gauge. The organized samples failed in the center of the sample along the particle boundaries as shown in the figure below.

Figure 18: Tensile test of organized specimen showing failure at particle boundary.

Figure 19 below shows experimental results of tensile tests for multiple organized specimens compared with plain nylon properties. Plain nylon has approximately six times the tensile strength as the organized graphene-nylon specimens. Data from sheared specimens will be attempted to be collected before the oral defense.

Figure 19: Experimental results of tensile strength for multiple organized specimens compared with plain nylon properties.

Table 1 shows a comparison of the electrical and mechanical properties of the specimens alongside the properties of the raw material used to form the composites: nylon and graphene.

		Conductivity (S/m)	Flexural Strength (MPa)	Tensile Strength (MPa)
Experimental	Average Organized	5.34E-01	12.13	8.32
	Average Sheared	2.35E-02	40.27	13.17
Literature	Plain Nylon	1E-11	48	48
	Graphene xGnp-M parallel to surface	1.E+08	N/A	5000
	Graphene xGnp-M perpendicular to surface	1.E+03	N/A	N/A

Table 1: Electro-mechanical comparison of average experimental data for graphene-nylon composites with literature of plain nylon and graphene.

Although the tensile data for the sheared specimens is listed as N/A, it is known they outlived the organized specimen stress before the sample slipped from the test grips. As would be expected, the conductivity of the experimental specimens are values between the plain nylon and raw graphene properties. There was no manufacturer data provided for flexural strength of the graphene, or for tensile strength in the perpendicular-to-surface direction. Both organized and shear specimens have lower mechanical properties than plain nylon and raw graphene, but this is inherent in the segregated macro-compo-site design. The mechanical experiments were not testing a single solid sample, but rather the stress needed to break apart the bonds between the segregated raw materials (graphene and nylon).

The next chapter explores a very different fusion of nylon and graphene composites using nylon yarn.

CHAPTER 4

NYLON-GRAPHENE TEXTILES

A preliminary investigation was accomplished to demonstrate the feasibility of fabricating graphene-nylon textiles. Several trial production methods were explored and one resulted in successfully demonstrating electrical conductivity.

Numerous industry techniques for treating and dyeing textiles were researched. One intriguing method called mercerization is used to dye and strengthen cellulose materials such as cotton. Mercerization is a process involving a chemical reaction that causes swelling of cellulose fibers so they are more receptive to smaller particles and absorption of dyes. Although nylon is non-cellulose, the absorption mechanism of mercerization was noted as inspiration. A solvent-graphene mixture was created and it was decided to utilize a smaller version of the “few-layered graphene” used in Chapter 3 for nylon-pellets composites.

The nylon textile obtained for this research is called “nylon fluffy yarn”.

Figure 20: Nylon fluffy yarn.

The first attempt to create a graphene nylon-yarn composite with electrical conductive properties was unsuccessful. The yarn was wetted with Methyl Ethyl Ketone (MEK) and then rolled in dry graphene powder (xGnp-M) to coat the outside of the yarn. It was immediately assembled into the mold in a horizontal crossing pattern. This was done to explore the potential for complexity in composite design with the ideal result being a sheet of fabric. Before the yarn dried in the mold, epoxy was poured over and allowed to harden. The textile-graphene epoxy sample was removed from the mold and cut to expose the graphene yarn on all sides. The sides were painted with silver conductive paint and a wire attached similar to the method in Chapter 2. However, no reliable electrical data was collected. It is speculated that either a complete conductive network was never formed or that during cutting the sample melted the epoxy and coated the exposed ends of the graphene-yarn.

Figure 21: Preliminary attempt at overlapping graphene nylon-yarn in epoxy matrix.

