Mechanical Performance Of Graphene Enhanced Nitrile Rubber

Torkel Nord Bjaerneman

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MECHANICAL PERFORMANCE OF GRAPHENE ENHANCED NITRILE RUBBER

A Thesis
Presented in partial fulfillment of requirements
For the degree of Master of Science in Engineering Science
The University of Mississippi

Torkel Nord Bjaerneman
May 2020
ABSTRACT

After the discovery in 2004, graphene and its different forms have been studied as nanofillers into a wide range of polymers and elastomers. It is now known that these nanofillers can have a significant effect on the polymer’s or elastomer’s mechanical performance. One area that has been overlooked is the effect these nanofiller can have on the cutting resistance – an essential mechanical property when it comes to occupational safety products – when they are being incorporated into the polymer or elastomer matrix. Reported are the effects on the mechanical performance after adding graphene nanoplatelets, and a functionalized form thereof, to nitrile rubber. The mechanical properties reported are storage modulus and tensile strength, as well as the cutting resistance when being coated on a nylon substrate. The procedure followed three distinct phases. Phase 1 served as a screening phase. Phase 2 followed a statistical design-of-experiments approach to get an objective understanding of the effect of nanofiller concentration and curing temperature on the mechanical properties mentioned above. Lastly, Phase 3 explored the possibility of adding non-functionalized graphene nanoplatelets to reduce the cost of production as well as the coating thickness’ effect on the cutting resistance. In Phase 1, it is reported that by just adding 0.2 parts per hundred rubber (phr) of functionalized graphene nanoplatelets (fGNP) to the nitrile rubber, a 171% increase in tensile strength was achieved. Similarly, by adding 1 phr of fGNP, a 58% increase in storage modulus was obtained.
Phase 2 reports that in order to maximize the storage modulus, the optimized combination is for the nanocomposite to be cured at 140°C with a concentration of 1.8 phr. However, due to the degradation of the nylon substrate at higher curing temperatures, the curing temperature was fixed at 130°C and the new optimal concentration was found to be 1.6 phr. During Phase 2, a 95% increase in storage modulus was obtained for a specimen with a 2.34 phr concentration and cured at 135°C. Lastly, in Phase 3 it was found that the thickness of the coating seem to have a greater effect on the cutting resistance than the concentration of the nanofiller. However, the coating with 1.6 phr of graphene nanoplatelets, cured at 130°C and with a 1 mm thickness, increased the cutting resistance by 29% in comparison to the pure nitrile rubber coating cured at the same temperature and with the same thickness. In conclusion, it was found that both the curing temperature and nanofiller concentration had a significant effect on storage modulus. An increase in storage modulus was found to increase the cutting resistance. Whilst the nanofiller concentration had an effect on the cutting resistance, the coating thickness was found to be of greater significance.
DEDICATION

To my Mother, for your unconditional love and for being there every step of the way.

To my Father, for undoubtedly expressing the highest level of confidence in me.

To my Brother, for supporting me from day one.

And, to Myrtle & Ed, for without whom this journey wouldn’t ever have been possible.
ACKNOWLEDGMENTS

I would like to express the deepest appreciation to my academic advisor and committee chair, Professor Ahmed Al-Ostaz, who has followed me and supported me all the way from my undergraduate studies to graduate studies. Professor Al-Ostaz has helped me prepare for what comes next after graduation. Without his guidance and help this thesis would not have been possible.

I would like to thank my committee members, Professor Sasan Nouranian and Professor Hunain Alkhateb, for their guidance, dialogue and insight. In addition, I would also like to thank Dr. Xiaobing Li, who taught me a great deal in the lab and for being invaluable to this thesis, as well as Mrs. Grace Rushing for all of her help and for being a great colleague. Also, thank you to Professor Clay Dibrell and Professor Robert VanNess from the School of Business for helping me with the business portion of this thesis.

To the former Executive Director of the National Graphene Association, Dr. Zina Jarrahi Cinker, thank you for taking me under your wing and for continuously including me in global initiatives for graphene and related materials commercialization.

Lastly, at the Office of Technology Commercialization, I would like to express appreciation to Allyson Best, Michael Mosher, and Gregory Sechrist for letting me work with them, and for teaching me about technology transfer and patent law.
ABBREVIATIONS

2D       Two-dimensional
1LG      Graphene
2LG      Bilayer graphene
FLG      Few-layer graphene
GNP      Graphene nanoplatelet
GO       Graphene oxide
GRMs     Graphene and related materials
ISO      International Organization for Standardization
IEC      International Electrotechnical Commission
fGNP     Functionalized graphene nanoplatelet
XPS      X-ray Photoelectron Spectroscopy
EDS      Energy Dispersive X-ray Spectroscopy
SEM      Scanning Electron Microscopy
AFM      Atomic Force Microscopy
BET      Brunauer-Emmett-Teller theory
PSD      Particle Size Distribution
SSA      Specific Surface Area
TEM      Transmission Electron Microscopy
PSA      Particle Size Analyzer
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<tr>
<td>TDS</td>
<td>Technical detail specification</td>
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<tr>
<td>NBR</td>
<td>Nitrile butadiene rubber</td>
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<td>MWCNT</td>
<td>Multi-walled carbon nanotubes</td>
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<td>PEI</td>
<td>Polyethylenimine</td>
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<tr>
<td>DMA</td>
<td>Dynamic mechanical analyzer</td>
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<tr>
<td>DOE</td>
<td>Design of experiments</td>
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<td>OFAT</td>
<td>One-Factor-At-a-Time</td>
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<td>CCD</td>
<td>Central composite design</td>
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<td>RSM</td>
<td>Response surface methodology</td>
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<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>LSD</td>
<td>Least Significant Difference</td>
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<td>TRGO</td>
<td>Thermally reduced graphene oxide</td>
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<td>phr</td>
<td>Parts per hundred rubber</td>
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<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>CAGR</td>
<td>Compound annual growth rate</td>
</tr>
<tr>
<td>ISO/TC229</td>
<td>ISO Technical Committee 229</td>
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<tr>
<td>TAG</td>
<td>Technical advisory group</td>
</tr>
<tr>
<td>WG</td>
<td>Working group</td>
</tr>
<tr>
<td>EHS</td>
<td>Environmental, health and safety</td>
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GR2M  
Graphene-related 2D materials

TDS  
Technical detail specification

ECHA  
European Chemicals Agency

EPA  
Environmental Protection Agency

TSCA  
Toxic Substances Control Act
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CHAPTER 1: INTRODUCTION

1.1 SYNOPSIS

Chapter 1 covers the theoretical background and gives the reader a perspective for the reason why this study is performed. It provides an understanding of the details of graphene and related materials, why this area is interesting to study and the challenges that comes with two-dimensional materials.

Chapter 2 is a brief overview of the materials, equipment and methods used in this study. It also covers the in-house functionalization and purification process that was used to modify the surface chemistry of the graphene nanoplatelets.

In Chapter 3, the study on the mechanical properties of nitrile butadiene rubber (NBR) with different conventional forms of graphene added as the reinforcement is reported, as well as the process of how those results were obtained. The overarching goal of Chapter 3 was to investigate the tensile strength and storage modulus of NBR and NBR nanocomposites, and then correlate those properties to the cutting resistance when being coated on a nylon substrate. The chapter is divided into three distinct phases. Phase 1 served as a screening phase where curing procedure, mixing method, type of nanofiller, and nanofiller surface chemistry were investigated. After it was determined that functionalized graphene nanoplatelets (fGNPs) had the best performance, initial results for cutting resistance were gathered for NBR/fGNP nanocomposites coated on a nylon substrate. Additional screening experiments using design of experiments was also performed. After determining that an increased storage modulus seem to result in an
increase in cutting resistance, a central composite design was developed in Phase 2 to better understand the interaction between the functionalized GNPs (fGNP) concentration and the curing temperature, their individual significance on the storage modulus, and to find an optimized combination of the two factors that maximizes the storage modulus. The cutting resistance for nylon substrates coated with either NBR or different concentrations of NBR/fGNP nanocomposites was also investigated. Lastly, in Phase 3, non-functionalized graphene nanoplatelets was investigated as the nanofiller to see if there would be a possibility to exclude the functionalization process covered in Section 2.1.1. This was done to understand the significance of the functionalization process and also to potentially lower the final cost of production of the nanocomposites. The coating thickness’ effect on cutting resistance was also investigated. Throughout Chapter 3, the unexpected results and challenges that occurred during material processing, experimentation and testing, dispersion difficulties, defects, scattered data, and so on; as well as the necessary precautions and actions taken to deal with them, is discussed.

Chapter 4’s purpose is to reinforce the argument why studying graphene and related materials is interesting from a commercial standpoint by giving a short environmental analysis of the industry. This is an important area to cover for the reader to understand some of the industry-wide challenges that are currently present and why graphene and related materials are not necessarily used in products on the mass-scale yet albeit their huge potential to increase product performance and value.

Chapter 5 covers the conclusions drawn from the study and the possible future work of interest.
1.2 THEORETICAL BACKGROUND

1.2.1 GRAPHENE: THE FIRST TWO-DIMENSIONAL MATERIAL

In 2004, at the University of Manchester in the UK, Professor Sir Andre Geim and Professor Sir Kostya Novoselov discovered and isolated an atomic layer of carbon for the first time. What they found was the first so called two-dimensional (2D) material that became known to the world as graphene. Due to this discovery, they received the Nobel Prize in Physics in recognition of their breakthrough in 2010 (“The history of graphene”, 2017).

Ever since the discovery, graphene has been called ‘the Wonder Material of the 21st Century.’ Academia has explored its worth and found it to have the potential to revolutionize an endless number of industries. This is because graphene is the thinnest and strongest material on Earth, having remarkable electrical, mechanical, thermal and optical properties (Mertens, 2017). Graphene is harder than diamond (another allotrope of carbon) yet extremely flexible and stretchable; much more conductive than copper; almost completely transparent; and filters out every type of liquid gas while allowing water to flow through (“Graphene Goes to Market”, 2016). Other materials may have one of the properties mentioned above, but graphene stands out because it has them all. Therefore, over the last decade, an excitement has arisen in graphene both scientifically and commercially. It is an understatement to say that graphene has caught the attention and lighted the imagination of countless researchers, innovators, businesses, entrepreneurs and investors around the world—all eager to bring it to the market, rather sooner than later (Nord Bjaerneman, Tillery, Moore, & McKemey, 2019). Over the last decade, after the discovery of graphene, multiple new 2D materials have been discovered, such as hexagonal boron nitride, 2D molybdenum disulfide, and phosphorene, to name a few. A large movement has arisen for using these unique materials as nanofillers in already existing materials to enhance
their properties. Throughout the day, look around you and think: “What materials would be more valued if they were also electrically conductive? Thermally conductive? Lighter? Stronger? If they absorbed more energy?” This could be anything from the rubber in your running shoes to the many different materials that makes up your car. Or the parts that makes up your computer to even the concrete that makes your apartment building stand up. The exciting part is that there are no limitations to your imagination of what can be done with the use of 2D materials—it is now realistic to think that it’s possible.

1.2.2 GRAPHENE AND RELATED MATERIALS

A 2D material is a material consisting of one or several layers with the atoms in each layer strongly bonded to neighboring atoms in the same layer. It has one dimension (the thickness) at the nanoscale or smaller, combined with having the two other dimensions at scales larger than the nanoscale (International Organization of Standardization, 2017). When one says nanoscale, it typically refers to between 1 nm to 100 nm, or smaller (International Organization of Standardization, 2010). Graphene is simply a single layer of sp² carbon atoms arranged in a honeycomb structure, having a reported thickness ranging from approximately 0.390 nm – 0.410 (Wang, Jing, Jiang, Lin, Han, & Li, 2017; Yao, Ren, Gao, & Li, 2017). It is also known as monolayer graphene or single-layer graphene and can be abbreviated 1LG to avoid any confusions since the word graphene is commonly used interchangeably with other forms of graphene (International Organization of Standardization, 2017). These forms can be for example bilayer graphene (2LG), few-layer graphene (FLG), graphene nanoplatelets (GNPs), graphene oxide (GO), and so on. Hereinafter, this report will refer to all of these different forms as graphene and related materials (GRMs), which also includes 1LG. All GRMs possess somewhat
different properties because they are made up different structurally and also, most commonly, chemically. For example, GO has been heavily studied as a nanofiller since its compatibility is usually better with common base materials. This is because GO is a chemically modified form of graphene, that is synthesized by exfoliating graphite using strong oxidizing agents—a method known as the Hummers’ method. What this does is introducing oxygen atoms to the carbon atoms that makes up the graphene, turning it into a nonconductive hydrophilic carbon 2D material (Marcano, Kosynkin, Berlin, Sinitskii, Sun, Slesarev, … Tour, 2010). Why this is important to understand is because when one hears the word graphene, the properties that are mentioned (e.g. two hundred times stronger than steel or ten times more conductive than copper), refers to 1LG. However, the products currently on the market that claim to use “graphene” as the nanofiller are in reality most likely using one, or a combination, of the GRMs mentioned above.

Currently, an ongoing discussion is taking place of what should be classified as a “graphene-related” material and what should not. The International Organization for Standardization (ISO), along with the International Electrotechnical Commission (IEC), has been working, and continues to work, with academia and industry to reach consensus in this matter. According to ISO and IEC, at this point in time it has been decided that the number of layers are what determines if a material is classified as 2D or just a bulk (three-dimensional) material. To be “graphene-related” and be classified as a 2D material, it has been determined that the restriction is ten layers thick for electrical measurements. After that it becomes graphite since the electrical properties are no longer distinct from one another (International Organization of Standardization, 2017). For industry this causes an issue because, many of the so-called “graphene” companies don’t necessarily supply and/or use 1LG, 2LG or even FLG in their products, but perhaps rather GNPs or functionalized forms thereof. Note that in a batch of GNP
powder, some of the platelets might be one, two or a few layers, but it can also include platelets of ten to multiple of layers. According to ISO and IEC (2017), anything above ten layers is classified as graphite (International Organization of Standardization, 2017). If one goes back to Section 1.2.1 and look at the properties mentioned, one can see that graphene’s properties aren’t limited to electrical properties alone. Not all companies are interested in electrical properties but might rather use the mechanical benefits that are still obtainable beyond the ten-layer-restriction. A GNP for example, is distinctive because it is a nanoplate made up of layers of graphene. By definition, this means that it has a thickness in the nanoscale with lateral dimensions ranging from approximately 100 nm to 100 μm and still holds most of the properties of 1LG but at “humbler” amounts. As a result, the unique small aspect-ratio (i.e. thickness over lateral dimension of the flake) of GNPs is a characteristic that one doesn’t get with traditional bulk graphite. Therefore, one can ask: If a carbon platelet, with a thickness exceeding ten layers but still within the nanoscale and with a very small aspect-ratio, is not “graphene-related” but still falls outside of the traditional graphite industry, then in what definition/material category does this carbon platelet fall? This is an industrial dilemma that is discussed in Chapter 4.

1.2.3 COMMON CHARACTERIZATION METHODS

As one can see in section 1.2.2, what determines the differences between GRMs are minute structural and chemical changes. Recall that graphene is no longer graphene, or 1LG, after the minute difference of having another layer stacked upon itself. Since 1LG is approximately 0.4 nm thick (think approximately a millionth of the thickness of a strand of hair), advanced, expensive and time-consuming characterization techniques are needed to be employed in order to determine these structural and chemical differences both precisely and accurately. As
one can imagine, this can be a challenging and costly operation for young companies that are trying to grow their presence in the GRMs industry. There are typically four different characterization methods that one can employ: microscopies, spectroscopies, electrical characterization, and mechanical characterization, respectively (Claudia Backes et. al., 2020). Most relevant to this paper are microscopies and spectroscopies, since those are the methods commonly used for powders and dispersions.

1.2.3.1 MICROSCOPIES

The use of microscopy methods is commonly employed during the characterization phase to investigate the structural nature of the flakes, or in other words, the flake morphology. Some of the common methods are Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM).

In order to determine the lateral size and the thickness distribution of flakes, AFM is a method that provides a fast and reliable characterization that let one investigate a large area (hundreds of μm²) when the flakes are deposited onto a substrate. Since AFM can measure both flake thickness and lateral dimensions, another asset of AFM is that the volume can be calculated (Claudia Backes et. al., 2020). AFM is a so-called scanning probe microscopy technique, made up of a cantilever with a sharp apex that measure the changes in topography with lateral and height resolution in the nanoscale. If one needs to analyze a large volume of flakes, one can use a theory called Brunauer-Emmett-Teller theory (BET) to obtain the average specific surface area. After having confirmed a 2D flake morphology through AFM as well as the particle size distribution (PSD) of that batch, a statistical representation of the structural nature of the batch can be created. The use of BET and PSD is specifically useful for industry, but not necessarily
for research purposes (see Section 1.2.3.3).

SEM is another method that can be used in combination with AFM. SEM can be used for good resolution imaging (tens of nanometers) of the lateral size of the flakes and is somewhat easier to use than AFM. SEM bombards the surface with electrons and then the collection of the electrons after the collision becomes an image of the structure of the surface.

Lastly, TEM is a high-resolution method that is commonly used in academia to investigate individual flakes. TEM measures not only the flake’s lateral size and thickness, but also its crystal structure and chemical composition which is very helpful in understanding the structural nature of that flake (Claudia Backes et. al., 2020). However, since TEM is only investigating a single flake, this method can be time-consuming, hence costly, when trying to characterize GRMs powders. Therefore, this method is not typically used within the GRMs powder and dispersions segment.

### 1.2.3.2 SPECTROSCOPIES

The use of spectroscopies can be helpful for a number of reasons, but the most sought-after for the characterization of GRMs are their ability to determine the specific number of layers, as well as the chemical nature. Two common spectroscopy methods are Raman spectroscopy (Raman) and X-ray photoelectron spectroscopy (XPS).

Raman is one of the most important characterization methods for GRMs. Raman can be used as a quick screening tool to determine presence of graphitic materials, but more importantly give one an understanding of the number and orientation of layers, the quality and types of edge, and the effects of perturbations. Why Raman is one of the most important characterization methods, is because of its ability to be fast and non-destructible, offer high resolution, give
structural, atomic and electronic information, and be applicable to both academia and industry (Claudia Backes et. al., 2020). In Figure 1.1, one can see a typical Raman spectrum of defect-free 1LG.

![Figure 1.1. Typical Raman spectra of defect free (top) and defective (bottom) 1LG (Ferrari, & Basko, 2013).]

XPS is another method that measures the kinetic energy of photoelectrons emitted from a sample irradiated with x-rays. The energy is then transferred to a core-level electron. This then measure the effective binding energy between atoms making up the material. For a given XPS analysis of GRMs, there are three main sources of information that can be obtained: presence of contaminants, coverage, and chemical state of the carbon atoms, which is critical to understanding the form of graphene that one is analyzing (Claudia Backes et. al., 2020).

1.2.3.3 INDUSTRIAL CHARACTERIZATION METHODS

As mentioned in Section 1.2.3.1, BET and PSD are two common methods to employ when one wants a statistical structural characterization of a larger batch. One can understand that
if dealing with flakes in the nanoscale for a batch with a weight of for example 1 kg, it is not practical to look at individual flakes since that batch may contain billions, or ever trillions, of flakes. Nor is it correct to assume that after having obtained images of couple of individual flakes, that those few flakes represent the structural nature of all the other of flakes in that particular 1 kg batch. This is a challenge for GRMs powder suppliers since they need to provide this information to their customers in a document called a technical detail specification (TDS). Therefore, if one can confirm that the material yield, from a particular exfoliation process with graphite as the feedstock material, has a flake or platelet morphology through AFM; then BET and PSD can be used to find the statistical representation of the average structural nature of that material yield.

This is simply done by first confirming the platelet morphology through AFM to know that the process didn’t yield some other shape such as spheres for example. Through BET the average specific surface area is then found and the PSD is found using a particle size analyzer (PSA). The average thickness can then be found using Eq. 1.1 below.

$$\textit{Average thickness} \ (t_{ave}) = \left( \rho_g \times SSA \times 1 \times 10^4 \right)^{-1}$$  \hspace{1cm} (Eq. 1.1)

Where $\rho_g$ is the density of graphite in g/cm$^3$ and SSA is the average specific surface area in m$^2$/g.

With the PSD, one gets the average lateral dimension of the batch. As mentioned in Section 1.2.3.1, this procedure can be very useful for industry that doesn’t necessarily own all the characterization equipment that established research labs typically have readily available. However, there are two drawbacks that one has to take into account: (1) It must be assumed that
the powder one is analyzing is a pure graphitic material. If it’s not, the density will be different which means that one would get an incorrect value. Therefore, Raman confirmation might be needed to confirm the assumption, and (2) BET has a tendency for strong agglomeration in the dry state which might result in an incorrect representation of the powder in its pristine form.

1.2.4 DESIGN OF EXPERIMENTS

In the simplest terms possible, experimentation is performed in order for researchers or engineers to observe changes to a system or process, or to confirm a hypothesis. In the book Design and Analysis of Experiments by Douglas C. Montgomery (2017), it says that an experiment is a series of runs where changes are made to the input variables so that one can understand changes to the output response and what input variable(s) is/are responsible for those changes (Montgomery, 2017). As simple as it may sound, experimental design can be very challenging, especially when one is dealing with many input variables.