A second method was developed to construct a graphene-nylon yarn composite. Instead of coating the outside of the yarn, traditional industry methods were investigated to explore depositing graphene inside the nylon yarn fibers. Traditional dyeing techniques use a liquor ratio of 100:1, which is the ratio of liquid to the material being dyed. [17] Though this turned out to be much more liquid solvent

than was needed, the industry liquor ratio was still followed. The yarn was cut into pieces approximately 5 inches long and massed to be .7856 g. This equated to 78.56 g of graphene-MEK (Methyl Ethyl Ketone) solution total. It was decided to retain the 0.3% volume ratio of graphene to MEK. The graphene was changed from xGnP-M to xGnP-C-500 as these were physically much smaller particles of few-layered graphene (6nm thick vs. 1-3nm thick). The nylon yarn was allowed to soak in this liquor to absorb the graphene within its fibers.

Figure 22: Nylon yarn soaking in graphene-MEK solvent.

As can be seen from the photo above, the yarn turned grey in the solvent mixture. To assure that an electrical conductive channel was formed in the next mold production, half the yarn was then coated with dry graphene powder (x-GnP-C-500). Both sets of graphene nylon yarn were placed immediately into the mold before allowed to dry. The soaked and coated graphene-nylon yarn was on one side while the single soaked graphene-nylon yarn was on the other side. The yarn was lain across

horizontally without crossing each other and the side panels were bolted on. Polyurethane was selected as the matrix material for its ability to not adhere to the mold when mold release is applied. Polyurethane was poured on top and allowed to set per manufacturer's instructions.

Figure 23: (A) A single uncoated nylon yarn shown secured in the mold. (B) Graphene-nylon yarn with polyurethane matrix in the mold.

After curing was complete, the polyurethane-graphene-nylon samples were cut into long rectangular sections measuring $5 \times 1/2 \times 1/8$ inches. Silver conductive paint was used on the exposed graphene-nylon-yarn ends of the samples, and wires were attached. Figure 24 shows Samples 1 and 2 which were prepared by both soaking and coating the nylon yarn with graphene, while samples A, B, and C only soaked the nylon yarn with graphene.

Figure 24: Graphene-nylon yarn samples in polyurethane matrix. The yarn in specimens 1 and 2 were soaked and coated with graphene, while specimens A, B and C were only soaked in graphene solvent.

All samples were tested for electrical conductivity but only specimens 1 and 2 produced results. Specimens A, B, and C likely did not have enough graphene to form a conductive pathway. Adding the step to roll the graphene-soaked yarn in more dry powder graphene establish electrical conductivity throughout the full length of the yarn.

The polyurethane in the sample simply provides the structure for the conductive nylon-graphene yarn and does not contribute to the electrical properties. Therefore the cross-sectional area of the yarn, the diameter, was used in conductivity calculations rather than including the cross sectional area of the polyurethane matrix.

	Conductivity (S/m)
Specimen 1	9.86E-02
Specimen 2	2.50E-03
Average	5.06E-02

Table 2: Experimental results for electrical conductivity of graphene-nylon yarn.

Figure 25: Graph comparing experimental results of graphene-nylon yarn with graphene-nylon pellets both sheared and organized, against plain nylon pellet properties.

The average conductivity value for the single-yarn method (5.06E-02 S/m) is the same order of magnitude as the shear graphene nylon-pellet sample average value from Chapter 3, Table 1 (2.35E-02 S/m).

The fabrication method successfully produced graphene nylon-yarn conductive specimens; however, there may be room for improvement to achieve better electrical results. Unlike the graphene-nylon pellet specimens which were compressed in the mold after heating to form tight efficient graphene networks, the graphene nylon-yarn

specimens were allowed to remain “fluffy” and spread out within the polyurethane matrix. When a cellulose material such as cotton goes through the mercerization process, the resulting yarn is always shorter in length and stronger when it dries. This would work to stack the graphene nano-platelets in one direction.