In design of experiments (DOE), the input variables are referred to as factors (e.g. concentration and surface treatment) that can take on different levels. The levels can be either numerical (e.g. 0.2 phr and 2 phr) or categorical (e.g. GNP and fGNP). An output (e.g. storage modulus) is referred to as a response. In today’s lab settings, DOE is not commonly used. Instead there are two common approaches that are utilized for experimentation: the best-guess approach and the One-Factor-At-a-Time (OFAT) approach. The best-guess approach simply means that for a set of factors, the scientist selects an arbitrary combination and make an observation. From this observation, one or two or more of the factors might be changed while holding the factors fixed, and another observation is made. According to Montgomery, the best-guess approach, switching the levels of factors based on the outcome of the tests, could be continued almost
indefinitely and is commonly used by scientists (Montgomery, 2017). The OFAT approach means that the researcher varies one factor while keeping all other factors in the experiment fixed. This approach is a simple one where a series of graphs can be developed to visually show how the response is affected. However, both the best-guess and OFAT approach fails to consider any interactions between the factors. In Jiju Antony’s book Design of Experiments for Engineers and Scientists (2014), one can read that: “an interaction between two factors exists when the effect of one factor on the response is different at different levels of the other factor(s).” (Antony, 2014). These approaches are also less efficient than other statistical DOE methods and can lead to the risk of spending a lot of time and money on avoidable runs.

Montgomery (2017) defines statistical DOE as a process where appropriate data is collected and analyzed by statistical methods, which results in valid and objective conclusions. He continues by saying that if the data analyzed are subject to experimental error, then statistical methods are the only objective approach (Montgomery, 2017). In statistical DOE there are two important aspects to consider: the actual design of the experiment and the statistical analysis of the data. There are many designs that one can choose from, but in this paper, it was decided to use a central composite design (CCD).

A CCD is a design that falls under the response surface methodology (RSM). RSM are techniques especially useful for the modeling and analysis when the response of interest might be affected by several factors and when the main objective is to optimize the response (Montgomery, 2017). The response surface can be represented graphically for a straightforward visual understanding to what is happening to the system. An example can be seen in Figure 1.2. In Figure 1.3, one can see the structure of a CCD when analyzing two factors (i.e. x1 and x2).
Figure 1.2. Example three-dimensional response surface showing the expected yield as a function of temperature ($x_1$) and pressure ($x_2$). (Montgomery, 2017).

Figure 1.3. CCD with two factors (e.g. $x_1 =$ concentration, $x_2 =$ curing temperature). (Montgomery, 2017).
Why CCD is useful is because of its rotatability, or in other words the ability to provide equal precision of estimation in all directions. Since the end purpose of RSM is optimization and the optimum location is unknown prior to experimentation, this trait is very helpful. As can be seen in Figure 1.3 above, a CCD is performed by choosing two factor levels of interest for each of the factors (i.e. +1 and -1). The center point between these levels are then added, which is known as center runs (i.e. 0, 0). The number of center runs is needed to provide reasonable stable variance of predicted response and is usually three to five runs (Montgomery, 2017). The software then calculates two extreme points for each factor (i.e. +a and -a). If the number of center runs is five, then for two factors it becomes a total of thirteen runs. If the statistical analysis turns out successful, CCD can predict with 95 percent confidence, the response for any combination of factor levels within the box seen in Figure 1.3.

1.3 INTEREST & HYPOTHESIS

Due to GRMs’ excellent mechanical properties, coupled with the unique combination of being both thermally and electrically conductive, they have the potential to be an ideal reinforcement in composites. For example, Wang et al. (2017) reported ultra-low percolation threshold and ultra-high electrical conductivity for a graphene-based polymer at only 2.45 wt.% loading. This improvement was also coupled with better thermodynamic properties, tensile strength, and toughness (Wang, Chong, Zhang, & Lu, 2017). Similarly, Pang et al. (2019) found that by adding thermally reduced graphene oxide (TRGO) to the matrix for polymers with already superior mechanical properties, such as polyethylene, their properties increased even more (Pang, Yang, Curtis, Luo, Huang, Feng, . . . Luo, 2019). For elastomeric materials, such as rubbers, there has traditionally been tradeoff between the wear resistance and application specific
functionality. Recent research has shown that by adding GRMs to the elastomer matrix can significantly improve both wear resistance and performance functionality simultaneously (Feddy, 2020). Valentini et al. (2018) examined the effects of thermally reduced graphene oxide (TRGO) and MWCNTs when being incorporated into nitrile butadiene rubber (NBR) matrix either on their own or a combination of the two. For tensile strength, a 293% increase was reported for the sample with 1 phr (parts per hundred rubber) of TRGO and 5 phr MWCNT (Valentini, Bittolo Bon, Hernández, Lopez-Manchado, & Pugno, 2018). In another study, Xue et al. (2019) reported that natural rubber enhanced with graphene oxide (GO) and reduced graphene oxide showed tremendous potential for tensile strength. It was also found that the surface roughness of the flakes had an effect of strengthening and toughening the rubber (Xue, Gao, Hu, & Hu, 2019). However, because of graphene’s crystalline structure, the graphene plane is perfectly smooth. If used in polymer-based composites, the interaction between the polymer and graphene may be poor. Additionally, graphene is much more rigid and stiffer than any polymer. Therefore, the compatibility and the mechanical properties of the composite still may not be satisfactory (Al-Ostaz, Li, Rushing, & Nord Bjaerneman, 2019).

With their unique viscoelastic nature, elastomers serve as essential strategic materials with multiple applications in industries and national defense. To gain acceptable mechanical properties or other functionalities, generally inorganic fillers are necessary (Yang, Guo, & Zhang, 2017). Nitrile butadiene rubber (NBR) is an oil-resistant synthetic elastomer that is commonly used in fuel hoses, gaskets, roller, and occupational safety products (“Nitrile rubber”, 2016). For occupational safety products, the NBR is usually coated on a substrate that is worn by the workers. The coating increases grip when handling different materials; provides a layer of protection from water and oil; and acts as a safety barrier for cuts. An area that has not been
studied in depth is NBR’s mechanical performance when it comes to cutting resistance – an important property when it comes to occupational safety products. Typically to improve the cutting resistance, the coating has been held fixed and instead the substrate has been modified with (e.g. switching the substrate made of nylon fibers with Kevlar fibers). Since GRMs has been shown to significantly improve the mechanical performance of elastomeric materials from the literature search presented earlier in this section, it can be assumed that the cutting resistance can be increased as well. Therefore, the starting hypothesis becomes if the NBR coating is reinforced with conventional forms of graphene, the mechanical properties such as tensile strength and storage modulus will be increased which may result in better cutting performance when the substrate is held fixed.

1.4 OBJECTIVES

Table 1.1: Objectives of Study

| Overarching Objective(s) | (1) Investigate the effect of adding conventional forms of graphene to nitrile butadiene rubber on the mechanical performance  
(2) Increase the cutting resistance of a nylon substrate by reinforcing the NBR-coating with a selected form of graphene |
|--------------------------|-------------------------------------------------------------------------------------------------------------|
| Phase 1 Objective        | (1) Investigate whether adding conventional forms of graphene to nitrile butadiene rubber have an effect on tensile strength, storage modulus, and cutting resistance  
(2) Evaluate different effect parameters |
| Phase 2 Objective        | (1) Investigate the optimal condition of selected effect parameters to increase cutting resistance |
| Phase 3 Objective        | (1) Investigate thickness’ effect on cutting resistance  
(2) Lower cost of production |
CHAPTER 2: MATERIALS, EQUIPMENT & METHODS

2.1 MATERIALS USED

The main GRMs that was used in this study was GNPs with an average SSA of 39.2764 m$^2$/g and an average lateral diameter of 50 μm (XG Sciences, Inc., Lansing, MI). Using Eq. 1.1, the average thickness could therefore be calculated to be 11.2 nm. Functionalized GNPs (fGNPs) derived from GNPs was prepared in the lab (see Section 2.2.1). Uncured nitrile butadiene rubber (NBR) latex, as well as the nylon substrate, was supplied by a confidential source.

GO was bought from Graphenea, Spain. Multi-walled carbon nanotubes (MWCNTs) were bought from Nanostructured & Amorphous Materials, Inc. Calcium nitrate tetrahydrate (99+ %) was bought from Fisher Scientific International, Inc., NH. Calcium nitrate tetrahydrate was dissolved in methanol to prepare 4 wt.% solution for 6-second impregnation of nylon substrate prior to coating. This was done to prevent the NBR latex (liquid) from bleeding through the substrate since the goal for the coating was to only stay on the surface. The surfactant was Polyethylenimine (PEI) from Sigma-Aldrich, MO. A release agent of 44-NC bought from Northern Composites, LLC, NH, was used to coat a glass substrate to facilitate the demolding of NBR and NBR composite sheets.
2.1.1 FUNCTIONALIZATION & PURIFICATION

As stated earlier, due to graphene’s crystalline structure as well as its rigidity, stiffness and hydrophobic nature; poor compatibility with the NBR was assumed. Also taken into account, the Van de Waals forces between the GNP normally cause agglomeration, so another issue addressed was dispersion. To address these problems, functionalization of the GNPs was assumed to be needed to produce a proper GNP-enhanced nanocomposite. The functionalization and purification process developed in house and highlighted in Alharith Manasrah’s dissertation (2016), is summarized as follows:

GNPs were mixed with concentrated sulfuric acid (95% or higher) and nitric acid (70%). The volume ratio of sulfuric acid to nitric acid was 3:1. The whole mixture was magnetically stirred in a three-neck glass flask and heated to around 70°C to 90°C for a period approximately 12 hours. The acid vapor was condensed and refluxed by a water-condenser attached to the flask during the entire reaction process. After the reaction, the resulting mixture was filtered through a porous film for, where the acid and water were sucked with a water-jet vacuum for purification. The now collected fGNP were re-dispersed in 500ml of distilled water, stirred and sonicated for 1 minute, then filtered again. After at least 5 cycles of water washing, sonication, and filtration, the filter paper was switched to Whatman quality filter paper for 5 additional cycles of water washing, sonication and vacuum filtration to complete the purification process. The purified fGNP were dried in the oven at 70°C for 1 hour. In later stages, it was instead left as a wet paste to investigate the effect on dispersion (Manasrah, 2016).

Figure 2.1 displays examples of the results from XPS for GNP and fGNP, respectively. It can be seen that the relative intensity of oxygen in the fGNP was increased, indicating that more
oxygen groups were introduced. Deconvolution of C1s analysis gives information on specific chemical bonds associated with carbon atoms in GNP. Table 2.1 summarizes the results for both GNP and fGNP, and it shows more oxygen groups were generated onto fGNP. EDS analysis also indicates that the oxygen content increased from 4.1% in GNP to 28.1% in fGNP (Table 2.2). There was some difference between these results because XPS measures the top few nanometers while EDS can go up to several micrometers in-depth. SEM images in Figure 2.2 shows the platelet structures of GNP and fGNP, respectively. That was no structural difference between GNP and fGNP observed (Al-Ostaz, Li, Rushing, & Nord Bjaerneman, 2019). Please note that, as stated in Section 1.2.3, a complete structural and chemical characterization process should also include Raman and AFM for example, but it was assumed that the supplier’s TDS was trusted. Therefore, the only characterization methods used in this work were SEM and XPS, respectively, to investigate the yield of the in-house functionalization process highlighted above.
Figure 2.1. Results of XPS for: (a) GNP; (b) fGNP
Table 2.1: XPS results for GNP and fGNP

<table>
<thead>
<tr>
<th></th>
<th>C conc. (%)</th>
<th>O conc. (%)</th>
<th>C1s sub-peak binding energy (eV) (bond-allocated carbon concentration [atomic%])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-C</td>
</tr>
<tr>
<td>GNP</td>
<td>91.5</td>
<td>8.5</td>
<td>284.34 (68.5)</td>
</tr>
<tr>
<td>fGNP</td>
<td>82.0</td>
<td>18.0</td>
<td>284.25 (59.8)</td>
</tr>
</tbody>
</table>

Table 2.2: EDS results for GNP and fGNP

<table>
<thead>
<tr>
<th></th>
<th>C conc. (%)</th>
<th>O conc. (%)</th>
<th>S conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP</td>
<td>95.9</td>
<td>4.1</td>
<td>0</td>
</tr>
<tr>
<td>fGNP</td>
<td>70.0</td>
<td>28.1</td>
<td>1.9*</td>
</tr>
</tbody>
</table>

*Sulfur was likely due to small residue from functionalization treatment.

Figure 2.2: SEM image of (a) GNP; (b) fGNP
2.2 EQUIPMENT & TESTING METHODS

The Instron tensile tester was model 5982 (Instron Corporation, MA). The tensile test followed ASTM 412-C in which the grip separation speed was 500 mm/min. Specimens for this procedure are usually of the "dogbone" variety (also known as dumbbell shape). However, the specimens were created by cutting rectangular strips with the same thickness as the narrow portion of the “dogbone” (i.e. approximately 6 mm thick) using a regular paper cutter, since the “dogbone” molds didn’t yield satisfactory specimens.

A dynamic mechanical analyzer (DMA) of model Q800 from TA Instruments, DE was used to measure the storage moduli under room temperature (RT). In more detail, rectangular strips of NBR or NBR/nanofiller composites were tested using film tension mold at a frequency of 1 Hz. No heating was carried out and the tests were isothermal at RT since the storage modulus and loss modulus were indicated directly by the DMA.

The cutting resistance of the specimens was measured at a confidential facility and followed ANSI/ISEA 105-2016. For each nylon substrate coated with either NBR or NBR/nanofiller composite, two specimens were created by cutting the coated substrate with a pair of scissors at a 45-degree angle to the nylon fibers. For each specimen, multiple cuts were performed. The cutting resistance was determined by loading a sharp blade and record how far it can travel across the coating surface before it cuts through both the coating and the substrate. The average load, in grams, that let the blade travel 20 mm before cutting through, is the recorded cutting resistance. In other words, the standard uses a nine (9) level scale. The level of cut resistance extends from 0 to 6,000 grams, based on tests by a Tomodynamometer (TDM), which moves a blade across the material. The higher the weight required to cut the materials, the higher the cut resistance rating (see Figure 2.3).
Figure 2.3: Schematic of ANSI/ISEA procedure and cut rating

Figure 2.4: Typical results of the cutting resistance
The sonicator was a Fisher Scientific FS30 Ultrasonic Cleaner. Specifications are as follows:

- Tank capacity: 1 gallon
- Tank dimensions (L x W x D): 9.5” x 5.5” x 6”
- Overall dimensions (L x W x H): 10.4” x 8.9” x 11.3”
- Ultrasonic power: 130 W
- Heater power: 109 W
- Operating frequency: 40 kHz
CHAPTER 3: RESULTS & DISCUSSION

3.1 OVERVIEW

The procedure for the experimentation followed three phases. The first phase served as a trial and error phase (i.e. screening) where curing procedure and curing temperature, mixing methods, manufacturing methods, nanofiller concentration, and nanofiller surface chemistry were investigated. Also, a first trial for coating the nylon substrate and cut resistance tests were performed. This was done to get an initial understanding of the correlation (if any) between tensile strength, storage moduli and cut resistance. Additional screening experiments was also performed for a DOE screening for a quick check of the individual factor’s significance.

The second phase followed a statistical DOE approach, where a CCD was developed to better understand the interaction between (A) the fGNP concentration and (B) the curing temperature and their significance on storage moduli. The cut resistance for nylon substrates coated with NBR and different concentrations of NBRfGNP was also investigated.

Lastly, in Phase 3, GNP was investigated to see if there would be a possibility to exclude the functionalization process covered in Section 2.1.1. This was done to both understand the significance on the functionalization process but also to potentially lower the cost associated with the manufacturing process of the nanocomposites. The coating thickness’ effect on cut resistance was also investigated.

Hereinafter, symbols and abbreviations for NBR reinforced with GNP, fGNP, MWCNTs and GO, are NBRGNP, NBRfGNP, NBRCNT and NBRGO, respectively.
3.2 PHASE 1

As stated above, in Phase 1, a number of screening experiments were carried out to investigate the best mixing method, curing procedure and curing temperature, type of nanofiller, and nanofiller surface chemistry.

3.2.1 CURING PROCEDURE & MIXING METHOD

The first area of interest was the mixing procedure to create NBRfGNP specimens. Two different procedures were investigated: (1) mixing by switching between short intervals of magnetic stirring and sonication, and (2) mixing by first sonicating the mixture, followed by 3-roll milling.

Before it was possible to investigate what mixing method to use, the curing procedure needed to be determined. Therefore, numerous experiments were performed on NBR alone. Uncured, NBR latex is a white liquid solution. It was found that the NBR latex has to be dried at room temperature (RT) for at least 24 hours before being gradually curing in an oven at elevated temperature. If the samples were placed in the oven to cure immediately, a skin was formed on the surface, preventing further evaporation of the liquid underneath it. The recommended curing procedure was found as follows:

1. pre-dry samples in RT for a minimum of 24 hours
2. cure in oven and heat from RT at 1°C/min to a target curing temperature
3. keep the oven isothermal for 40 min
4. cool samples to RT
Figure 3.1a displays the failed samples that were immediately placed in the oven. Figure 3.1b shows successful curing of NBR and NBR composites after the samples were cured following the recommended curing procedure above. Curing in the molds shown in Figure 3.1 produced specimens with up-curved sides because of capillary phenomenon. Therefore, it was decided to pour the NBR solution onto a glass plate coated with a release agent before curing that after curing produced a rubber sheet that was then cut into specimens with proper sizes for tests. Through experimentation it was found that the yield of cured NBR was 45.6% by weight. This means that 45.6 g cured NBR can be produced from 100 g of uncured NBR latex liquid solution. This result was used as a basis to guide the formulations to control the concentrations of nanofillers.

Figure 3.1. (a) NBR samples cured immediately in oven, (b) NBR samples after recommended procedure.
After the curing procedure was determined, NBR latex was then mixed with a selected nanofiller and further dispersed with sonication or sonication with 3-roll milling. Since it was found that 46.5 g solid NBR was produced from curing 100 g latex, to control for example 2 phr GNPs in NBR, 0.93 g of GNPs was mixed into 100 g NBR latex to be cured. This was simply calculated by multiplying the ratio 0.465/1 by the phr concentration. For sonication, each mixture was placed in a closed glass jar and processed with cycles of 5-minute sonication and 5-minute magnetic bar stirring. The total mixing time was about 30 min. In Figure 3.2 below, one can see the time effect of this method for a sample of NBRGO mixture. To see if 3-roll milling enhanced the properties of the mixture, NBR latex with the same concentration was sonicated as described above and passed once through the 3-roll mill. Figure 3.3 compares the effects of sonication and sonication plus 3-roll milling. It appeared that sonication resulted in better storage moduli. For maximum tensile strength, there was no distinct difference between the two mixing methods. However, because there was some improvement in the storage moduli when only sonication was employed, it was decided that 3-roll milling was not necessary.

Figure 3.2. NBRGO mixture (a) after 5 min sonication, (b) 15 min, (c) 30 min
Figure 3.3. Storage moduli (a) and maximum tensile strengths (b) of NBRfGNP samples dispersed by sonication and sonication with 3-roll milling. Curing condition: heating rate of 1°C/min to 110°C isothermal for 40 min.
Lastly, out of scientific curiosity, mixing of NBR with TRGO and NBR mixed with MWCNTs was also investigated. It was quickly found that due to the hydrophobicity of both TRGO and MWCNTs, when mixed with NBR, the two caused significant agglomerations. During 3-roll milling TRGO and MWCNTs stuck to the rolls and were lost. Therefore, results for NBR/TRGO/MWCNT composites were unobtainable.

3.2.2 TYPE OF NANOFILLER & SURFACE CHEMISTRY

GNPs, fGNPs, and MWCNTs were formulated into the NBR matrix, respectively, to observe how the mechanical properties of the resulting composite would be affected. In Figure 3.4, the concentrations of these nanofillers are fixed at 0.67 phr. It can be seen that fGNP has a better performance than the rest. Therefore, fGNP was selected for further experiments.

Figure 3.4. NBR reinforced with different nanofillers. Curing condition: heating rate of 1°C/min to 110°C isothermal for 40 min.
As stated in Section 1.2.2, GO is a nanofiller that has been heavily studied since its compatibility is usually better with common base materials. It was therefore assumed that it may have better interaction with the NBR matrix. Therefore, another experiment was performed that compared fGNP to GO. Figure 3.5 shows the comparison results for NBRfGNP and NBRGO, respectively, both fixed at a concentration of 0.6 phr. Out of curiosity, a new curing temperature was also tested. It was found that if cured at 110°C, GO significantly improved the storage modulus but resulted in a lower tensile strength. If cured at 160°C, there was no distinct different between the two. Considering the high price and availability of GO, fGNP was decided to be used for further experimentation.
Figure 3.5. Comparison of mechanical properties of NBR, NBRfGNP and NBRGO: (a) cured at 110°C isothermal for 40 min; (2) cured at 160°C isothermal for 40 min. Heating rate was 10°C/min in both cases.
3.2.3 ADDITIONAL SCREENING EXPERIMENTS

After the observation during previous experimentation that the curing temperature seem to have an effect on both the storage modulus and tensile strength results, it was of interest to investigate it further. Storage modulus and tensile strength tests were performed on NBRfGNP composites for concentrations of 0 to 1 phr (in increments of 0.2 phr) at curing temperatures of 110°C and 160°C, respectively. To analyze the significance of the factors (i.e. concentration and curing temperature) and to get a visual representation of the results, a statistical DOE design was developed. The layout of this design can be seen in Table 3.1. The two responses, storage modulus and tensile strength, were analyzed separately.