APPENDICES

APPENDIX A: DETAILS OF MATERIALS

Graphite Nanoplatelets

Acquired from XG Sciences, Lansing, MI (www.xgsciences.com)

Catalog No. xGnP-M-25 (used with nylon pellets)

Description: xGnP Graphene Nanoplatelets: Grade M

Thickness: ~ 6 nm

Surface Area: $120 - 150 \text{ m}^2/\text{g}$

Particle Diameter: 25 microns

Density: $2.2 \text{ g}/\text{cm}^3$

Carbon content: $>99.5\%$

Tensile Modulus:

Parallel to surface: 1,000 GPa

Perpendicular to surface: N/A

Tensile Strength:

Parallel to surface: 5 GPa

Perpendicular to surface: N/A

Electrical Conductivity:

Parallel to surface: 10^7 S/m

Perpendicular to surface: 10^2 S/m

Catalog No. xGnP-C-500 (used with nylon yarn)

Description: xGnP Graphene Nanoplatelets: Grade C

Thickness: ~ 1 -3 nm (depending on surface area)

Surface Area: 500 m²/g

Particle Diameter: less than 2 microns

Nylon Resin (Polyamid 612)

Acquired from DuPont, USA (www.dupont.com)

Catalog No. Zytel LC7601 NC010

Description: Nylon Resin Zytel LC7601 NC0101, PA612-IP

Melting Temp. at 10°C/min: 209 °C (408 °F)

Stress at Break: 48 MPa (7.0 kpsi)

Strain at Break: 50 mm/min, 400%

Tensile Modulus: 500 MPa (72 kpsi)

Flexural Modulus: 500 MPa (72 kpsi)

Flexural Strength: 48 MPa (6.9 kpsi) [average of comparable materials]

APPENDIX B: GRAPHENE-NYLON PELLET FABRICATION PROCEDURE

APPENDIX B: Templating Procedure for making Nylon/GNP composites

Materials: **Matrix:** Zytel LC7601 NC010 Nylon Resin (DuPont, Inc.)

Filler: xGnP Nanoplatelets M-25 (XG Sciences, Inc.)

I. **Organized GNP/Nylon Particle Templated Composites**

1. Measure out 60g of Nylon pellets in a glass beaker.
2. Measure out 0.3927g GNP.
3. Combine Nylon and GNP in glass jar. Seal and shake vigorously to allow for
4. complete coating of nylon pellets.
5. Spray interior of mold with a light coating of extreme temperature ceramic lubricant to prevent the plastic from sticking to the walls of the mold.
6. Place coated Nylon into mold and insert four heating cartridges into the mold in the designed holes. Place the thermocouple in the middle of the center mold to read the sample's temperature.
7. Set Rodix Feeder Cube heater cartridges to 9V and set the temperature control processor heater cartridges to desired temperature (200°C).
8. Cover the mold setup with mylar blanket to trap heat and use a space heater in the enclosed room if necessary.
9. Thermocouple will report desired temperature reading in approximately 4 hours. When temperature is reached, turn off and remove heater cartridges.

10. Press to 10 metric tons and maintain pressure for 20 seconds. Release, then cool immediately under water.

II. Shear-modified GNP/Nylon Particle Templated Composites

1. Follow steps 1-8, ensuring steel ball bearings are in place on the top and bottom pistons.
2. Press to 5 metric tons.
3. Using the spanner wrench, rotate both pistons to desired angle and press to 10 metric tons.
4. Release pressure and cool immediately in cool bath of water.

APPENDIX C: RECOMMENDATIONS FOR FUTURE WORK

Graphene-polymer composites:

- Vary polymer type and shearing method. For example instead of rotary shearing, perhaps a single directional lateral shear.
- Vary percent volume of graphene to polymer ratio.
- Further quantify the gradation of the material in both x and y axis.
- Measure defects of the material using high resolution photos.
- Mechanical testing of elastic modulus.
- Determine if air is left in the specimens and investigate removal with vacuum or spinning.
- Dynamic experiments with live electrical testing. For example if the composite is compressed, is there a moment when the conductive networks are forced together and conductivity actually improves?
- Smart sandwiches as sensor for internal damage. For example, can a drop in electrical readings predict internal damage?
- Develop material that is conductive in one direction and insulating in the other direction.

Graphene-textile composites:

- Use graphene-oxide to promote chemical bonding with textile.
- Incorporate graphene using textile industry equipment for spinning or dying
- Utilize mercerization or cationic reagent with cellulose fibers (such as cotton) as an efficient way of incorporating graphene into the fibers and improving fiber strength.

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