After the data was confirmed normal with a constant variance, it was found that the concentration was the significant factor for storage modulus. This can be seen in Figure 3.6. As one follows the concentration axis at a specific curing temperature, the storage modulus increases drastically, but if one instead follows the curing temperature axis at a specific concentration it is just a slight change. For tensile strength, this scenario was reversed. It was found that the curing temperature was the significant factor. This can be seen in Figure 3.7 by following the same logic as for Figure 3.6 explained above.
Table 3.1. Screening DOE layout based on performed test

<table>
<thead>
<tr>
<th>STD ORDER</th>
<th>RDM ORDER</th>
<th>Concentration</th>
<th>Temperature</th>
<th>Storage Mod</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>phr</td>
<td>ºC</td>
<td>MPa</td>
<td>MPa</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>0</td>
<td>110</td>
<td>1.26</td>
<td>1.37</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0.4</td>
<td>110</td>
<td>1.55</td>
<td>2.08</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0.6</td>
<td>110</td>
<td>2.16</td>
<td>1.94</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
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<td>110</td>
<td>2.33</td>
<td>1.52</td>
</tr>
<tr>
<td>5</td>
<td>8</td>
<td>0</td>
<td>160</td>
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<td>2.5</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>0.2</td>
<td>160</td>
<td>1.83</td>
<td>3.84</td>
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<td>7</td>
<td>7</td>
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<tr>
<td>8</td>
<td>1</td>
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<td>2.03</td>
<td>3.31</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>1</td>
<td>160</td>
<td>2.37</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Figure 3.6. Response surface plot for storage modulus in Phase 1. Plot developed using Design-Expert.
3.2.4 PRELIMINARY CUTTING RESULTS

Since it was found that both storage modulus and tensile strength were higher when cured at 160°C, the curing temperature was fixed at this value for the preliminary cut results. For the first trial of coating the nylon substrate, the 4 wt.% solution of Calcium nitrate tetrahydrate in methanol mentioned in Section 2.1 was not used, resulting in the NBRfGNP mixture bleeding through, or in other words impregnating the substrate (see Figure 3.8). Nylon substrate with NBR and NBRfGNP of concentrations of 0.2 phr, 0.4 phr, 0.6 phr, 0.8 phr, and 1 phr were tested, respectively. Figure 3.9a below summarizes the preliminary results for cut resistance at different levels of concentration. It can be seen that as concentration increases, so does the cutting resistance. If one compares that cutting resistance at 0 phr with the cutting resistance at higher concentrations, the least significant difference (LSD) bars are not overlapping, which
suggests that nanofiller concentration is in fact significant for cutting resistance. In Figure 3.9b and 3.9c the cutting resistance is plotted against storage modulus and tensile strength, respectively. It can be seen that there is a clear trend when cutting resistance is plotted against storage modulus. If one compares the cutting resistance at higher results of storage modulus versus at lower results, then the LSD bars are not overlapping which indicates that a higher storage modulus helps increase the cutting resistance. In contrast, if one compares cutting resistance and tensile strength, the higher values’ LSD bars overlaps the lower values, which indicates that tensile strength doesn’t affect the cutting resistance.

Figure 3.8. Example of impregnated substrate of NBRfGNP for cut test
Figure 3.9. Plot: (a) cut resistance vs fGNP concentration, (b) cut resistance vs storage modulus, (c) cut resistance vs tensile strength. Cured at 160°C.
To verify that the cutting resistance seem to correlate to storage modulus rather than tensile strength, specimens of the same concentrations as for the cut tests, cured at 160°C, were manufactured and tested. In Figure 3.10, one can see the results. It was verified that storage modulus seems to correlate to the cutting resistance since the cutting resistance vs concentration graph in Figure 3.9a somewhat resembles the same pattern for storage modulus in Figure 3.10a. Therefore, a new hypothesis became that maximizing storage modulus may then also maximize future cutting performance results. It was decided that by finding an optimized combination of the fGNP concentration and curing temperature that maximizes the storage modulus was the next objective of the study.
Figure 3.10. (a) storage modulus results for NBRfGNP, (b) tensile strength results for NBBfGNP. Cured at 160°C.
Lastly, in Figure 3.11, one can see a comparison of the stress-strain curves for NBRfGNP with a 0.2 phr concentration cured at 110°C and 160°C, respectively. Note that by changing the curing temperature, a 31% increase in tensile strength was observed. If one looks at Figure 1.15b above, one can see that the greatest increase for tensile strength was found for the 0.2 phr NBRfGNP, increasing from 1.4 MPa for NBR to 3.8 MPa (171% increase).

Figure 3.11. Stress-strain curve for NBR formulated with 0.2 phr fGNP, cured at 110°C and 160°C, respectively.
3.3 PHASE 2

3.3.1 CCD RESULTS

As mentioned in Section 1.2.4, a CCD was chosen to be followed in Phase 2. The high and low levels of the two factors was decided to be 0.34 phr and 2 phr for concentration and 110°C and 160°C for curing temperature. The center point for each then became 1.17 phr and 135°C, respectively. The two extreme points for each factor became 0 phr and 2.34 phr for concentration, and 100°C and 170°C for curing temperature. In Table 3.2 below, the design layout is shown.

Table 3.2: Design Layout for CCD

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>phr</td>
<td>°C</td>
</tr>
<tr>
<td>1</td>
<td>12</td>
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<td>13</td>
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<td>1.17</td>
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</table>
For each combination, tests for storage modulus and cut performance were performed. The cut tests were performed with the NBRfGNP coating on the surface of the substrate rather than impregnated, made possible by the pre-dipping the substrate in Calcium nitrate tetrahydrate solution as mentioned in Section 2.1. In Figures 3.12 through 3.14, one can see examples of the cut specimens. In Table 3.3, the responses from the tests have been added to the matrix.

Figure 3.12. NBR (0 phr) coated on substrate without impregnation. Cured at 135°C.

Figure 3.13. NBRfGNP (1.17 phr) coated on substrate without impregnation. Cured at 100°C.
Figure 3.14. NBRfGNP (1.17 phr) coated on substrate without impregnation. Cured at 170°C.

Table 3.3. Design Layout CCD with response results

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<tbody>
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<td>-</td>
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<td>g</td>
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<td>135</td>
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</table>
In Section 1.2.4, one can read that in statistical DOE the two important aspects to consider are the actual design of the experiment and the statistical analysis of the data. Hence, for the responses above, a statistical analysis was the next step. Below, a series of figures are included to verify that the statistical model for storage modulus and cut resistance were significant.

For storage modulus, after having confirmed that the data was normal with a constant variance, the fit statistics can be seen in Table 3.4 and the analysis of variance (ANOVA) can be seen in Table 3.5. As can be seen in Table 3.4, the coefficient of determination (i.e. R2) was 0.92 which indicates that the data is close to the fitted regression line, which suggests a good model. However, the predicted R2-value was found to be 0.4359, which indicates that the regression model might not provide a good prediction.

For the ANOVA in Table 3.5, it can be seen that the p-value was 0.0012. Since this value is less than 0.05, it means that the model as a whole is significant. If one looks at the individual factors, both of their p-values are also less than 0.05, which indicates that both the concentration and curing temperature had a significant effect on the storage modulus. Since the p-value for concentration and curing temperature was 0.0003 and 0.012, respectively, it indicated that the concentration was more significant than the curing temperature. This result also validated the preliminary results in Section 3.2.3, that the storage modulus was significant, but it also indicated that curing temperature actually had a significant effect on the response. That means that an optimized combination could found. However, the interaction AB was found to have a p-value of 0.1212 which indicated no significance.
In Figure 3.15 and Figure 3.16, the response surface plot and contour plot for storage modulus can be seen. It can be observed that there is a peak value somewhere in the orange region of plots. It was found that an optimized combination for concentration and curing temperature to maximize storage modulus was 1.8 phr, cured at 140°C. However, if one looks at Figure 1.19 above, it can be noted that the substrate started to degrade at higher curing temperature. Due to this, an optimization was performed when the curing temperature was fixed at 130°C, resulting in the optimal concentration to be 1.6 phr. This combination served as the baseline for Phase 3.
Figure 3.15. Response surface plot for storage modulus. Developed using Design-Expert.

Figure 3.16. Contour plot for storage modulus. Developed using Design-Expert.
To validate the DOE results for storage modulus above, additional tests for NBRfGNP with concentrations of 0 to 1 phr (at 0.2 phr increments) cured at 130°C were performed. In Figure 3.17 below, one can see the expected values for storage modulus at these concentrations when being fixed at 130°C, as well as the actual test results plotted. It can be noted that all of the actual results except at 0.2 phr fall within the confidence interval expected by statistical DOE.

Recall, the only concentrations in the CCD matrix that was tested below 1 phr were 0 phr and 0.34 phr. There were no tests performed at 130°C. Yet, it was possible to successfully predict results at this curing temperature for numerous concentrations that fall within the CCD box.

Figure 3.17. Comparison between predicted vs. actual results for storage modulus. Cured at 130°C.
For recollection, Table 3.6 below shows the CCD layout with the results for cut resistance only. Notice that for the five center runs’ results (highlighted in red), the data fluctuates from 673 g to 925 g. Comparing this to NBR alone, this is a percent increase range from 28% to 76%. This caused a major problem which can be seen in the statistical analysis in Tables 3.7 and 3.8. First, it was observed that the data was non-normal with a non-constant variance. The predicted R2-value was -0.5363 which says that the mean of the results is a better indicator for prediction of response than the model itself. For the ANOVA, one can also see that all p-values are greater than 0.05 which means that the model nor the factors are significant. The only two options that a conclusion could be drawn from was that either there was no correlation between concentration, curing temperature and cut resistance, or due to experimental errors, coating defects, dispersion issues and possible non-uniform thickness of coating, the results didn’t represent the true nature. It was concluded that the latter was more likely to be true since an obvious increase in cut performance for some NBRfGnP coated specimens was observed in comparison with the NBR (0 phr) coated specimens. Therefore, further investigation of why this scattered data for cut resistance occurred was performed.
Table 3.6. Design Layout with cut results

<table>
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<tbody>
<tr>
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Table 3.7. Fit Statistics for Cut Resistance

<table>
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<tr>
<th>Std. Dev.</th>
<th>Mean</th>
<th>R²</th>
<th>Adeq Precision</th>
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<tr>
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<tr>
<td>Mean</td>
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<td>Adjusted R²</td>
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<tr>
<td>C.V. %</td>
<td>14.89</td>
<td>Predicted R²</td>
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</table>
3.3.2 FURTHER INVESTIGATION

Since the results for cut resistance were so scattered, further investigation was needed in order to understand the phenomenon. Initially, there were two areas of interest: dispersion and defects. To examine a given specimen that was used for cutting resistance tests, optical microscopy was employed. In Figure 3.17, a NBRfGNP coated substrate with concentration of 1.17 phr cured at 135°C can be seen under optical microscopy. Note that fGNP agglomeration can be seen as well as areas of poor dispersion. To address this issue, it was decided to employ longer sonication as well as the use of surfactants. NBR latex with fGNP was subjected to 10 cycles of 3 minutes magnetic stirring/ 3 minutes bath sonication for a total of 1 hour. The surfactant PEI was also used. No clear difference was observed after the use of PEI. Therefore, it was decided not to use surfactant and just to extend the time of stirring/sonication.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squ.</th>
<th>df</th>
<th>Mean Squ.</th>
<th>F-Value</th>
<th>p-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
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<td>10884.73</td>
<td>0.8612</td>
<td>0.4518</td>
<td>not signif.</td>
</tr>
<tr>
<td>A: Conc.</td>
<td>19683.81</td>
<td>1</td>
<td>19683.81</td>
<td>1.56</td>
<td>0.2405</td>
<td></td>
</tr>
<tr>
<td>B: Temp.</td>
<td>2085.66</td>
<td>1</td>
<td>2085.66</td>
<td>0.1650</td>
<td>0.6931</td>
<td></td>
</tr>
</tbody>
</table>
Another issue was defects. There were two types of defects that could be observed. The first one was bubble formation during curing in the oven, and the second was rivers that formed during being placed out in RT from a minimum of 24 hours. To address the latter, vacuum degassing and casting on a non-stick Teflon substrate or glass plate heavily coated with a release agent was employed. To address the bubble formation, a slower temperature sweep was employed. A sample with a severe bubble formation can be seen in Figure 3.18.
Figure 3.18. Bubble formations for NBR coating after curing.
3.4 PHASE 3

As stated earlier, in Phase 3, cutting resistance for NBRGNP and NBRfGNP was compared to see if there was a way to decrease the cost associated with manufacturing since the functionalizing process is labor intensive hence expensive. Also, the effect of the coating’s thickness on cut resistance was investigated. The thickness was controlled by the weight of poured NBR latex/NBRGNP or NBRfGNP solution. For a thick coating, it was poured twice with at least 30 minutes in between to avoid the formation of rivers. Evaporation of solvent was done in the ventilation hood at RT. Substrate was always pre-dipped into the 4 wt% calcium nitrate tetrahydrate/methanol solution for 6 seconds.

Figure 3.19 summarizes the results for all samples. It can be seen that the thickness plays a vital role in controlling cut resistance. There is no clear correlation between concentration and cutting performance. For example, if one compares the cut resistance for NBR with NBRGNP and NBRfGNP, keeping the concentration fixed at 1.17 phr for both 0.6 mm and 1 mm thickness, there is just a slight increase in cut resistance. In other words, for a thickness of 0.6 mm, the results for NBR, NBRGNP, and NBRfGNP was 524 g, 594 g (13%), and 569 g (9%), respectively. For 1 mm the results were 705 g, 750 g (6%), 749 g (6%), respectively. NBRGNP at 1.6 phr/1 mm thickness gained the largest cut resistance (908 g), a 29% increase from NBR of the same thickness (705 g). As discussed in Section 3.3.1, this occurred where the storage modulus was maximized so it might suggest that cut resistance is in fact correlated to the storage modulus of the nanocomposite.
Figure 3.19. Cut performances of samples of NBR, NBRGNP, or NBRfGNP coated on nylon substrate.

p: GNP.

f: fGNP.

ap: added test results of NBRGNP

op: overall test results of NBRGNP

af: added test results of NBRfGNP

of: overall test results of NBRfGNP.
CHAPTER 4: THE GRAPHENE AND RELATED MATERIALS INDUSTRY

4.1 INTRODUCTION

Graphene and related materials certainly have unique properties that are attractive to many industries. For example, in Chapter 3 it’s reported that when 0.2 wt.% of functionalized graphene nanoplatelets was added to the nitrile butadiene rubber matrix the tensile strength increased by 171%. When 1.17 wt.% was added, the storage modulus increased by 66%. This is certainly encouraging! One could assume that enhancing a material with graphene and related materials is an obvious thing to do, hence for a composites manufacturer the decision to do so should be clear. There is no doubt that bringing new materials like these into the marketplace can have tremendous effects on industries as a whole, but what is important to remember is that it doesn’t come without a challenge – it is not as straightforward as one might think. As Van de Voorde (2015) stated: “The challenge for the global economy is in the development and implementation of a development path for nanotechnology that goes from the research laboratory, through pilot processing and development, into mass production and commercialization.” (Van De Voorde, 2015). For graphene and related materials there are an endless number of opportunities, but before it makes sense for companies to commit to the capital requirements and risks associated with adding new nanomaterials to their production, processes and supply chain, there are many areas that first needs assessment. These can be internal on the firm-level, such as a cost-benefit assessment, or it can be external forces influencing the industry as a whole such as regulations or a complex supply chain. Other
challenges for the industry include finding better ways to produce at a low-cost and consistent quality; the lack of international standards that is much needed for clear supplier-customer communication; and unknown health risks, to name a few. Ultimately, these are all examples of areas that will influence industrial adoption and companies’ internal decisions on whether or not to invest. The graphene and related materials hype depend solely on material performance benefits or added value. But what it’s important to remember is that when it comes to industrial adoption, performance is just a part of the picture and don’t comprise the whole equation. Commercialization comes first after the industry and market also accepts the technology.

This chapter argues that before companies will start incorporating graphene and related materials into their products at the mass scale, the industry as a whole will need to overcome challenges that are currently present. Individual firms will also need a clear picture of how the industry as a whole look like to better make an assessment of the risks, costs, and challenges that ultimately will influence their decision-making. Therefore, this chapter looks at the graphene and related materials industry from a macro perspective so shed light over these challenges. Since there are many broad industries where graphene and related materials serves a purpose, with unique lifecycles, challenges and opportunities, it is not practical to dive deep into these industries separately.

4.2 INDUSTRY OVERVIEW

Material development takes time, yet in today’s age people assume that it can be as quick as software development. Not only that, the development of new materials can be so complex and expensive that it is more likely that it doesn’t achieve industrial adoption than that it does (Reiss, Hjelt, & Ferrari, 2019). For the development of new materials and products trying to
incorporate GRMs this fact certainly holds true. The activity around GRMs is often referred to as the graphene industry, but to stay consistent with terminology used in this report it will be referred to as the GRMs industry. This goes back to Section 1.2.2, where one has to understand that the term graphene is commonly used interchangeably with other forms of GRMs, which is incorrect and creates confusion because 1LG itself doesn’t necessarily serve a wide range of industries, but GRMs does. As one will realize reading this text, the GRMs industry certainly has a bright forecast relative to its young age but there are many forces that can be quite difficult to navigate around.

The number of applications where GRMs can be useful are multifold (see Figure 4.3). GRMs has the potential to revolutionize a wide range of applications from aerospace engineering to digital electronics to biomedicine. Therefore, when one talks about the GRMs industry, it can be quite difficult to understand what exactly one is referring to. For example, does it refer to GRMs as raw materials or is it the end products containing GRMs? A simplified way to look at the GRMs industry is as raw materials but through segmentation. That is, GRMs used individually (e.g. 1LG as a component in electronics) and GRMs in bulk (e.g. GNP powder as a nanofillers within other material matrices). Alternatively, the GRMs industry can be divided into (1) GRMs produced by bottom-up production and (2) GRMs from top-down production (Barkan, 2019). The first one, tends to serve high end, high quality with relatively low volume requirements (e.g. electronics), while the second one large-scale production at competitive pricing for applications with a range of quality requirements (e.g. composites).

Recall that the outstanding electrical properties of some GRMs depends profoundly on the number of graphene layers and the quality of those layers. In this case, quality typically refers to how defect-free the graphene layers are. To control the quality and number of layers, a
production method known as chemical vapor deposition (CVD) is typically used. CVD produces (or grows) graphene layers in units of area on a substrate from a carbon bearing gas. According to experts, when this so-called bottom-up production method is used, one gets a form of graphene that is the closest to pristine graphene as one can achieve. When the process yields a defect-free single layer, one would simply have produced 1LG. The drawback is the (current) inability to produce at scale. By this method, the GRMs produced can potentially be used as individual components for products in the electronics, optoelectronics and/or photonics industries, for example. GRMs produced by a bottom-up production method is regarded as individual materials because the performance is measured for the materials alone. In comparison, for GRMs in bulk, the performance is measured in combination with the base material – similar to what was done in Chapter 3. CVD grown graphene is therefore commonly compared to silicon (Si) which also is viewed as an individual material. After the discovery of Si, it took 124 years before the creation of the first Si chip that is now used in almost all modern electronics (Reiss, Hjelt, & Ferrari, 2019). This is just an example of how time enters the equation when it comes to material development and the road to industrial adoption. GRM-industry-experts have stated that it should take at least 20-30 years following the discovery of graphene before one can see significant industrial adoption for GRMs (Reiss, Hjelt, & Ferrari, 2019). This will certainly be the case for GRMs as individual components within technologies but, again, what’s promising with GRMs is the potential to be used within multiple industries, not just one or two. That means that it can be assumed that it will be much quicker for industrial adoption in some areas.

If one instead looks at GRMs in bulk, one can already see industrial adoption – just fifteen years after the original discovery – which is very promising. GRMs in bulk are produced by a top-down production method. Recall that graphite is just made up by graphene layers
bonded together by Van der Waals forces. To break these forces to produce powders and
dispersions, the most common method is using graphite as a feedstock material and then
applying an exfoliation method, either chemical, electrochemical or physical exfoliation to
separate the graphene layers (Barkan, 2019). This segment in particular is most relevant to this
paper and will hereinafter be the main focus.

For the GRMs industry lifecycle, it is evident that some areas are in an emerging stage
whilst other areas have transitioned into a growth stage. With that being said, in some areas there
are many new entrants and no dominant players, where the industry is becoming more and more
fragmented. These are all characteristics of an emerging industry. In other areas, such as the
GRMs in bulk powders for example, the industry can be argued to be in a growth stage. This
stage is characterized by fragmentation, increased profits and some initial consolidation. The
growth stage is an expansive period for many companies because they are using extensive
resources while developing critical partnerships to establish their position in the industry (Allen,
2016). This makes sense because currently there are GRMs companies that are partnering up
with large, established companies to develop GRM enhanced products. Take for example XG
Sciences, an American GNPs producer, that recently developed GNP-enhanced parts with the
Ford Motor Company.

If one looks at the GRMs in bulk segment one can see some threats to substitutes since
there are many so-called “graphene” powder suppliers, but as time goes by most of these
suppliers will cease to exist since they will not be able to keep up with the technological changes
or quality requirements. An interesting combination for this segment is that both supplier’s
bargaining power and the buyer’s bargaining power are quite strong. This is because there are
very few suppliers that can produce GRMs at a large scale with consistent quality and the buyers
of these GRMs also have bargaining power since they are generally very large firms that can force down prices through volume purchases (Nord Bjaerneman, Tillery, Moore, & McKemey, 2019). For an investor, this combination indicates a less attractive industry. This also causes a scenario commonly known as the chicken-and-egg dilemma. With that being said, the buyer, which in this case is the company trying to incorporate GRMs in their products, will not advance past demonstration performance in the absence of proved ability to securely and safely offer consistent supply, whilst the GRMs supplier find it difficult to raise and invest capital faced with no confirmed orders and with speculative orders (Collins, 2019). This dilemma causes stagnation which is not good for a growing industry. Lastly, the GRMs industry does have high barriers to entry due to the significant requirements in capital, which signifies an attractive industry for investors since competitors are therefore less likely to enter the industry.

4.2.1 FORECAST

When one is analyzing a particular market, a market forecast is an important component to include in order to assess the economic potential. As been stated above, the GRMs industry is quite complex to analyze since it’s stretched over the two aforementioned segments – both of which being at different stages in their lifecycles with unique forecasts and time to industrial adoption. Not only that, within these segments there are multiple individual industries that themselves have different forecasts and where the adoption times for GRMs to be used within those industries are different. Therefore, there are multiple ways to analyze the GRMs market. Reiss et al. (2019) made a market forecast for the GRMs industry as a whole by collecting data from multiple sources. Their approach was to first assume that the numbers collected represented the revenue of GRMs as raw materials, not the revenue of the end products containing GRMs.
The second assumption they made was that the numbers are estimated by mapping the whole GRMs production sector and the current prices and production volumes for all relevant players in the field (Reiss, Hjelt, & Ferrari, 2019). The market forecast that they presented can be seen in Figure 4.1 below. The estimated projection has a range that goes from approximately $200 million to $2 billion, which is a huge difference. This is just an evidence of how difficult it can be to make valid evaluations of complex markets.

Figure 4.1. GRM market forecast 2010 to 2025. Graph showing max, min and mean revenues (Reiss, Hjelt, & Ferrari, 2019).
Figure 4.1 only take the revenue projections up until 2025 into account. By also taking the time-argument into account, it can be assumed that the segment contributing to this market forecast the most is GRMs in bulk. This argument can be backed up by looking at Figure 4.2, where the market value for GNP (that falls within the GRMs in bulk segment) is projected to be $112 million in 2023, a compound annual growth rate (CAGR) of 37.53% through 2023. If one compares that to the mean value in Figure 4.1, one can see that in 2023 the entire market is expected at approximately $400 million, so almost a third of that would be compromised by GNP sales alone. If one assumes that the CAGR of the whole market from 2023 to 2025 (approximately 41%) can be applied to the GNP market, then the market value of GNP in 2025 can be calculated to be approximately $223 million, which is also approximately a third of the market. This assumption can be somewhat validated by Figure 4.3 that was made by The Graphene Council to illustrate the estimated market share for numerous potential GRMs applications. As one can see, the blue slice, representing the applications where GNP are most likely to be used, is approximately a third of the circle as a whole.
Figure 4.2. Market value of GNPs worldwide, in million USD. Figure generated by Statista.

Figure 4.3. Relative market share for GRMs by application (Barkan, 2019).
To get a better understanding of the estimated market size, one can compare it to the graphite market. In Figure 4.4 below, one can see the market forecast for graphite. The graphite market is estimated to have a revenue of about $27 billion in 2025. If one compare this to the forecasted mean value of $800 million for GRMs in the same year, the GRM market size looks quite underwhelming in comparison. Still, since the GRMs industry is at a young age, it can be concluded that the outlook looks promising.

Figure 4.4. Market forecast for graphite from 2015 to 2025 in billion USD. Figure generated by Statista.
Again, it is very difficult to make valid assumptions for the GRMs industry. Let the information above serve as a comparison tool rather than facts. It is important to remember that the GRMs industry faces many challenges, that will ultimately influence these projections and the environment as a whole. In the next few sections, this paper will briefly cover a couple of the industry-wide challenges that the industry is currently subjected to.

4.3 INDUSTRY-WIDE CHALLENGES

4.3.1 STANDARDIZATION

As been stated in this paper before, there are numerous industries that could potentially reap the benefits of adding nanomaterials, such as GRMs, into products. However, before it’s possible for effective industrialization, an area that needs work for the GRMs community is standards development, or standardization. In Standardization Essentials (2000), the importance of standardization is stressed with the argument that new standards development for an industry simply means progress. Standards help shape technologies, defines the terms of commerce, sustains our environment and makes the public safe. They are crucial for purchasing and contractual agreements, quality assurance, and many other areas (Spivak, & Brenner, 2000). In the book The Nano-Micro Interface (2015), it’s also stated that standardization of measurement, test, and characterization techniques is a prerequisite to the implementation of industrialization (Van De Voorde, 2015).

The main global body for standardization that is the most active in nanotechnology standardization, where GRMs falls as a subcategory, and that has been mentioned in this paper before, is the International Organization for Standardization. ISO has over 300 technical committees that are established for different industries. ISO Technical Committee 229
(ISO/TC229) is the committee solely focusing on nanotechnology. The IEC has a similar committee called IEC TC 113. Each country involved in the development of standards has their own governing body. For example, in the United States the governing standardization body is American National Standards Institute (ANSI). Each body have domestic experts, or representatives, that participate in an international group called a technical advisory group (TAG). For the ISO/TC229 TAG, each country has five separate working groups (WGs) that focus on different areas within the field of nanotechnology. Each group has their own members providing input. For example, WG1 focuses solely on terminology and nomenclature, while WG2 is responsible for measurements and characterization. The other WGs have their respective focus in the areas of environmental, health and safety (EHS), material specifications, and products and applications.

By looking at these areas, each of them is important components for the GRMs industry. With that being said, recall the argument about how the term “graphene” is used interchangeably with other GRMs. Without WG1, this term would certainly be continued to be used in the wrong way which creates confusion and causes distrust between stakeholders. Imagine the scenario when a buyer, interested in purchasing few-layer graphene powder to enhance their polymer by making it electrically conductive, contacts a certain supplier that claim that they’re selling “graphene powder of the highest quality” but in reality are selling some sort of carbon flakes with varying thicknesses of 15 to 30 nm. In this case, the buyer would have to trust the supplier and realize that, to their dissatisfaction, their newly “graphene-enhanced” polymer didn’t get the performance that they wanted. In the emerging stage for the GRMs in bulk segment, when the hype of graphene was at its peak, this scenario commonly occurred. Instead of industrial adoption, the outcome of this almost resulted in industrial rejection since the expectations of
what graphene promised was not set correctly. Without standardization for terminology there is no way for suppliers to communicate effectively with customers and would instead promote false advertising. Dr. Denis Koltsov, the current chair of ISO/TC229 and an expert within this field, stated that it’s clear that since adopting a strict definition of “graphene” and other forms in ISO TS 80004-13:2017, the terminology used by industry and academia has become clearer (Koltsov, 2019). If developed well, terminology has the power to promote the growth of the GRMs industry because it simply builds trust between stakeholders and sets true expectations. With all of this said, there is a lot of work still to be done. As stated in Chapter 1, there is currently an ongoing discussion of what should be classified as a “graphene-related” material and what should not. For example, the abbreviation used in this paper (i.e. GRMs) is just a made-up term by the industry that makes it simpler when talking about all the different forms of graphene. So instead of saying “the industry where companies sell either 1LG, 2LG, FLG, GO, rGO, GNP and/or another forms of graphene,” one can instead just say the GRMs industry. However, this term has not reached global consensus and is not an accepted term by ISO. So, one of the current activities for WG1 is to come up with an umbrella term that covers all of these forms. At the time this paper is written, the most recent term that has been suggested by ISO experts is graphene-related 2D materials (GR2M), which first seems like a good term. However, part of the GRMs industry is not happy with it because note that it says “2D materials” which, as we can see in Section 1.2.2, excludes everything above 10 layers. This means that many of the GNP’s suppliers that doesn’t necessarily produce flakes below 10 layers, are left out. Recall what was stated in Section 1.2.2, that if a carbon material, with a thickness exceeding 10 layers but still falls within the nanoscale and with the other dimensions significantly larger, is excluded from suggested term GR2M but at the same time falls outside the traditional definition of graphite, then in what
category does this carbon material fall? The current GNPs producers that have put extensive resources in developing their businesses into becoming well-trusted, established “graphene” suppliers, can’t accept the fact that based on ISO’s definitions they are technically seen as graphite suppliers. The very unique low aspect ratio of GNPs is a characteristic that one doesn’t get with traditional bulk graphite. If this community falls outside of the realm of GR2M, then the majority of the so-called “graphene-enhanced” products we see today on the market (e.g. Callaway’s graphene-enhanced golf balls and Ford Motor’s graphene-enhanced components) should not be called “graphene-enhanced,” and neither should this paper (recall that the GNPs used in this study was approximately 11 nm thick). That would mean that the industry, referred to as the GRMs industry in this paper, certainly is not as developed as what is stated by advocates of the industry. The definitions set by ISO are often developed by personnel in academia with limited input from industrial entities. Yet, academics continuously highlights the benefits of using “graphene” in composites, coatings, and infrastructure, to name a few large industries. However, if it’s also decided that due to “scientific correctness” everything outside 10 layers should not be classified as a “graphene-related” material then they are also continuously contradicting themselves. Therefore, with 80004-13:2017 up for revision within this year, the WG1 need to work hard to figure out a solution to this that academia and the industry can reach consensus around. Hopefully by the time this paper is publicly published, this issue has been resolved.

Another standards area is measurements and characterization. This discussion was initiated in Section 1.2.3. Recall that the definitions set out in 80004-13:2017 mostly depends on minute structural and chemical changes. Currently up for publishing is a document developed for the structural characterization for graphene powders and dispersion (ISO/PDTS 21356-
This document highlights many of the characterization techniques covered in Section 1.2.3. However, the discussion surrounding this document has been around how useful the document is for industry. The document sets out standard procedures to investigate the structural nature of individual flakes by using methods such as AFM, TEM, and SEM. With that being said, recall that if dealing with a batch of powder, it is not practical to look at individual flakes only since that batch may contain billions, or ever trillions, of flakes. Nor is it correct to assume that after having characterized of couple of individual flakes, that those flakes represent the structural nature of all the other of flakes in that particular batch. So, the argument has been made that the ISO/PDTS 21356-1:2020(E) document is not necessarily relevant to industrial settings. Instead, a document like this can be very useful for the lab scale. For the industry to grow however, standardized methods need to be developed for clear communication between suppliers and customers using technical detail specifications (TDS), and for quality control and assurance. Ray Gibbs, the former CEO for Haydale Graphene Industries, said that after testing powders supplied from 230 so-called “graphene” producers, none was of the same quality/structure, even between different batches within the same company (Critchley, 2018). Similarly, the powder supplied from 60 different producers were tested and it was reported that many highly priced products that claims to be “graphene” consisted mostly of bulk graphite powder (Bøggild, 2018). Again, without clear standards, companies risk wasting money on graphite powder advertised as high-grade “graphene” powder, which sets incorrect expectations and can result in industrial rejection.

Before ISO begin developing a characterization document better suited for industrial settings where statistical meaning is important, an area to evaluate is recent shifts in the supply chain. With that being said, for the past couple of years two challenges for graphene powder...
suppliers has been the buyer’s lack of experience working with GRMs and re-agglomeration issues. Recall that due to graphene’s crystalline structure and hydrophobic nature, compatibility issues with other material is often assumed. However, if one lack experience and knowledge, it might be assumed that the powder received can simply be mixed into the material matrix of interest, which one know by now is not the case. Therefore, the buyer might be dissatisfied with the powder and discontinues the relationship with that particular supplier. This scenario is clearly not ideal for the suppliers. Another issue is re-agglomeration. The interlayer forces that is needed to be broken up in order to produce GRMs, have a tendency to cause re-agglomeration in the dry state. This can be during production, which ultimately affect the batch, but can also be during shipment and storage. That means that when a supplier sells a batch that is characterized in-house, the structural nature of the flakes might actually differ once delivered to the customer. This might also result in dissatisfactory end-performance for the buyer when mixed with their materials, disregarding their experience level. To address these issues the powder suppliers has started to focus on a new business model where the type of GRMs they’re selling are already dispersed in common base materials used in large industries. This is done to eliminate the risk of the aforementioned issues with dry powders. Since the suppliers are the experts on how to deal with the mixing and re-agglomeration issues, they can control this process more easily and instead sell these GRM-enhanced materials directly to industries. This is a business model that has been proven to work for many industries. If the suppliers are shifting their focus to a business model like this, then a document that includes a standard way to characterize large batches of powders might not be much relevant anymore. A performance-based standards document might be the correct choice.
4.3.2 RISK FOR NEW REGULATIONS

As of today, it doesn’t appear to be any federal or state regulations for the GRM industry in the United States. However, as a nanomaterial, GRMs are likely regulated by the United States Environmental Protection Agency (EPA) under the Toxic Substances Control Act (TSCA) (Kaplan, & Woloschyn, 2014). While it is a little bit unclear of the regulations in the US, Europe has already established regulations. Therefore, if a company want to reach globally, it needs to be familiar with these regulations as well. The key regulation that covers the European market is called REACH, which stands for Registration, Evaluation, Authorization, and Restriction of Chemicals in Europe. As of May 31, 2018, companies that manufactures or imports chemical substances into the EU over one metric tonnes per year, are required to register with the ECHA (National Graphene Association, 2018). This means that suppliers (from any country that want to do business in Europe), and importers need to get approved by the ECHA before a GRM-enhanced product can be commercialized. Similar regulations are being developed in Korea, Turkey, and China, with more countries following (Nord Bjaerneman, Tillery, Moore, & McKemey, 2019). Since there is a huge interest in using 2D materials to enhance consumer products, it is likely that there will be new regulations emerging that might affect the growth of the industry.

4.3.3 LACK IN GOVERNMENTAL FUNDING

In the U.S. there is both a lack of funding within the GRM industry as well as an opportunity for federal funding. The US government is currently in an active discussion about whether GRMs requires more funding. This is because other countries around the world are way ahead of the U.S. when it comes to funding for GRMs research and commercialization. The EU
have invested around $1.4 billion into graphene research and commercialization, and China about $1 billion. Other countries, such as Korea, the UK and Singapore is also way ahead the US. The US have currently invested around $200 million, so there is definitely a need for greater funding. If the US push through an initiative to increase the funding for graphene, there might be a great opportunity for companies to receive money for their GRMs commercialization efforts (Nord Bjaerneman, Tillery, Moore, & McKemey, 2019).

4.3.4 UNKNOWN HEALTH RISKS

In order for companies to feel safe to incorporate GRMs into their products, they need to be certain of the risks associated with these materials. Unfortunately, this is a topic that, when faced with questions, experts like to avoid. It is however crucial to be able to address these concerns before it is possible for industrial adoption on the mass scale (Nord Bjaerneman, Tillery, Moore, & McKemey, 2019). This topic has been discussed at numerous conferences and workshops. For instance, Al-Ostaz et al. (2014) said that in a workshop organized by the U.S. Environmental Protection Agency (EPA), “risk” was defined as the human risk as a result of using any material and that the “likelihood of hazard” can be defined as the potential of a compound or material to produce harm. They continued by saying that “exposure to hazard” is the harm that might result if humans get in contact with the material or compound. The different types of risks related to GRMs can be exposure to GRMs, toxicology of GRMs, the ability to extrapolate GRMs toxicity using existing particle and fiber toxicological databases, environmental and biological fate, transport, persistence and transformation of GRMs; and recyclability and overall sustainability of GRMs (Al-Ostaz, Ettouney, & Cheng, 2014). As one can see, there are many areas that need investigation, but unfortunately, there is not a lot of work
done in these areas for GRMs in particular. According to a report by the European Commission in 2015, most GRMs risk assessment has been made in comparison to the use and safety of carbon nanotubes (CNTs) since CNTs has been investigated for many years. With that being said, in order to speculate on the safety of GRMs, the existing knowledge and experience from CNTs was used. It was found that the extent and mechanism by which cells interact and uptake GRMs is considered critically important and that exposing the body to carbon nanomaterials could result in either their accumulation in the tissues or elimination through excretion (SCU, 2015). More recently experts have said that there should not be a risk when being exposed to GRMs. But “should not” is not good enough for one to be entirely confident, nor when being faced with a lawsuit. As Delgado (2010) mentioned in a report, one should not assume that nanotechnology will be different from other industrial innovations when it comes to having the potential to present both benefits and risks to human and environmental health. He continues by saying that when it comes to toxicity, environmental impact and the biodegradability of nanostructures with possible effects on human health is significant given their presumed interference in vital functions (Delgado, 2010). At later stages in the paper, it is reported that there have been some scientific investigations that indicated possible hazards. The reported studies included, but not limited to, a study based on rats that affirm that carbon nanoparticles can enter through the nose to the brain, and another reporting that the introduction in the abdominal cavity of rats resulted in pathogenicity similar to asbestos (Delgado, 2010). As one can understand, this area is critical to understand before it is possible for industrialization on the mass-scale.
CHAPTER 5: CONCLUSIONS & FUTURE WORK

5.1 CONCLUSIONS

In summary, this report has presented improved mechanical performance in NBRfGNP and NBRGNP nanocomposites fabricated by a sonication method. In Phase 1 it was reported that with a 0.2 phr concentration of fGNP to NBR, a 171% increase in tensile strength was obtained. When 1 phr of fGNP was added, a 58% increase in storage modulus could be achieved. Phase 1 also showed likelihood that storage modulus was correlated to cutting resistance. Phase 1 and 2 reported a statistically significant effect for both curing temperature and concentration on the nanocomposite’s tensile strength and storage modulus. Whilst the curing temperature showed to have a greater effect on tensile strength, concentration displayed a greater significant effect on storage modulus. The interaction between concentration and curing temperature didn’t display a significant effect. During Phase 2, the optimal combination for curing temperature and concentration was found to be 130°C and 1.6 phr, respectively, in order to maximize storage modulus. Also, during Phase 2, a 95% increase in storage modulus was obtained for a specimen with a 2.34 phr concentration and cured at 135°C. Lastly, in Phase 3 it was found that the thickness of the coating seem to have a greater effect on the cutting resistance than the concentration of the nanofiller. However, the coating with 1.6 phr of graphene nanoplatelets, cured at 130°C and with a 1 mm thickness, increased the cutting resistance by 29% in comparison to the NBR coating cured at the same temperature and with the same thickness.
5.2 FUTURE WORK

This report certainly reports some interesting findings. However, there are still areas that could need further exploration. For instance, it is reported that a 171% increase in tensile strength was achieved for a concentration of 0.2 phr. This report focuses on maximizing cutting performance, so since it was determined that tensile strength didn’t seem to have a correlation with cutting resistance, it was not investigated further. However, in the future there may be an interest to investigate the low concentrations further to see if the tensile strength can be maximized.

Another area that would be interesting to investigate is the effect of coating thickness on cutting performance. A simple DOE design can be set up for this. Along with the thickness it would also be interesting to investigate the contribution of the substrate versus the contribution of the coating for cutting resistance. That said, if the substrate shows a significant contribution to the cutting performance and the coating does not, then it might be financial incentive to modify the substrate rather than the coating. A cost-benefit analysis could be done.

Lastly, since the cutting performance is just one property that is tested for occupational safety products, it should be interesting to investigate the other properties as well. These properties are abrasion resistance and puncture resistance. Even if only one of these properties are significantly improved, it might be enough as an incentive for safety companies to enhance their products with nanofillers.
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VITA

Torkel Nord Bjaerneman was born and raised in Gothenburg, Sweden. At the age of seventeen, he moved to pursue his dream of studying in the United States of America. In May 2018, he received a bachelor’s degree in Civil Engineering from the University of Mississippi with an emphasis in Structural Engineering and a minor in Business Administration. In the Spring of 2018, Torkel also received the Senior Excellence Award from the Department of Civil Engineering for his achievements during his time as a student at the University. Over a period of almost three years, from 2017 to 2020, he worked for the Center for Graphene Research & Innovation as a Research Assistant. Part of this time, Torkel also worked for the Office of Technology Commercialization as an Undergraduate and Graduate Engineering Student Analyst. Additionally, at three occurrences, he served as a team member for the National Graphene Association by help organizing and helping out at conferences focusing on the commercialization of graphene and related materials. From August to December in 2019, Torkel served as the Interim Business Development Manager for the National Graphene Association, actively identifying and promoting graphene commercialization within a number of industries.

Following graduation, Torkel will continue his involvement in the graphene and related materials industry by starting a position as the Business Developer/Research & Innovation Engineer for the Cambridge Graphene Centre at the University of Cambridge in Cambridge, United Kingdom, starting in May 2020.